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# Cu(I) Coordination Polymers as the Green Heterogeneous Catalysts for Direct C-H Bonds Activation of Arylalkanes to Ketones in Water with Spatial Confinement Effect

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S Supporting Information

ABSTRACT: To develop coordination polymers (CPs) as catalysts to selectively catalyze the reaction of C-H bond activation of arylalkanes to their homologous ketones, three new Cu(I)-based coordination polymers  $(Cu^{I}-CPs) [CuI(aas-TPB)]_{n}$ (1),  $[CuBr(ass-TPB)CH_3CN]_n$  (2), and  $\{[Cu(ass-TPB)]Cl\}_n$  (3) (TPB = N, N, N-tris(3-pyridinyl)-1, 3, 5-benzenetricarboxamide)were synthesized. Structural variations from a herringbone fashion one-dimensional framework of 1 to a two-dimensional framework of 2 containing a 48-membered macrocycle and a cationic threedimensional framework of 3 filled with Cl<sup>-</sup> anions were observed arising from the different halogen ions (I<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup>). 1-3 were used as the green heterogeneous catalysts to catalyze direct C-H bond activation reactions of arylalkanes to ketones under mild reaction conditions with water as solvent. Handy product



separation, convenient reaction procedures, and recyclability of these catalysts make the catalytic system fascinating. Moreover, the Cu<sup>1</sup>-CPs performed the reaction with high regioselectivity due to the unique spatial confinement effect of CPs.

### INTRODUCTION

Coordination polymers (CPs) made from metal ions linked by organic ligands are the structurally and compositionally diversified class of function materials of which the physical and chemical properties are investigated intensively for numerous applications including drug delivery,<sup>1</sup> gas liquid/ solid separations,<sup>2</sup> sensing,<sup>3</sup> luminescence,<sup>4</sup> catalysis,<sup>5</sup> and so on. In particular, by introducing catalytically competent moieties via either self-assembly or postsynthetic modification methods, solid CPs-based catalysts have provided a versatile tunable platform to engineer molecular catalysts that are immobilizing, well-defined, and perform a broad range of organic transformations, such as the formations of C-C bond, aldol condensations, oxidations, epoxidations, etc.<sup>6-</sup>

The most vital virtue of CPs is that they can imitate the siteisolation of many catalytic enzyme assembled in nature, because the active catalytic sites are immobilizing and atomistically welldefined, isolated with certain fixed azimuth and distance in the solid.<sup>10</sup> These active catalytic sites can not only increase catalytic activity via eliminating multimolecular catalyst deactivation approaches but also possess exceptional chemo-, size-, shape-, and enantioselectivity. Interestingly, solid CPbased catalysts often display higher activity than that of the corresponding homogeneous catalysts. Besides, several groups including ours have reported other virtues of CP-based catalysts

that are deficient in classic porous carbons and various other solid supports. For example, synergistic interactions with substrates can be facilitated by CPs via the sequential or cooperative manner to obtain the tandem or cooperative catalytic products without isolating intermediates.<sup>11</sup> In particular, when substrates have more than one reaction functional group, the lack of reaction selectivity happens in typical homogeneous system. By contrast, CPs can possess spatial confinement effect and regioselectivity, taking into consideration the uniformly distributed single active sites in CPs with specific coordination geometry, symmetry, and steric configuration, making these materials attractive catalytic selectivity.12

However, for the chemical transformation of methylene groups of arylalkanes to ketones, besides the traditional oxidation using KMnO<sub>4</sub> as an oxidant, the homogeneous,<sup>13</sup> heterogeneous,<sup>14</sup> and metal-free<sup>15</sup> catalysts catalyze C-H bond activation of arylalkanes to form the homologous ketones, which have been rapidly developed in recent years. However, these methods lack selectivity. Overoxidation products are always afforded when substrates have more than one methylene group, so that it is still a challenge to find strategies to realize

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selectivity. Enlightened by the virtues of CPs, especially its spatial confinement effect and regioselectivity, we are interested in developing the oxidation of alkanes catalyzed by CPs as heterogeneous catalysts, and meanwhile high catalytic selectivity can be achieved.

