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### FULL PAPER

# In situ stabilization of Pd(0) nanoparticles into a mixture of natural carbohydrate beads: A novel and highly efficient heterogeneous catalyst system for Heck coupling reactions

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Email: rahmatió1@yahoo.com Ardeshir Khazaei, Faculty of Chemistry, Bu-Ali Sina University, PO Box 651783868, Hamedan, Iran. Email: khazaei\_1326@yahoo.com A convenient, mild and cost-effective synthesis of palladium nanoparticles stabilized by a mixture of natural carbohydrate beads (gum arabic and pectin) as a new bio-organometallic catalyst is reported. Powder X-ray diffraction, transmission and scanning electron microscopies and energy-dispersive X-ray and UV–visible spectroscopies were employed to characterize this supported Pd nanoparticles/ gum arabic/pectin catalyst. The nanocatalyst exhibited efficient activity in Mizoroki–Heck cross-coupling reactions between various aryl halides and *n*-butyl acrylate under solvent-free conditions. The catalyst can easily be recovered from the reaction system and reused several times with high yields. The products were obtained in short reaction times with excellent yields.

### KEYWORDS

gum arabic, Mizoroki-Heck reaction, palladium nanoparticles, pectin, solvent-free

# **1 | INTRODUCTION**

In recent years, the synthesis of metal nanoparticles with a variety of geometries has been an especially important issue because their optical, electronic, magnetic and biomedical properties can be tuned by controlling their shape and size.<sup>[1]</sup> Also design and development of green catalysts have attracted a large number of studies by academic and industrial groups to reduce or eliminate the use of hazardous substances.<sup>[2]</sup>

Recently, immobilization of palladium nanoparticles on solid supports to prepare active and stable catalytic systems has attracted interest, and various supports have been employed to stabilize the nanoparticles, such as silica-based materials,<sup>[3–8]</sup> dendrimers,<sup>[9]</sup> metal oxides,<sup>[10–12]</sup> carbon nanotubes,<sup>[13–15]</sup> polymers,<sup>[16]</sup> ionic liquids,<sup>[17–20]</sup> polyvinylpyrrolidone,<sup>[21,22]</sup> gelatin,<sup>[23]</sup> polyaniline<sup>[24]</sup> and carbohydrate-based materials.<sup>[25–27]</sup>

In order to develop the use of carbohydrate-based materials as supports for palladium nanoparticles, we decided to introduce a gum arabic/pectin mixture as a suitable and naturally degradable support for the stabilization of palladium nanoparticles. Gum arabic, also known as acacia gum, is a natural gum made of hardened sap taken from two species of the acacia tree.<sup>[28]</sup> Gum arabic is a biologically active branched polysac-charide<sup>[29]</sup> with wide applications in food and pharmaceutical industries.<sup>[30]</sup> This natural carbohydrate has also been used for stabilization of nanostructures.<sup>[31–33]</sup>

Pectin is a natural polymer extensively employed in the food industry, as a thickener or stabilizing agent. It is a polysaccharide that is found extensively in citrus peel. Some unique properties of pectin, such as biodegradability, flexibility, non-toxicity and carrying freely available hydroxyl groups, make it suitable for many applications in various areas of science.<sup>[34,35]</sup> Pectin contains free carboxyl groups on its backbone which can form complexes with Pd(II) ions in solution and reduce them to Pd(0) without using any extra reducing agent such as NaBH4, hydrazine or molecular hydrogen. This slow-rate in situ reduction of Pd(II) to Pd(0) causes the formation of small-size and well-distributed palladium nanoparticles on the surface of pectin.<sup>[36]</sup> Therefore gum arabic/pectin mixture being used as a new support for palladium species has two advantages: first, it can reduce Pd(II) to Pd(0) via its available free carboxyl groups by liberation of CO<sub>2</sub> gas; and, second, it acts as a highly

1

functionalized support that can stabilize the reduced form of the palladium nanoparticles by ligation.

The Mizoroki–Heck coupling reaction is among the most important and widely used reaction for the formation of carbon–carbon bonds, which allows the arylation, alkylation or vinylation of various alkenes through their reactions with aryl, vinyl, benzyl or allyl halides, acetates or triflates in the presence of palladium and a suitable base in a single step under mild conditions.<sup>[37]</sup>

It is of current interest to develop new catalytic systems which meet the goals of simple operation procedure, low catalyst loading and high activity towards aryl halides. Herein, we report that palladium nanoparticles supported on gum arabic/pectin mixture ( $Pd_{np}$ /gum arabic/pectin) generated from  $PdCl_2$  *in situ* showed high activity in Mizoroki–Heck cross-coupling reactions between activated and non-activated aryl halides and *n*-butyl acrylate under solvent-free conditions.

