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A highly efficient heterogeneous rhodium(I)-catalyzed C–S coupling reaction of thiols with polychloroalkanes or alkyl halides under mild conditions

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Heterogeneous C–S coupling reaction of thiols with polychloroalkanes or alkyl halides was achieved at 30 or 80 °C in the presence of 5 mol% of an MCM-41-immobilized bidentate phosphine rhodium complex (MCM-41-2P-RhCl(PPh_3)) and triethylamine, yielding a variety of formaldehyde dithioacetals, ethylenedithioethers and unsymmetric thioethers in good to excellent yields. This heterogeneous rhodium catalyst can be easily recovered and recycled by simple filtration of the reaction solution and used for at least 10 consecutive trials without significant loss of activity. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: rhodium; C–S coupling; functionalized MCM-41; thiol; heterogeneous catalysis

Introduction

Thioethers are useful synthetic intermediates in many aspects of organic and medicinal chemistry, with applications in organic, inorganic, bioorganic, medicinal and heterocyclic synthesis.[1] Numerous synthetic methods have been developed for the preparation of thioethers;[2] such methods typically involve the condensation of a thiol (or disulfide) with an activated halide in the presence of a base.[3] In addition, a variety of other methods have been used for their preparation.[4] Even so, there still are synthetic difficulties that need to be addressed. High temperatures, several equivalents of base or strong reducing agents are often required.[5] The development of efficient methods for the formation of carbon–sulfur bonds has been a subject of interest in synthetic chemistry since Migita *et al.* first reported cross-coupling reactions of aryl halides with thiols in the presence of a palladium catalyst.[6] A wide range of transition metals have been used to catalyze this coupling reaction, including palladium,[7] nickel,[8] cobalt,[9] copper[5,10] and indium.[11] Recently, Tanaka and Ajiki reported a $RhCl(PPh_3)_3$-catalyzed reaction of thiols with polychloroalkanes or alkyl halides, which provides a convenient new method for the preparation of formaldehyde dithioacetals, ethylenedithioethers, thioformates, dithiocarbonic esters and unsymmetric thioethers under mild reaction conditions.[12] However, industrial applications of homogeneous rhodium complexes remain a challenge because they are expensive, cannot be recycled and difficult to separate from the product mixture, which is a particularly significant drawback for their application in the pharmaceutical industry. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. The high costs of transition metal catalysts coupled with toxic effects associated with many transition metals have led to an increased interest in immobilizing catalysts onto supports. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[13] So far, supported palladium catalysts have successfully been used for the Heck reaction, the Suzuki–Miyaura reaction, the Sonogashira reaction, the Stille reaction, etc.[14] However, carbon–carbon or carbon–heteroatom bond formation reactions catalyzed by heterogeneous rhodium complexes have received less attention.[15]

The discovery of the mesoporous material MCM-41 has given an enormous stimulus to research in heterogeneous catalysis and provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[16] MCM-41 has a regular pore diameter of *ca* 5 nm and a specific surface area $> 700\ m^2\ g^{-1}$.[17] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach the surfaces of channels.[18] It is generally believed that a high surface area of a heterogeneous catalyst results in high catalytic activity. Considering the fact that the MCM-41 support has an extremely high surface area and the catalytic rhodium species is anchored on the inner surface of the mesopore of the MCM-41 support, we expect that an MCM-41-immobilized rhodium complex catalyst will exhibit high activity and good reusability. Shyu *et al.* reported a phosphinated MCM-41-supported rhodium complex for catalytic hydrogenation of olefins and found that it is an excellent hydrogenation catalyst with turnover frequency three times higher than that of $RhCl(PPh_3)_3$ in the hydrogenation of cyclohexene.[19]