Herein, a series of Cu(I)-based coordination polymers (Cu<sup>I</sup>-CPs) [CuI(*aas*-TPB)]<sub>n</sub> (1), [CuBr(*ass*-TPB)CH<sub>3</sub>CN]<sub>n</sub> (2), and {[Cu(*ass*-TPB)]Cl}<sub>n</sub> (3) (TPB = N,N,N-tris(3-pyridinyl)-1,3,5-benzenetricarboxamide) were prepared and characterized. It shows that 1 and 2 are efficient heterogeneous catalysts and display high regionselectivity for direct C–H bond activation reactions of arylalkanes to ketones in H<sub>2</sub>O under room temperature. In addition, we proposed a plausible mechanism for the catalytic reaction, and the relationship of reactivity– structure was further clarified.

## EXPRTIMENTAL SECTION

Materials and Physical Measurements. *N,N,N*-Tris(3pyridinyl)-1,3,5-benzenetricarboxamide (TPB) was synthesized through a modified method in the literature.<sup>16</sup> All chemical reagents were purchased from commercial suppliers without further purification. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained on Bruker Avance-400 spectrometers. Fourier transform infrared (FT-IR) spectra were performed on a Bruker-ALPHA spectrophotometer with KBr pellets in the 400–4000 cm<sup>-1</sup> region. Powder X-ray diffraction patterns were achieved by using Cu K $\alpha$ 1 radiation on a PANalytical X'Pert PRO diffractometer. High-resolution mass spectrometry–electrospray ionization (HRMS-ESI) was performed on a Micro Q-TOF mass spectrometer. Atomic absorption spectroscopy (AAS) was performed on a Z28000 graphite-oven atomic absorption spectrophotometer.

**Synthesis of [Cul(***aas***-TPB)**]<sub>*n*</sub>**(1).** The mixture of CuI (5.7 mg, 0.03 mmol), TPB (17.6 mg, 0.04 mmol), and 7 mL of acetonitrile was added in a 25 mL Teflon-lined stainless steel container and heated at 120 °C for 3 d. After the mixture cooled to room temperature at a rate of 5 °C/h, yellow block-shaped crystals of 1 were obtained in a yield of 80% based on CuI. Anal. Calcd for  $C_{24}H_{18}$ CuIN<sub>6</sub>O<sub>3</sub>: C, 45.84; H, 2.88; N, 13.36. Found: C, 45.82; H, 2.91; N, 13.74%. IR (KBr, cm<sup>-1</sup>): 3328 (m), 3250 (m), 2162 (vw), 1672 (s), 1653 (vs), 1597 (s), 1525 (vs), 1413 (vs), 1297 (s), 926 (vw), 898 (w), 858 (vw), 800 (s), 724 (w).

**Synthesis of [CuBr**(*ass*-**TPB**)**CH**<sub>3</sub>**CN**]<sub>*n*</sub> (2). The synthesis of 2 was similar to that of complex 1, except that CuBr was used instead of CuI. Yellow block-shaped crystals of 2 were obtained when the mixture was cooled to room temperature at the rate of 5 °C/h in a yield of 40% based on CuBr. Anal. Calcd for  $C_{26}H_{21}$ CuBrN<sub>7</sub>O<sub>3</sub>: C, 50.13; H, 3.40; N, 15.74. Found: C, 50.15; H, 3.37; N, 15.72%. IR (KBr, cm<sup>-1</sup>): 3339 (m), 3258 (m), 2252 (vw), 1683 (vs), 1584 (s), 1525 (vs), 1410 (vs), 1285 (s), 937 (w), 866 (w), 802 (vs), 768 (s), 735 (vw), 722 (m).

