

Combined Experimental and Computational Study on Catalytic Cyclocoupling of Epoxides and CO₂ Using Porphyrin-Based Cu(II) Metal-Organic Frameworks with 2D Coordination Networks

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Abstract

The cyclocoupling of epoxides and CO_2 was investigated using porphyrin-based Cu(II) metal-organic frameworks with 2D coordination networks. A variety of mono- and disubstituted epoxides were transformed into cyclic carbonates under mild and neat conditions. Several control experiments were carried out to elucidate that the catalytically active site is the dicopper paddle wheel unit rather than the copper porphyrin complex moiety. The proposed mechanism was corroborated by density functional theory calculations of a model paddle wheel unit.

1. Introduction

Metal-organic frameworks (MOFs) are organic-inorganic hybrid materials, in which characteristic uniform porous structures are assembled by coordination networks of metal ions and organic linkers.¹ MOFs have garnered enormous attention from the scientific community over the last decade, because the judicious combination of a wide variety of metals with rationally designed organic linkers enabled access to diverse new MOFs.² Moreover, because of their robust porous structures, MOFs find extensive applications in gas storage and separation, removal of toxic chemicals, (opto-)electronic devices, energy storage, heterogeneous catalysts, and drug-delivery systems among others.^{1,3}

Among these applications, the selective transformation of small organic raw materials into valuable functional molecules

using MOFs has been a topic of intensive studies. The molecular recognition owing to the distinct pore size and intrinsic coordination ability of metal components enable adsorption and catalytic conversion of small molecules.⁴ Moreover, robust coordination networks allow the efficient separation and reuse of MOFs. Although these features are similar to those of conventional porous solid materials such as zeolites, MOFs are advantageous because their topologies, pore sizes, and functions can be readily tunable through rational design of the starting components.² For example, the development of CO₂ fixing technologies that utilize the CO₂ adsorption ability of MOFs⁵ is fundamental to harnessing the major greenhouse gas as an abundant renewable C1 resource.⁶ Various MOFs have been investigated as catalysts for cyclocoupling of epoxides and CO₂.⁷ In a pioneering study, Cu₃(btc)₂ (HKUST-1, btc: benzene-1,3,5-tricarboxylate, Figure 1a)⁸ catalyzed cyclocoupling of epichlorohydrin under CO₂ pressure (7 bar) at elevated temperatures (70-100 °C) to furnish the corresponding cyclic carbonate in a modest yield.⁹ Later, the catalytic performance was greatly improved using different types of Cu MOFs, MMPF-9 and MMCF-2, in which tetrakis(3,5-dicarboxybiphenyl)porphine (H₁₀tdcbpp) or 1,4,7,10-tetrazacyclododecane-N,N',N"',N"'-tetra-p-methylbenzoic acid (H4tactmb) were used as polycarboxylate linkers, respectively.¹⁰ The cyclocoupling of propylene oxide proceeded under atmospheric pressure CO₂ at ambient temperature in the presence of tetrabutylammonium bromide (TBAB) as a cocatalyst, producing the corresponding cyclic carbonate in higher yields than those obtained with the benchmark catalyst, HKUST-1. In these



Figure 1. (a) Copper paddle wheel units and polycarboxylic acid ligands used for previous Cu MOFs, HKUST-1, MMPF-9, and MMCF-2; (b) Porphyrin-based Cu MOFs developed by Toyota Central R&D Labs.

examples, copper complexes of the porphyrin or cyclic polyamine ligands boosted the catalytic efficiency, although copper paddle wheel units, $Cu_2(OCOR)_4$, have been recognized as catalytically active sites. Moreover, a copper porphyrin-based MOF has been reported to be effective for CO_2 capture and subsequent activation.¹¹

We investigated the catalytic activity of porphyrin-based Cu MOFs **1a** and **1b**, developed by Toyota Central R&D Labs, toward the cyclocoupling of epoxides and CO₂ (Figure 1b).¹²

Table 1. Cyclocoupling of styrene oxide and CO₂ using Cu MOFs

Ph 2a 1 mmol	Cu MOF (10 mg), 10 mol % TBAB CO ₂ , 28 °C, 48 h		► 0 - 0 Ph - 0 3a	
Entry	Cu MOF	CO ₂ /MPa	Yield/% ^a	
1	HKUST-1	0.1	47	
2	1a	0.1	52	
3	1b	0.1	66	
4^b	1b	0.1	46	
5	1b	2.5	77	
6	1b	5.0	74 ^c	

^{*a*}Yields of isolated products. ^{*b*}TBAI was used instead of TBAB. ^{*c*}Crude yield determined by ¹HNMR analysis.