#### 2 | EXPERIMENTAL

#### 2.1 | Synthesis of Pd<sub>np</sub>/Gum arabic/Pectin

Pectin (0.5 g) and gum arabic (0.5 g) were dissolved in water (100 ml) at room temperature. To this solution was added a solution of  $PdCl_2$  (100 ml, 1 mM) and diluted with water (100 ml). The reaction mixture was refluxed at 100°C for 5 h so that the complete conversion of Pd(II) to Pd(0) was ensured. The mixture was cooled to room temperature and the solvent was evaporated. The obtained dark grey composite was dried by a flow of air over night and then under vacuum for 24 h.

# 2.2 | General method for Mizoroki–Heck reaction using nanocatalyst

To a flask were added  $Pd_{np}/gum$  arabic/pectin (0.05 g of the composite), aryl halide (1 mmol), *n*-butyl acrylate (1.5 mmol, 0.21 ml) and *n*-Pr<sub>3</sub>N (1.5 mmol, 0.29 ml) under solvent-free conditions. The mixture was stirred at 140°C in air. The reaction having been completed (monitored by TLC), ethyl acetate (10 ml) was added to the flask. The catalyst was separated by simple filtration. Water (3 × 15 ml) was added to the ethyl acetate phase and decanted. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the crude product was purified by column chromatography.

**Product 1a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.81 (t, 3H, J = 8 Hz), 1.29 (sex, 2H, J = 8 Hz), 1.62 (M, 2H, J = 8 Hz), 4.11 (t, 2H, J = 8 Hz), 6.31 (d, 1H, J = 16 Hz), 7.17 (M, 2H), 7.28 (M, 1H), 7.50 (M, 1H), 7.90 (M, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 11.61, 13.62, 19.09, 30.65, 55.56, 64.48, 77.24, 120.81, 127.50, 130.09, 134.71. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1716 (C=O).

**Product 2a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz,  $\delta$ , ppm): 0.89, (t, 3H, J = 8 Hz), 1.35 (sex, 2H, J = 8 Hz), 1.62 (sex,

2H, J = 8 Hz), 4.03 (t, 2H, J = 8 Hz), 6.39 (d, 1H, J = 16 Hz), 7.3 (t, 3H), 7.44 (M, 2H), 7.6 (d, 1H, J = 16 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz,  $\delta$ , ppm): 13.74, 21.02, 30.78, 60.37, 64.41, 118.3, 128.07, 130.19, 134.48, 144.53, 167.08. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1714.17 (C=O).

**Product 3a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.86 (t, 3H, J = 8 Hz), 1.33 (quint, 2H, J = 8 Hz), 1.60 (sex, 2H, J = 8 Hz), 3.17 (s, 3H), 4.11 (t, 2H, J = 8 Hz), 6.40 (d, 1H, J = 8 Hz), 6.71 (m, 2H), 7.20 (m, 1H), 7.39 (m, 1H), 7.8 (1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 13.72, 19.21, 30.82, 55.40, 64.31, 77.15, 111.11, 120.62, 123.39, 128.88, 131.46, 139.98, 158.3, 167.6. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1710.62 (C=O).

**Product 4a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.87 (t, 3H, J = 8 Hz), 1.35 (sex, 2H, J = 8 Hz), 1.60 (m, 2H), 2.21 (s, 3H), 4.11 (d, 2H, J = 8 Hz), 6.28 (d, 1H, J = 16 Hz), 7.11 (d, 2H, J = 8 Hz), 7.30 (d, 2H, J = 8 Hz), 7.50 (d, 1H, J = 16 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 11.27, 13.79, 19.22, 21, 44, 30.81, 64.32, 117.20, 128.04, 131.75, 144.50, 167.27. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1714 (C=O).

**Product 5a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.89 (t, 3H, J = 8 Hz), 1.37 (sex, 2H), 1.62 (quint, 2H), 2.44 (s, 3H), 4.15 (t, 2H, J = 4 Hz), 6.40 (d, 1H, J = 16 Hz), 7.59 (d, 1H, J = 8 Hz), 7.82 (d, 1H, J = 16 Hz), 7.98 (quarter, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 13.66, 13.7, 13.75, 19.16, .68, 64.85, 121.37, 123.33, 125.45, 127.28, 138.98, 139.73, 148.14, 166.17. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1716 (C=O).