**Synthesis of {[Cu(***ass***-TPB)]Cl}<sub>n</sub> (3).** The mixture of CuCl (9.9 mg, 0.1 mmol), TPB (17.6 mg, 0.04 mmol), and 7 mL of acetonitrile was placed in a 25 mL Teflon-lined stainless steel container and heated at 120 °C for 3 d. The yellow block-shaped crystals of 3 were obtained when the mixture was cooled to room temperature at the rate of 5 °C/h in a 60% yield based on CuCl. Anal. Calcd for  $C_{24}H_{18}CuClN_6O_3$ : C, 50.23; H, 3.27; N, 14.68. Found: C, 50.58; H, 3.34; N, 14.62%. IR (KBr, cm<sup>-1</sup>): 3232 (m), 3180 (m), 2092 (vw), 1696 (s),

1586 (m), 1541 (s), 1486 (vs), 1420(vs), 1292 (s), 948 (vw), 907(m), 810(vs), 698(s), 648(w), 645(w).

Typical Procedure for Direct C–H Bonds Activation of Arylalkanes to Ketones in Water. Arylalkanes (1.0 mmol, 1.0 equiv), *tert*-butyl hydroperoxide (TBHP; 1.5 mmol, 1.5 equiv) and catalyst (0.05 mmol, 0.1 equiv based on Cu ion) were added in water (5 mL). The resulting mixture was first ultrasonically treated for 0.5 h and then stirred for 3.5 h in room temperature in the air. For product separation, the aqueous phase was extracted with ethyl acetate (EtOAc;  $3 \times 15$ mL). The organic phases were combined, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The raw products were refined by column chromatography on silica gel, and the pure products were obtained.

**Crystal Data Collection and Refinement.** The data of the complexes 1–3 were collected on a Rigaku Saturn 724 CCD diffractomer (Mo K $\alpha$ ,  $\lambda = 0.710$  73 Å) at a temperature of 20 ± 1 °C. Absorption corrections were used by multiscan program. The Lorentz and polarization effects were corrected by the data. The structures were solved by direct methods and refined on  $F^2$  by the full-matrix least-squares technique with the SHELXL-97.<sup>17</sup> The hydrogen atoms were generated geometrically and refined the using riding model. The details of the crystal data for 1–3 are listed in Table S1, and selected bond lengths and bond angles are listed in Table S2 in the Supporting Information. Crystallographic data for 1–3 were deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 988513, 988512, and 1565786, respectively.

### RESULTS AND DISCUSSION

**Crystal Structure of 1.** A single-crystal X-ray diffraction study indicated that 1 crystallizes in the monoclinic space C2/c. Each Cu(I) is coordinated by I1 and two nitrogen atoms (N1 and N4) of two ligands. The Cu(I) centers are bridged by ligand TPB ligands with *aas* conformation (Scheme 1), and a chain was constructed in the herringbone fashion along *a*-axis (Figure 1a).



a-Conformation means that the oxygen of amide and the nitrogen of pyridyl are in the opposite side. *s*-Conformation means that the two atoms of the ligand are in the same side.

It is noteworthy that the amide group is an interesting functional group due to the two types of hydrogen bonding sites, the -C=0 group working as an electron donor and the -NH moiety working as the electron acceptor. Thus, the amides induce hydrogen bonding interactions with itself, with the counteranions, and with the solvent. As expected, two-dimensional (2D) extended structure of the complex molecules is linked through the hydrogen-bonding interactions between



Figure 1. (a) View of the one-dimensional (1D) chain of compound 1. Hydrogen atoms are omitted for clarity. (b) View of the 3D supermolecular framework of 1 built from the 1D chains.



Figure 2. (a) View of the 2D network of compound 2. Hydrogen atoms are omitted for clarity. (b) View of the 3D supermolecular framework of 2.

the amide nitrogen atom (N5) and the carbonyl oxygen atom (O2) of the next chain (N5–H5…O2 = 2.983 Å; Figure S1b). Furthermore, these 2D structures are further immobilized by  $\pi-\pi$  interactions between parallel pyridyl rings (center-to-center distance of ca. 3.679 Å) to form the three-dimensional (3D) supermolecular structure (Figure 1b).