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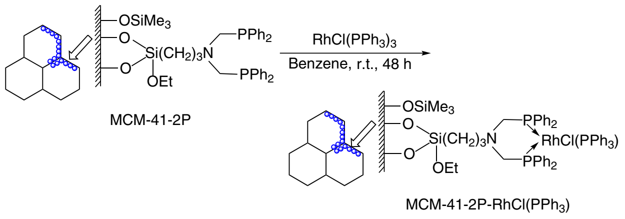
However, to the best of our knowledge, no C–S coupling reaction of thiols with alkyl halides catalyzed by an MCM-41-immobilized phosphine rhodium complex has been reported until now. In continuing our efforts to develop greener synthetic pathways for organic transformations, we herein report the application of an MCM-41-immobilized bidentate phosphine rhodium(I) complex (MCM-41-2P-RhCl(PPh_3)) as an extremely effective and recyclable heterogeneous catalyst for C–S coupling reactions of thiols with polychloroalkanes or alkyl halides.

Results and Discussion

The MCM-41-immobilized bidentate phosphine rhodium(I) complex MCM-41-2P-RhCl(PPh_3) was easily synthesized by the reaction of diphosphino-functionalized MCM-41 (MCM-41-2P) with $RhCl(PPh_3)_3$ according to our previous reported method (Scheme 1).[20] The P:Rh mole ratio of the MCM-41-2P-RhCl(PPh_3) was determined to be 4.5 from elemental analyses.

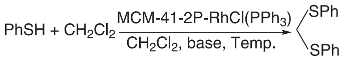
In our initial screening experiments, the heterogeneous C–S coupling reaction of thiophenol (0.5 mmol) with dichloromethane (2.0 ml) was chosen as a model reaction, and the influences of various reaction parameters such as bases, reaction temperatures and rhodium catalyst quantities on the reaction were tested. The results are summarized in Table 1. At first, the effect of base was examined, and a significant base effect is observed. It is evident that a good yield is obtained when Et_3N is used as base (entry 1), whereas DBU, *n*-Bu_3N, *n*-Bu_2NH and *n*-$BuNH_2$ are substantially less effective (entries 2–5). The reaction is completely blocked when inorganic bases such as K_2CO_3 and Cs_2CO_3 are used, presumably due to the poor solubility of these salts in organic solvents (entries 6 and 7). So, Et_3N was finally selected as the base for the reaction. To our delight, employing excess amounts of Et_3N (0.5 ml) affords the desired bis(phenylthio)methane in excellent yield (entry 8). We then investigated the effect of reaction temperature on the reaction. Reducing the temperature to 20 °C results in a decrease in yield and the reaction also proceeds smoothly at 40 °C (entries 9 and 10). Finally, the amount of supported rhodium catalyst was also screened, and 5.0 mol% MCM-41-2P-RhCl(PPh_3) is found to be optimal; a lower yield is observed and a longer reaction time is required when the amount of the catalyst is decreased (entry 11). Increasing the amount of rhodium catalyst could shorten the reaction time, but does not increase the yield of bis(phenylthio)methane (entry 12). No reaction is observed in the absence of rhodium catalyst (entry 13). Therefore, the optimal catalytic system involves the use of MCM-41-2P-RhCl(PPh_3) (5 mol%), Et_3N (0.5 ml) in CH_2Cl_2 (2.0 ml) at 30 °C under argon for 24 h (entry 8).

To examine the scope for this heterogeneous C–S coupling reaction, we investigated reactions using a variety of thiols and different polychloroalkanes as substrates under the optimized reaction conditions (Scheme 2). The results are summarized in Table 2.



Scheme 1. Preparation of MCM-41-2P-RhCl(PPh_3) complex.