**Product 6a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.86 (t, 3H, J = 8 Hz), 1.34 (sex, 2H), 1.59 (sex, 2H), 3.70 (s, 3H), 4.09 (t, 2H, J = 4 Hz), 6.19 (d, 1H, J = 16 Hz), 6.8 (d, 2H, J = 8 Hz), 7.3 (d, 2H, J = 12 Hz), 7.5 (d, 1H, J = 16 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 10.16, 10.15, 12.7, 15.68, 18.1, 29.67, 47.47, 63.81, 112.31, 120.89, 126.93, 130.69, 137.75, 165.5. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1711 (C=O).

**Product 7a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.88 (t, 3H, J = 7.2 Hz), 1.36 (sex, 2H), 1.63 (sex, 2H), 4.15 (t, 2H, J = 8 Hz), 6.42 (d, 1H, J = 16 Hz), 7.55 (t, 3H, J = 12 Hz), 7.60 (d, 2H, J = 8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 10.16, 12.7, 18.06, 29.67, 53.24, 63.841, 112.31, 117.34, 120.89, 127.06, 130.69, 165.2. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1713 (C=O).

**Product 8a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.88 (t, 3H, J = 8 Hz), 1.36 (quint, 2H), 1.62 (sex, 2H), 4.10 (t, 2H, J = 8 Hz), 6.43 (d, 1H, J = 8 Hz), 7.54 (t, 3H, J = 8 Hz), 7.61 (quart, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 13.7, 19.14, 30.66, 64.78, 113.29, 118.34, 121.87, 128.33, 132.61, 138.73, 142.07, 166.18. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1715 (C=O).

**Product 9a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.2 MHz, *δ*, ppm): 0.88 (t, 3H, J = 4 Hz), 1.35 (sex, 2H), 1.63 (quint, 2H, J = 8 Hz), 4.10 (t, 2H, J = 8 Hz), 6.30 (d, 1H, J = 16 Hz), 7.26 (d, 2H, J = 8 Hz), 7.36 (d, 2H, J = 8 Hz), 7.52 (d, 1H, J = 16 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz, *δ*, ppm): 11.24, 13.75, 16.83, 19.19, 30.75, 54.1, 64.55, 118.88, 128.12, 132.96, 166.85. FT-IR ( $\nu$ , cm<sup>-1</sup>): 1715 (C=O).

#### 2.3 | Procedure for reusability of nanocatalyst

After the completion of the reaction for the first run, the reaction mixture was cooled to room temperature and ethyl acetate (5 ml) was added to the reaction mixture in order to extract the organic layer. The ethyl acetate phase was removed using a syringe and the catalyst was dried under vacuum. The dry catalyst was reused for subsequent reaction. This process was repeated three times with success (Table 1).

#### 2.4 | Optimizing reaction conditions

The coupling reaction of iodobenzene with *n*-butyl acrylate was used as a model reaction to investigate the catalytic performance of  $Pd_{np}/gum$  arabic/pectin. The influence of bases, solvents and reaction temperature on the yield was investigated (Table 2). Employing dimethylsulfoxide (DMSO) as the solvent in the presence of *n*-Pr<sub>3</sub>N at 140°C gave 100% conversion of the starting material after 17 min (Table 2, entries 1 and 2). The use of other protic and organic solvents (Table 2, entries 2–4) was not beneficial to the process. We also studied the reaction under solvent-free conditions. The results clearly show that the reaction under solvent-free conditions (Table 2, entry 8) proceeded better than in solvents with an excellent yield and shorter reaction time. The reaction was also studied at various temperatures under

**TABLE 1** Recycling for the reaction of iodobenzene with *n*-butyl acrylatecatalysed by  $Pd_{np}/gum$  arabic/pectin

Run	1	2	3
Time (min)	6	8	11

**TABLE 2** Optimization studies for reaction of iodobenzene with *n*-butylacrylate in presence of  $Pd_{np}$ /gum arabic/pectin<sup>a</sup>

Entry	Base	Solvent	<i>T</i> (°C)	Time (min)	Yield (%) <sup>b</sup>
1	<i>n</i> -Pr <sub>3</sub> N	DMSO	140	17 min	94 (100)
2	<i>n</i> -Pr <sub>3</sub> N	EtOH	Reflux	900	36 (41)
3	<i>n</i> -Pr <sub>3</sub> N	$H_2O$	Reflux	900	18 (12)
4	<i>n</i> -Pr <sub>3</sub> N	Toluene	Reflux	900	8 (16)
5	<i>n</i> -Pr <sub>3</sub> N	Solvent free	100	360	70 (79)
6	<i>n</i> -Pr <sub>3</sub> N	Solvent free	120	145	89 (100)
7	n-Pr <sub>3</sub> N	Solvent free	130	40	90 (100)
8	<i>n</i> -Pr <sub>3</sub> N	Solvent free	140	6	95 (100)
9	DABCO	Solvent free	140	80	90 (100)
10	KOAc	Solvent free	140	900	81 (87)
11	$K_2CO_3$	Solvent free	140	900	89 (94)
12	NaOH	Solvent free	140	900	62 (70)