**Crystal Structure of 2.** X-ray diffraction revealed that **2** belongs to the triclinic space group  $P\overline{1}$  and contains a fascinating zeolite-like network. Cu(I) is coordinated in a distorted tetrahedral coordination environment with a bromine atom and three nitrogen atoms (N1, N4, and N6) from three ligands. The  $C_3$ -symmetic triangular ligand is the *ass* 

conformation (Scheme 1). The Cu(I) ions bridge ligands to construct a 48-membered macrocycle formed 2D network that three  $C_3$ -symmetric triangular facial ligands connect with three Cu(I) centers (Figure 2a). In addition, the plane networks are further packed by hydrogen bonds (N3–H3…Br1 = 3.578 Å, N5–H5A…Br1 = 3.398 Å) to build a 3D zeolite-like framework (Figure 2b and Figure S2b).

**Crystal Structure of 3.** A single-crystal X-ray diffraction study on 3 indicated that it crystallizes in the orthorhombic space *Pbca*. Each Cu(I) is coordinated by N1, N4, and N6 from three ligands. In 3, the  $C_3$ -symmetic triangular ligand TPB in *ass* conformation links Cu(I) ions forming a 2D framework



Figure 3. (a) View of the 2D network of compound 3. Hydrogen atoms are omitted for clarity. (b) View of the 3D supermolecular framework of 3.

structure (Figure 3a). Overall, the cationic framework is filled with Cl<sup>-</sup> ions (Figure 3b). On the basis of charge balance, the asymmetric unit contains one Cl<sup>-</sup> ion occupied in the channels. Furthermore, the -NH hydrogen bond with the Cl<sup>-</sup> anions (N5-H5...Cl = 3.333 Å; N2-H2...Cl = 3.234 Å; N3-H3...Cl = 3.326 Å) connecting these layers to generate the 3D framework (Figure S3b). The framework of 3 is similar to a Ag-MOF (MOF = metal–organic framework) reported by Tzeng group.<sup>18</sup>

The Catalytic Effect of 1–3 for Direct C–H Bond Activation of Hydrocarbons. We selected the optimized conditions of the direct C–H functionalization reaction using diphenylmethane as the substrate. The results of the optimization experiment were shown in Table 1. After extensive screening of the temperature, atmosphere, and solvents, the optimized conditions were obtained in the presence of TBHP as an oxidant and 5 mol % of crystal samples as catalysts in  $H_2O$ under air at room temperature for 4 h, producing the desired

Table 1. Optimized Conditions of the Reaction<sup>a</sup>

Û	+	₩ООН	$\longrightarrow $	
entry	catalyst	atmosphere	solvent	yield, %
1	CuI	air	H <sub>2</sub> O	19
2	1	air	H <sub>2</sub> O	99
3	2	air	H <sub>2</sub> O	97
4	3	air	H <sub>2</sub> O	70
5	none	air	H <sub>2</sub> O	0
6	1	$N_2$	H <sub>2</sub> O	<5
7	1	Ar	H <sub>2</sub> O	<5
8	1	air	acetonitrile	48 <sup>b</sup>
9	1	air	dioxane	51 <sup>b</sup>
10	1	air	DMF	<5
11	1	air	DMA	58
12	1	air	dilyme	<5
13	1	air	NMP	<5
14	1	air	toluene	<5 <sup>b</sup>

<sup>*a*</sup>Reagents and conditions: diphenylmethane (1.0 mmol), TBHP (1.5 mmol), and catalyst (0.05 mmol), room temperature, 4 h. <sup>*b*</sup>Reaction performed at refluxed temperature.

ketone products in the yields of 70%, 97%, and 99%. It showed that 1 worked as an excellent heterogeneous catalyst for the C– H bond activation reaction, while CuI was a less effective homogeneous catalyst with a yield of 19% under the same conditions. 2 and 3 could also work as heterogeneous catalysts for the reaction with the yields of 97% and 70%, respectively. With inert gases such as nitrogen and argon, only a trace amount of the desired compound was produced. The C–H activation proceeded with moderate effectiveness in acetonitrile (48%) and dioxane (51%), but dimethylformamide (DMF), dimethylacetamide (DMA), diglyme, *N*-methyl pyrrolidone (NMP), and toluene were unsuitable solvents. In view of environment, efficiency, cost, simplicity, and stability, we identified  $1/\text{TBHP/H}_2\text{O}/\text{air}$  as our standard conditions for the C–H functionalization reactions.