MOFs 1a and 1b have a 2-dimensional 2.2 nm square-grid coordination network consisting of a copper paddle wheel unit, $Cu_2(OCOR)_4$, and a copper tetra(4-pyridyl)porphyrin ligand (CuTPyP). In 1a, the 2D sheets are slip-stacked through hydrogen bonds between the H atoms of the methyl groups of one 2D sheet and the carbonyl oxygens of an adjacent 2D sheet to form an overall 3D structure, in which the square cavities are not aligned. In 1b, acetate ligands are replaced by 1-naphthoates. In contrast to the 3D structure of 1a, that of 1b has 2D sheets stacked through CH- π interactions between 1naphthoate groups on the faces and edges of the adjacent 2D sheets. Because of the bulky 1-naphthyl groups, 1b has lower gas adsorption ability, albeit with higher CO2/N2 selectivity than 1a. We hypothesized that the porous structures of 1a and 1b, together with two different copper environments, could lead to unprecedented molecular recognition and catalytic ability. Unlike conventional Cu MOFs, the networks of 1a and **1b** are assembled by coordination between the pyridyl moiety on the porphyrin ligand and the copper paddle wheel units. Therefore, no apparent vacant site of the paddle wheel unit is available for activation of epoxides. Herein, we report the results of our study on catalytic cyclocoupling of epoxides and CO₂ using Cu-MOFs 1a and 1b with particular emphasis on the substrate scope and elucidation of catalytic activity origin.

2. Results and Discussion

The cyclocoupling of styrene oxide **2a** with CO₂ was conducted using Cu MOFs **1a** and **1b** along with commercial HKUST-1 (Basolite $300^{\text{(B)}}$) as a benchmark (Table 1). The reaction was performed by adding 10 mg of MOFs and 10 mol % "Bu₄NBr (TBAB) to 1 mmol of **2a** without a solvent under atmospheric pressure (0.1 MPa) of CO₂ at 28 °C for 48 h. When HKUS1 was used as the reference catalyst, the expected carbonate **3a** was obtained in 47% yield (Entry 1). A slightly higher yield of 52% was obtained using 2D-MOF **1a** (Entry 2). The 1-naphthoate analog **1b** was used as the catalyst under the same conditions, affording **3a** in an improved yield of 66% (Entry 3). When "Bu₄NI (TBAI) instead of TBAB was used as the cocatalyst together with **1b**, the yield of **3a** decreased to 46% (Entry 4). The effect of CO₂ pressure was then examined using **1b**. The yield of **3a** increased to 77% when the reaction

Table 2. Cyclocoupling of styrene oxide and CO₂ using Cu catalysts^{*a*}



1	rtone	00
2	Without TBAB	0
3	Without 1b	22^{b}
4	2.85 mol % Cu(OAc) ₂ instead of 1b	45
5	$2.85 \text{ mol } \% \text{ Cu}(\text{Naph})_2 \text{ instead of } 1b$	67
6	2.85 mol % CuTPP instead of 1b	15^{b}
7	AcOEt extract was used instead of 1b	25^{b}

^{*a*}Naph: 1-naphthoate, TPP: 5,10,15,20-tetraphenylporphinate. Yields of isolated products are shown. ^{*b*}Crude yield determined by ¹H NMR analysis.

was carried out under 2.5 MPa CO_2 (Entry 5). An increase in CO₂ pressure to 5.0 MPa did not lead to further improvement (Entry 6).