Table 1. Reaction condition screening for the reaction of thiophenol with CH_2Cl_2[a]

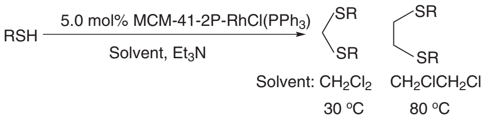


Entry	Base	Temp. (°C), time (h)	Catalyst amount (mol%)	Yield[b] (%)
1	Et_3N	30, 36	5.0	67
2	DBU	30, 36	5.0	52
3	*n*-Bu_3N	30, 36	5.0	54
4	*n*-Bu_2NH	30, 48	5.0	46
5	*n*-$BuNH_2$	30, 48	5.0	42
6	Cs_2CO_3	30, 36	5.0	0
7	K_2CO_3	30, 36	5.0	0
8[c]	Et_3N	30, 24	5.0	95
9[c]	Et_3N	20, 36	5.0	79
10[c]	Et_3N	40, 20	5.0	93
11[c]	Et_3N	30, 48	2.5	75
12[c]	Et_3N	30, 16	10	94
13[c]	Et_3N	30, 24	0	0

[a] Reaction was performed using 0.5 mmol of thiophenol, 1.0 mmol of base in 2.0 ml of CH_2Cl_2 under argon.

[b] Isolated yield based on thiophenol used.

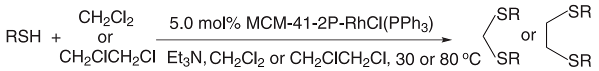
[c] Et_3N (0.5 ml) was used.



Scheme 2. Reactions of thiols with polychloroalkanes catalyzed by MCM-41-2P-$RhCl(PPh_3)_3$.

The C–S coupling reactions of CH_2Cl_2 with a variety of substituted thiophenols proceed smoothly in the presence of 5.0 mol% MCM-41-2P-RhCl(PPh_3) and Et_3N at 30 °C affording the corresponding formaldehyde dithioacetals **3b–3d** in excellent yields (entries 2–4). Various electron-donating and electron-withdrawing groups such as $-CH_3$, –Cl and –F on aryl thiols are well tolerated. The reactions of alkyl thiols with CH_2Cl_2 also proceed smoothly under the same conditions to furnish the desired products **3e–3 g** in good yields (entries 5–7). A hydroxyl-substituted alkanethiol can be used as the substrate, affording selectively the desired coupling product **3 g** in 67% yield (entry 7). The reaction of a vicinal dichloride (CH_2ClCH_2Cl) with thiophenol does not occur at 30 °C due to its lower reactivity compared with CH_2Cl_2. However, the reaction can proceed effectively at 80 °C to afford the corresponding ethylenedithioether **3 h** in 93% yield (entry 8). The reactions of a variety of substituted thiophenols and alkyl thiols with CH_2ClCH_2Cl also proceed smoothly at 80 °C to furnish the corresponding ethylenedithioethers **3i–3 m** in good to excellent yields (entries 9–13). We attempted to carry out the heterogeneous rhodium-catalyzed reactions of $CHCl_3$ and CCl_4 with thiol to prepare a thioformate and a dithiocarbonic ester starting from a thiol. Unfortunately, although high catalyst loading and diluted conditions were used, the reactions of $CHCl_3$ and CCl_4 with thiols do not take place at 30 °C or even at reflux (entries 14–17). This heterogeneous rhodium catalyst exhibits as high an activity as $RhCl(PPh_3)_3$. For example, the coupling reaction of *p*-thiocresol (0.5 mmol) with CH_2ClCH_2Cl in the presence of 5.0 mol% of MCM-41-2P-RhCl(PPh_3)

Table 2. Reaction of thiols with polychloroalkanes catalyzed by MCM-41-2P-RhCl(PPh$_3$)[a]