<sup>a</sup>Reactions carried out using 1 mmol of idobenzene, 1.5 mmol of *n*-butyl acrylate and 1.5 mmol of base.

<sup>b</sup>Yields are given for isolated products. The data presented in parenthesis refer to the conversion of iodobenzene.

-WILEY-Organometallic 3 Chemistry

solvent-free conditions. The results demonstrated that the temperature plays a significant role in the reaction rate. The activity of the catalyst increased with increasing temperature (Table 2, entries 5–8) with the activity being very high at 140°C. During our optimization studies, various bases were examined and the catalyst was found to be very active and selective for the reaction in the presence of *n*-Pr<sub>3</sub>N (Table 2, entry 8) as a liquid organic base, while the reaction rate was very slow when inorganic bases were used (Table 2, entries 10–12). Entry 8 (bold) shows our selected conditions for the Mizoroki–Heck reaction.

#### **3** | RESULTS AND DISCUSSION

 $Pd_{np}/gum$  arabic/pectin was prepared by addition of an aqueous solution of  $PdCl_2$  (100 ml, 1 mmol) to pectin and gum arabic (0.5 g of each dissolved in 100 ml of water) without any extra reducing agent under reflux conditions for 5 h (Figure 1). This solution was refluxed giving a grey solution and, after drying in vacuum, afforded a dark grey solid.

UV-visible spectroscopic data for the resulting supported Pd nanoparticles indicate the conversion of Pd(II) to Pd(0) by the disappearance of the peak at around 450 nm (Figure 2).



FIGURE 1 Preparation of Pd<sub>np</sub>/gum arabic/pectin.



**FIGURE 2** UV-visible spectra of (A) Pd(II) before reduction and (B) Pd(0) after reduction with gum arabic and pectin.

#### 4 Applied Organometallic Chemistry

This change shows that the mixture of pectin and gum arabic is able to form complexes with Pd(II) ions and reduce them to Pd(0).

The result of energy-dispersive X-ray analysis (EDX) shows the presence of palladium. Its loading amount is measured to be 1.83% (*w*/w) in the Pd<sub>np</sub>/gum arabic/pectin catalyst. In Figure 3, the EDX spectrum also shows signals of carbon, nitrogen and oxygen being present in the gum arabic and pectin.

The X-ray diffraction (XRD) pattern of the  $Pd_{np}/gum$  arabic/pectin catalyst confirms the formation of Pd nanoparticles. The XRD pattern shows that the characteristic peaks at (1 1 1), (2 0 0) and (3 1 1) can be clearly observed for Pd particles (Figure 4). These characteristic peaks indicate crystallographic planes of the Pd(0) nanoparticles. According to crystallographic planes from the diffraction pattern, a face-centred cubic crystalline structure is indicated for Pd(0).

A transmission electron microscopy (TEM) image of the catalyst shows that Pd nanoparticles with near-spherical morphology are formed onto the surface of gum arabic and pectin with relatively good monodispersity. The TEM image indicates that the size of the palladium particles must be in the range 3–6 nm (Figure 5). Also a field-emission scanning electron microscopy (FESEM) image of the Pd<sub>np</sub>/gum arabic/pectin catalyst shows the size of the particles to be in the range 3–6 nm (Figure 6).

In order to show the application of these nanoparticles in organic synthesis, we applied them as catalyst in the Mizoroki–Heck reaction. With the optimized reaction conditions, a range of aryl iodides and bromides with various substituent groups with *n*-butyl acrylate were examined in the Mizoroki–Heck reaction. The reaction was performed under



FIGURE 3 EDX spectrum of Pd<sub>np</sub>/gum arabic/pectin.



FIGURE 4 XRD pattern of Pd<sub>np</sub>/gum arabic/pectin.



**FIGURE 5** TEM image of the  $Pd_{np}/gum$  arabic/pectin catalyst showing the morphology of Pd nanoparticles on the surface.