Several control experiments were conducted to investigate the origin of the observed catalytic activity of 1a and 1b, as summarized in Table 2. No reaction occurred in the absence of TBAB, which implies that this cocatalyst is imperative (Entry 2). In contrast, TBAB alone catalyzed the cyclocoupling to afford **3a** with a low yield of 22% (Entry 3).¹³ Several copper compounds were tested as catalysts. Because 10 mg of **1b** corresponds to 2.85 mol % Cu, 2.85 mol % of Cu(O₂CR)₂ was used as the catalyst. Cu(II) acetate and 1-naphthoate exhibited significant catalytic activity, affording 3a in 45% and 67% yields, respectively (Entries 4 and 5). The use of CuTPP as a catalyst led to the formation of 3a in a lower yield than that obtained with TBAB alone (Entry 6).¹⁴ Therefore, the catalytic activity of the copper porphyrin was negligible, and the effect of the carboxylate ligands on the efficiency was the same as that observed for 1a/1b. These results suggest that the catalytically active sites of 1a and 1b are the copper paddle wheel units rather than the copper porphyrin moiety. This consideration is in striking contrast to the previous study that implied a significant contribution of the copper porphyrin moiety to the catalytic performance of MMPF-9 in epoxide-CO2 cyclocoupling. Moreover, the efficiency of 1a and 1b was greater than that of HKUST-1 despite the paddle wheel units in 1a and 1b with saturated coordination sites. Thus, the mechanism for the activation of epoxides deserves further discussion (vide infra). Finally, potential catalyst leaching was examined as follows: 10 mg of 1b was stirred in AcOEt at 28 °C for 24 h, and after centrifugation, the AcOEt supernatant was decanted and concentrated. Subsequently, 10 mol % TBAB and 1 mmol of 2a were added to the obtained extract, and the reaction mixture was stirred at 28 °C for 48 h to obtain 3a in 25% NMR yield (Entry 7). The contribution of catalyst leaching can be neglected because the observed yield was comparable to that of TBAB alone (Entry 2).

We then investigated the recyclability of the catalyst by taking advantage of the heterogeneous nature of the MOFs. The

Table 3.	Catalyst	recycling	experiments	using	1b	for	cyclo-	•
couplin	ig of $2a^a$							

Cycle	1b amt/mg	Yield/%	TON
1	10.0	74	26.0
2	8.7	68	27.4
3	6.5	54	29.1
4	5.4	47	30.5
5	4.9	42	30.1

^{*a*}All reactions were performed on a 1 mmol scale using 10 mol % TBAB under 2.5 MPa CO₂ at 28 °C for 48 h. Yields of isolated products are shown.

reaction of styrene oxide 2a was conducted using 1b under 2.5 MPa CO₂. After the completion of the first cycle, the reaction mixture was diluted with AcOEt and 1b was separated by centrifugation. The recovered 1b was dried under vacuum and reused in the next cycles. As summarized in Table 3, Cu MOF 1b could be reused over five cycles; however, the amounts of recovered 1b gradually decreased, and accordingly, the yields of **3a** lowered from 74% for the 1st cycle to 42% for the fifth cycle. Nevertheless, turnover number (TON) gradually increased over reaction cycles. These results indicate that recovered 1b maintained its catalytic activity, although the amount of recovered 1b decreased by partial degradation with unsticking of the 2D MOF sheets. The slight increase in TON can be attributed to the accumulated TBAB cocatalyst. In striking contrast, copper (II) 1-naphthoate (Naph), Cu(Naph)₂, could not be recycled in a similar manner, which indicates an advantage of the MOF catalyst regarding recyclability.

Previous studies on epoxide-CO₂ cyclocoupling with Cu MOF catalysts have reported limitations in epoxide scope. In general, epoxides larger than propylene oxide lowered the product yields. Functional-group compatibility was also neglected in those studies. We performed the reactions of various epoxides to establish the substrate scope as summarized in Table 4. The reaction of 2-(tert-butoxymethyl)oxirane (2b) was conducted under the standard conditions and at atmospheric pressure of CO₂ furnished cyclic carbonate **3b** in high yield (82%), indicating that the bulky *tert*-butoxymethyl substituent was tolerated by 1b (Entry 1). Acetoxymethyl derivative 3c, propargyloxymethyl derivative 3d, and hydroxymethyl derivative 3e were also obtained in 56-85% yields (Entries 2-4). The oxygen functionality in the substituent was unnecessary because both chloromethyl derivative 3f and but-3-enyl derivative 3g were obtained in 68% yields (Entries 5 and 6). Cyclic carbonates with perfluoroalkyl substituents have been claimed to be superior solvents for the electrolyte salt of lithium secondary batteries as compared to conventional ethylene and propylene carbonates.¹⁵ The perfluoroalkyl derivative **3h** was obtained in 71% yield from commercial epoxide 2h using our method (Entry 7). Accordingly, various functional groups including ester, alcohol, ether, terminal alkene, terminal alkyne, chloroalkyl, and perfluoroalkyl, were well tolerated, although unidentifiable byproducts were detected as trace impurities in some cases.¹⁶ In addition, 2,2-disubstituted epoxide 2i and cyclopentane-fused epoxide 2j could be used as substrates (Entries 8 and 9), but the yield decreased for bicyclic carbonate