Structurally diverse alkylarenes were employed in the benzylic Csp<sup>3</sup>-H bond activation to investigate the scope of the three Cu<sup>I</sup>-CPs catalytic processes (Table 2). The catalytic system proceeded smoothly to generate the corresponding carbonyl compounds in moderate or excellent yields. 5a and 6a were converted into the corresponding ketones with 1 in the yields of 93% and 90%, respectively (Table 2, entries 4 and 7). More importantly, to research the regioselectivity of 1-3 on this reaction, substrates with two symmetrical benzylic sites, such as 7a, 8a, 9a, and 10a (Table 2, entries10-21) were employed. Amazingly, it showed that their respective monoketones formed as the sole products by using CPs 1-3 as heterogeneous catalysts. Specifically, using 1 as catalyst, 7a, 8a, and 9a were selectively oxidized to their respective monoketones with yields ranging from 88 to 98% for 4 h (Table 2, entries10, 13, and 16). While for the bulky 10a, the desired monoketone 10b was obtained in a moderate yield of 72% for 8 h. The yield of 10b is significantly lower than other products (Table 2, entries 19-21), which indicates that the size of channels of CPs and substrates plays a significant role in the heterogeneous catalytic reaction. As an effective heterogeneous catalyst, large open channels are needed for CPs to transport organic substrates and products. It shows that the increasing size of the substrates leads to the declining reaction rate but has no effect on the reaction selectivity. In addition, when 2 and 3 were used as catalysts to perform these reactions under the same conditions, the substrates were converted into the respective sole monoketones with moderate yields. In contrast,

Ο

	R = H = F	OOH <u>catalyst (5 mo</u> H <sub>2</sub> O, r.t. air, 4h	1%) ► R∰	Ċ
Entry	Substrate	Product	Catalyst	Isolated Yield/%
1			1	99
2			2	97
3	<b>4</b> a	4b	3	70
4		O H	1	93
5	F		2	90
6	5a	5b	3	65
7	$\sim \sim \sim$	O II	1	$90^{a} 98^{b}$
8			2	$88^{a}96^{b}$
9	6a	6b	3	53 <sup><i>b</i></sup>
10			1	98
11			2	96
12	7a	7b	3	72
13	$\bigwedge \frown$	O A	1	98
14			2	97
15	8a	8b	3	41
16			1	88
17			2	85
18	9a	9b	3	64
19		O	1	$72^b$
20			2	$65^b$
21	10a	10b	3	$46^b$

Гable	e 2.	Direct	С–Н	Bonds	Activation	of .	Aryla	lkanes	to	Ketones	Catal	yzed	by	$1 - 3^{\circ}$	
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<sup>a</sup>Reagents and conditions: arylalkanes (1.0 mmol), TBHP (1.5 mmol), and catalyst (0.05 mmol), H<sub>2</sub>O (5 mL), room temperature, air, 4 h. <sup>b</sup>8 h.

this reaction under a series of catalytic conditions (KAuCl<sub>4</sub>, MnO<sub>2</sub>, ionic liquid, palladium complexes, ruthenium complexes, etc.) generally provided a mixture of mono- and bisketone compounds under strict operation conditions (high temperature, toxic solvents, complex reagents, etc.).<sup>19</sup> For example, CuI, a commonly used homogeneous catalyst for the direct C–H bond activation of diphenylmethane only gave monoketone benzophenone in a yield of 19% under the same reaction conditions (Table 1, entry 1). In addition, the similar selectivity could only be found using Fe(III)/THA (thymine-1-acetate) as catalysts and H<sub>2</sub>O<sub>2</sub> as an oxidant.<sup>13a</sup> Compared to other catalytic systems, CPs have great potential as heterogeneous catalyst for the reaction not only because their unique structural features, including crystallinity, active-site uniformity, high surface area, and porosity, but also due to their