**FIGURE 6** FESEM image of  $Pd_{np}$ /gum arabic/pectin catalyst that shows the morphology of Pd nanoparticles on the surface.

solvent-free conditions at  $140^{\circ}$ C and in the presence of n-Pr<sub>3</sub>N. The desired products are obtained in short reaction times with excellent yields (Table 3).

High reaction rates and yields are obtained with both activated and non-activated aryl iodides (Table 3, entries 1–7). Aryl iodides without any substituent and activated aryl iodides with electron-withdrawing substituents are reactive substrates in Mizoroki–Heck reactions and the corresponding reactions are completed in shorter times. As an example, the reaction of iodobenzene with *n*-butyl acrylate is completed within 6 min giving the desired product in 95% isolated yield (Table 3, entry 2). Non-activated aryl iodides with electron-donating substituents on the aromatic ring are not reactive substrates in Heck reactions and the corresponding reactions are completed in longer reaction times.

The Pd<sub>np</sub>/gum arabic/pectin catalytic system was also applied for reactions of substituted aryl bromides and 
 TABLE 3
 Reaction of aryl halides with *n*-butyl acrylate catalysed by Pd<sub>np</sub>/gum arabic/pectin



heteroaryl bromides giving the desired products in moderate to high yields (Table 3, entries 8 and 9).

To show the catalytic activity of the  $Pd_{np}/gum$  arabic/pectin system, we compare previously reported systems with the

present system in the Mizoroki–Heck reaction. Bhaumik and co-workers reported the application of Pd nanoparticles tethered into mesoporous polymer MPTA1 in the Mizoroki– Heck reaction of iodobenzene with *n*-butyl acrylate in the

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# 6 WILEY-Organometallic Chemistry

presence of K<sub>2</sub>CO<sub>3</sub> as a base in water under reflux. Under these conditions, the reaction was completed within 5 h,<sup>[38]</sup> while for a similar reaction with our catalytic system, the desired product is obtained within 6 min in 95% yield (Table 3, entry 2). Also, in another report, palladium supported on superparamagnetic nanoparticles was used as a catalyst for the Mizoroki-Heck reaction of iodobenzene with *n*-butyl acrylate. The reaction was completed within 5 h in the presence of K<sub>2</sub>CO<sub>3</sub> in N-methyl-2-pyrrolidone as solvent at 130°C,<sup>[39]</sup> whereas a similar reaction using the present catalyst, as mentioned above, is completed within 6 min. Wang and co-workers reported the application of Pd nanoparticles supported on functionalized mesoporous silica in the Mizoroki-Heck reaction of iodobenzene with *n*-butyl acrylate in the presence of  $Et_3N$  as a base in dimethylformamide at 120°C. Under these conditions, the reaction was completed within 1 h.[40] A similar reaction under our conditions gives the desired product within only 6 min in 95% yield (Table 3, entry 2).

The *in situ* generation of nanoparticles without addition of any external reducing agents, stability toward air and humidity, easy handling and recycle ability are some unique features of the  $Pd_{np}$ /gum arabic/pectin catalytic system. It is worth mentioning that some reactions proceeding in the presence of the  $Pd_{np}$ /gum arabic/pectin system under solvent-free conditions are among the fastest ever reported.

The reusability of heterogeneous catalysts is seen to be of great importance. The reusability of the catalyst was checked using the reaction of iodobenzene with *n*-butyl acrylate as substrates in the presence of the catalyst and *n*-Pr<sub>3</sub>N at 140°C. After the reaction was completed in the first run, the organic compounds were separated from the reaction mixture by a simple extraction and the resulting solid mass was reused three times. In the first run, the reaction is completed within 6 min with 95% yield. The nanocatalyst was reused three times with some decrease in the catalytic activity of the catalyst. For the third run, the reaction was completed within 11 min with 89% yield. It is interesting to note that during the recycling process the shape and size of the nanocatalyst do not change notably.

#### 4 | CONCLUSIONS

In summary, a novel, environmentally friendly, one-step method to synthesize stable Pd nanoparticles is reported here.  $Pd_{np}/gum$  arabic/pectin as a new category of nanocomposite was obtained easily under green conditions without addition of any external reducing agent. The nanoparticles immobilized on the mixture of gum arabic and pectin showed high catalytic activity in the Heck reaction for various aryl halides (iodides and bromides) under solvent-free conditions. This green approach for the synthesis of Pd nanoparticles may find various medicinal as well as technological applications. The yields for the reactions of aryl iodides and bromides, with respect to reaction time and amount of catalyst, show that the catalyst has excellent activity. The supported palladium nanoparticles can be easily recovered and reused.

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