	1 1		
Entry	Epoxide	Carbonate	Yield/ %
1	'BuO	⁷ ВиО 3b	82
2	AcO O	AcO 3c	85
3	oO 2d	o 3d	56
4	HOO 2e	HO 3e	70
5	ClO 2f	ClO 3f	68 ^b
6	Solution ⊂ Colored Co	0 3g	68 ^b
7	$F \xrightarrow{F} F \xrightarrow{F} F$	F = F = F	71
8			52 ^b
9	2j	3j	27 (41) ^c

 Table 4.
 Scope of epoxide substrates^a

^{*a*}All reactions were performed under standard conditions: **1b** (10 mg), TBAB (10 mol %), epoxide (1 mmol), CO₂ (0.1 MPa), 28 °C, 48 h. Yields of isolated products are shown. ^{*b*}Trace impurities derived from naphthoate were detected. ^{*c*}The yield of the reaction performed at 50 °C.

3j. Because the steric hindrance is assumed to hamper the nucleophilic attack of a bromide anion to **2j**, this reaction was repeated at an elevated temperature of 50 °C under otherwise identical conditions to improve the yield of **3j** to 41%.

Scheme 1a shows an accepted mechanism for the cyclocoupling of epoxides and CO₂ using Lewis acid (LA)/TBAB binary catalysts.¹⁷ The electrophilic activation of epoxides by LA, followed by the nucleophilic attack of a bromide ion, leads to opening of the oxirane ring. Subsequent incorporation of



Scheme 1. (a) General mechanism for cyclocoupling of epoxides and CO₂ using LA/TBAB binary catalysts;
(b) cyclocoupling of non-racemic epoxide (S)-2j using 1b as the catalyst.

 CO_2 into the LA–O bond of resultant intermediate **4** generates carboxylate intermediate **5**. The final ring closure from **5** occurs with concomitant restoration of a bromide ion, affording cyclic carbonates. Because the 1-naphthoate ligand is more electronwithdrawing than the acetate ligand, as indicated by the pK_a values of acetic acid and 1-naphthoic acid (4.76 and 3.70, respectively),¹⁸ the 1-naphthoate ligand renders the copper center more Lewis acidic than the acetate ligand. This prediction is consistent with the trend in catalytic efficiency found for the cyclocoupling of epoxides and CO_2 using Cu MOFs **1a** and **1b** or Cu(II) carboxylate salts.

According to this scenario, the attack of a bromide ion should take place at the less-substituted oxirane carbon in the $S_N 2$ mode with retention of configuration at the adjacent chiral center. To verify this assumption, we employed commercial chiral non-racemic 2-(chloromethyl)oxirane (*S*)-**2f** (97% *ee*, GC) as a probe (Scheme 1b). The reaction of (*S*)-**2f** under the standard conditions afforded the corresponding product (*S*)-**3f** in 70% yield. As expected, the optical rotation of the isolated product ($[\alpha]_D^{23} = +30.7^\circ$ in MeOH) was in good accordance with that previously reported for optically pure (*S*)-**3f** ($[\alpha]_D^{20} = +37.6^\circ$ in MeOH).¹⁹ Although the slight erosion of the enantiomeric purity was observed for the obtained sample (82% ee), the stereochemistry of the chiral center was mostly preserved during the reaction, indicating that the bromide ion attacked the less-substituted carbon.