atomistically well-defined isolated active sites with uniformly fixed configuration and suitable channel size throughout the solid, which endow them with spatial confinement effect and catalyze the reaction with regioselectivity. In addition, the catalytic active sites of the CPs **1–3** are arranged periodically with the distance of neighboring Cu(I) ions more than 6 Å, which can effectively avoid synergic activity among Cu(I) ions, yielding products with the high selectivity. Therefore, the catalytic systems with Cu<sup>I</sup>–CPs as catalysts in H<sub>2</sub>O under air at room temperature not only remain environmental friendly conditions but also express high selectivity in the reactions that C–H bonds of arylalkanes are directly activated to ketones.

The mechanism for the oxidation of alkanes to the corresponding ketones catalyzed by the Cu(I)-based CPs were proposed based on previous report (Scheme 2).<sup>20</sup> The

# Scheme 2. Proposed Mechanism for the Oxidation of Alkanes Catalyzed by Cu<sup>I</sup>-CPs



intermediates of <sup>*t*</sup>BuO· radical and HO-Cu<sup>II</sup>XL are first given by ultrasonic treatment of TBHP with Cu(I)-based CPs. Subsequently, the <sup>*t*</sup>BuO· radical abstracts one of allylic H atoms from the substrate to produce the allylic radical I, which further reacts with HO-Cu<sup>II</sup>XL to produce the corresponding peroxyether II. Finally, II reacts with O<sub>2</sub> to provide the expected ketone. Therefore, the activity centers in 1 are coordinated with I<sup>-</sup> anions, which may be easily cleaved and form the transient state (Cu···I) to make contact with active centers of substrates during the catalytic process. In contrast, the lowest catalytic activity of **3** may be caused by the dissociative Cl<sup>-</sup> anions, which are unfavorable for catalyzing decomposition of TBHP into <sup>*t*</sup>BuO· and HO· radicals.

To study whether the C-H functionalizations were heterogeneous or homogeneous, atomic absorption spectroscopy analysis of the filtrate showed the presence of slight leaching (<1 ppm) of copper from the crystalline sampes of 1 during the reaction. Next, a filtration experiment was conducted. After 25% conversion of 4a catalyzed by 1, we use a sand core funnel to filtrate the catalysts from reaction mixture. Then the filter liquor was stirred for 3 h. It was found that the conversion was constant in the process. The experiment data clearly demonstrated that 1 was a heterogeneous catalyst. Furthermore, the recyclability of the catalyst was investigated with 1 and diphenylmethane in this reaction. In the recyclability experiments, 1 could be easily recovered by filtrating from the reaction mixture. The reused catalyst indicated that only tiny catalyst was deteriorated after six runs (Figure 4a). Besides, the PXRD patterns of the crystalline



Figure 4. (a) The recyclability of the catalyst of 1 in this reaction. (b) Comparison of the PXRD patterns of 1 before and after recycle experiments.

samples of 1 after the sixth round of reaction completely matched the simulated 1 (Figure 4b) and displayed that the framework did not collapse, which revealed that the framework could retain integrated after at least six runs. Likewise, the powder PXRD patterns of 2 and 3 after catalytic cycle also closely matched the simulated **2** and **3**, respectively (Figures S2 and S3).

#### CONCLUSION

In summary, a series of catalytically active Cu(I)-based CPs 1– 3 were successfully regulated with different halogen ions (I<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup>) under the same reaction conditions. 1–2 could not only be used as the efficient and green heterogeneous catalysts to catalyze direct C–H bond activation reactions of arylalkanes to ketones in water under room temperature but also present spatial confinement effect, the reaction proceeding with high regioselecticity. We also showed that the CPs retained their integrated crystallinity after the catalysis. This work provides important insights into CPs-catalyzed regioselective reaction.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02106.

Experimental details for all new compounds and all reactions reported. Crystallographic information for complexes 1-3 in CIF format and additional figures and tables for structural, spectral, and computational characterization (PDF)

#### **Accession Codes**

CCDC 1565786 and 988512–988513 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/ cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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