According to the results from the control experiments summarized in Table 2, the catalytic activity of Cu MOFs **1a** and **1b** is ascribed to the copper paddle wheel units rather than the copper porphyrin moiety. However, the vacant sites of the paddle wheel units are occupied by the pyridyl ligands, and no Lewis acid sites are available for electrophilic activation of epoxides. This situation is also consistent with a recently reported 1D Cu MOF, Cu(Hip)₂Bpy (Hip: 5-hydroxyisophthalic acid, Bpy: 4,4'-bipyridyl), in which the coordination sites of each Cu(II) center are saturated with two carboxylate and two pyridyl ligands.²⁰ To avoid discrepancy between saturation of the coordination sites and high catalytic performance, the authors proposed that the coordination mode of the carboxylate ligand changed from κ^2 to κ^1 to open a vacant site (Scheme 2). A similar change in coordination mode is possible in the



Scheme 2. Proposed coordination-mode changes in active copper sites.

dinuclear situation of the paddle wheel units: one of the four bridging κ^2 carboxylate ligands is converted into a κ^1 ligand to provide an open Lewis acid site for the activation of epoxides. A possibility that Cu species derived from decomposition of Cu MOF **1b** promote cyclocoupling is less likely because the leaching species have virtually no catalytic activity (Table 2, Entry 7).

To evaluate the proposed possibility, density functional theory (DFT) calculations were performed for a model system corresponding to a single paddle wheel unit. Triplet states were calculated at the unrestricted B3LYP²¹ level because singlet states were unstable (see SI for details). Single-point energy calculations were carried out using the Truhlar's M06L functional, because this functional is more accurate in estimating medium-range correlation energy than the B3LYP functional.²² A smaller ligand system comprising formates and pyridines was used for calculation efficiency. Among the carboxylate ligands, one closely relevant to the reaction site was replaced by a benzoate ligand. A tetramethylammonium ion replaced a tetrabutylammonium ion, and ethylene oxide was chosen as an epoxide substrate.

As discussed above, the opening of the benzoate bridge would make a vacant coordination site. However, no transition state (TS) could be located for this change in coordination mode. Instead, we could find an alternative mechanism for opening a vacant site (Scheme 3). The bridging benzoate ligand underwent slippage via **TS**_{AB} with an activation energy of $\Delta G^{\ddagger} = +12.2 \text{ kcal/mol}$ to generate unsymmetrical complex **B**. In **B**, the benzoate ligand coordinates to Cu_b in a κ^2 coordination mode, and one of its two oxygen atoms still coordinates to Cu_a. Because the C(carbonyl)–O bond lengths (1.307 and 1.238 Å) and Cu_b–O distances (2.048 and 2.623 Å) are significantly different, the carbonyl oxygen readily dissociated to generate complex **C** with the κ^1 benzoate ligand. The ligand slippage process is kinetically feasible, even though the formation of **C** from **A** is endergonic by 8.5 kcal/mol.

The ring opening of ethylene oxide occurred from complex **D**, via nucleophilic attack of the epoxide by a bromide ion (Scheme 4). This process was estimated to proceed with an activation energy of $\Delta G^{\ddagger} = +11.2 \text{ kcal/mol}$, and the formation of copper bromoethoxide intermediate **E** is slightly endergonic. Therefore, this step is thermodynamically feasible and reversible, and it is concluded that the paddle wheel unit with a κ^1 carboxylate ligand has sufficient Lewis acidity to promote oxirane-ring opening. Notably, the ring opening of ethylene



Scheme 3. Benzoate ligand slippage step starting from model complex **A**. Relative Gibbs free energies (298 K, 1 atm) are indicated in parentheses. Atom distances (Å) are given in italic numbers.

oxide mediated by Me₄NBr only has a higher activation energy of $\Delta G^{\ddagger} = +32.0 \text{ kcal/mol}$ and is endergonic by 19.0 kcal/mol (Figure S1 in SI). Therefore, the activation with the copper center is imperative for the efficient oxirane ring opening. In addition, the control experiment showed that CuTPP was totally inefficient as a catalyst (Table 2, Entry 6). The geometry optimization of Cu porphyrin complex with oxiran and tetramethylammonium bromide afforded a stationary point (K, Figure S2 in SI). However, no transition state for the nucleophilic ring opening of oxiran from K could be located. This is probably because the interaction between the Cu center and oxiran is very week: the Cu-O distance is significantly longer in K (2.522 Å) than in D (2.197 Å). Moreover, Cu porphyrin complex has no appropriate low-lying vacant orbital to interact with the HOMO of oxiran, whereas a model dinuclear Cu complex with a κ^1 -benzoate ligand has a suitable LUMO on the unsaturated Cu center (Figure S3 in SI).

Subsequently, a CO₂ molecule was inserted into the Cu–O bond of the resultant Cu bromoethoxide ($\mathbf{F} \rightarrow \mathbf{TS}_{FG} \rightarrow \mathbf{G}$, Scheme 5). The insertion proceeded via four-center transition state \mathbf{TS}_{FG} , in which the Cu–O(alkoxide) bond was elongated and, the C(CO₂)–O(alkoxide) and Cu–O(CO₂) distances were simultaneously shortened. In the CO₂ fragment, one of the two C=O bonds is longer than the other (1.247 and 1.216 Å, respectively), and the bent angle is 137.8°. The activation



Scheme 4. Epoxide ring-opening step starting from model complex **D**. Relative Gibbs free energies (298 K, 1 atm) are indicated in parentheses. Atom distances (Å) are given in italic numbers.

barrier was calculated as $\Delta G^{\ddagger} = +18.7 \text{ kcal/mol}$ and the formation of Cu carboxylate intermediate **G** from **F** is slightly endergonic, which indicates that this process is also thermodynamically feasible and reversible. Subsequent ring closure of the 2-bromoethoxy carbonate moiety occurred via transition state **TS**_{GH} with an activation energy of $\Delta G^{\ddagger} = +8.6 \text{ kcal/mol}$, which is lower than that of the CO₂ insertion. The formation of carbonate complex **H** from **G** is exergonic by 9.6 kcal/mol. Therefore, the final ring closure step is important as a thermodynamic sink to irreversibly generate cyclic carbonates.

The overall energy surface is shown in Figure 2.23 As already discussed, each step is kinetically feasible as the activation barriers are lower than 20 kcal/mol. The most energetically severe step is that of CO₂ insertion. This is in good accordance with the fact that the yield of the product from styrene oxide was improved by increasing the CO₂ pressure. In contrast, previous DFT calculations on closely relevant cyclocouplings using binary catalyst systems suggested that epoxide ring opening rather than CO_2 insertion is the most difficult step.²⁴ The formation of cyclic carbonate complex H from the starting complex A is endergonic by 10.4 kcal/mol. This thermodynamic penalty can be mostly attributed to the benzoate ligand slippage step with endergonicity of 11.1 kcal/mol. Thus, the nature of the carboxylate ligand plays a critical role as 1b with the 1-naphthoate ligand superior to 1a with the acetate ligand. The efficiency of the cyclocoupling can further be improved by choosing other ligands that facilitate the ligand slippage.

3. Conclusion

We demonstrated that the combination of porphyrin-based Cu MOFs 1b with tetrabutylammonium bromide efficiently catalyzed cyclocoupling of epoxides and CO₂ under mild



Scheme 5. Final CO₂ insertion and ring-closure steps starting from model complex **F**. Relative Gibbs free energies at 298 K, 1 atm are indicated in parentheses. Atom distances (Å) are given in italic numbers.



Figure 2. Calculated energy surface for the overall process, with relative Gibbs free energies (298 K, 1 atm).

conditions without solvents. This catalyst system has a good substrate scope as epoxides with a long and bulky substituent could be used. A wide range of functional groups, including

alcohol, ether, ester, alkene, alkyne, and haloalkyl groups, were compatible with this catalytic system. However, epoxides with two substituents gave lower yields. The catalyst recycling studies revealed that **1b** could be reused several times for the cyclocoupling of styrene oxide, although the product yields gradually decreased.

The control experiments suggest that the catalytically active sites comprised the Cu paddle wheel unit, although no vacant site is seemingly available. It was proposed that the bridging carboxylate ligand dissociates from one of the two copper centers to assume a κ^1 coordination mode. As such, a vacant coordination site is available for the electrophilic activation of epoxides. This assumption was corroborated by the DFT calculations of a single paddle wheel unit as a model system. The computed energy surfaces suggest that the epoxide ring opening, CO₂ insertion, and the final carbonate ring closure occur at the single copper center and are both kinetically and thermodynamically feasible.

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Supporting Information

Experimental procedures and compound characterization data. This material is available on http://dx.doi.org/10.1246/bcsj.20170371.

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