Entry	Thiol	Polychloroalkane	Product	Yield[b] (%)
1	PhSH	CH$_2$Cl$_2$	PhSCH$_2$SPh (**3a**)[21]	95
2	4-ClPhSH	CH$_2$Cl$_2$	CH$_2$(SPhCl-4)$_2$ (**3b**)[22]	91
3	*p*-TolSH	CH$_2$Cl$_2$	CH$_2$(STol-*p*)$_2$ (**3c**)[12]	93
4	4-FPhSH	CH$_2$Cl$_2$	CH$_2$(SPhF-4)$_2$ (**3d**)[23]	89
5	PhCH$_2$SH	CH$_2$Cl$_2$	CH$_2$(SCH$_2$Ph)$_2$ (**3e**)[12]	80
6	CH$_3$(CH$_2$)$_3$SH	CH$_2$Cl$_2$	CH$_2$(SBu-*n*)$_2$ (**3f**)[24]	88
7	HO(CH$_2$)$_{11}$SH	CH$_2$Cl$_2$	CH$_2$[S(CH$_2$)$_{11}$OH]$_2$ (**3 g**)[12]	67
8[c]	PhSH	(CH$_2$Cl)$_2$	(CH$_2$SPh)$_2$ (**3 h**)[25]	93
9[c]	4-ClPhSH	(CH$_2$Cl)$_2$	(CH$_2$SPhCl-4)$_2$ (**3i**)[26]	87
10[c]	*p*-TolSH	(CH$_2$Cl)$_2$	(CH$_2$STol-*p*)$_2$ (**3j**)[12]	90
11[c]	4-FPhSH	(CH$_2$Cl)$_2$	(CH$_2$SPhF-4)$_2$ (**3 k**)[26]	85
12[c]	PhCH$_2$SH	(CH$_2$Cl)$_2$	(CH$_2$SCH$_2$Ph)$_2$ (**3 l**)[27]	82
13[c]	CH$_3$(CH$_2$)$_3$SH	(CH$_2$Cl)$_2$	(CH$_2$SBu-*n*)$_2$ (**3 m**)[12]	89
14[d]	CH$_3$(CH$_2$)$_3$SH	CHCl$_3$	*n*-BuSCHO (**3n**)	0
15[d]	PhSH	CHCl$_3$	PhSCHO (**3o**)	0
16[d]	CH$_3$(CH$_2$)$_3$SH	CCl$_4$	*n*-BuSCOSBu-*n* (**3p**)	0
17[d]	PhSH	CCl$_4$	PhSCOSPh (**3q**)	0

[a] Reaction was performed using MCM-41-2P-RhCl(PPh$_3$) (0.025 mmol), thiol (0.5 mmol), Et$_3$N (0.5 ml), polychloroalkane (2.0 ml) at 30 °C for 24 h under argon.

[b] Isolated yield based on thiol used.

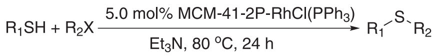
[c] At 80 °C.

[d] MCM-41-2P-RhCl(PPh$_3$) (0.1 mmol) and polychloroalkane (10 ml) were used at 30 °C or reflux.

using Et$_3$N (0.5 ml) as base at 80 °C for 24 h gives a 90% yield of the desired product **3j** (entry 10); the same reaction in the presence of 5.0 mol% of RhCl(PPh$_3$)$_3$ using Et$_3$N (0.5 ml) as base at 80 °C for 24 h gives **3j** in 87% yield.[12]

To broaden the scope of this methodology, we next investigated the heterogeneous rhodium-catalyzed reactions of thiols with alkyl halides. The results are summarized in Table 3. Generally, the reaction proceeds cleanly in Et$_3$N as both base and solvent without using excess alkylating reagents when a reactive primary alkyl chloride or a primary alkyl bromide is used as an alkylating reagent. For example, the reaction of thiophenol with benzyl chloride (1.0 equiv.) gives benzylphenylthioether in 91% yield (entry 1). The reactions of various substituted thiophenols, alkyl thiols with benzyl chloride (1.0 equiv) also proceed successfully under mild conditions to furnish the corresponding unsymmetric thioethers in good yields (entries 2–6). Additionally, the reaction of benzylthiol with pentyl bromide (1.0 equiv.) proceeds effectively, leading to the desired benzylpentylthioether in 83% yield (entry 7). No reaction of thiols with alkyl halides is observed in the absence of rhodium catalyst.

Table 3. Heterogeneous rhodium-catalyzed reaction of thiols with alkyl halides[a]



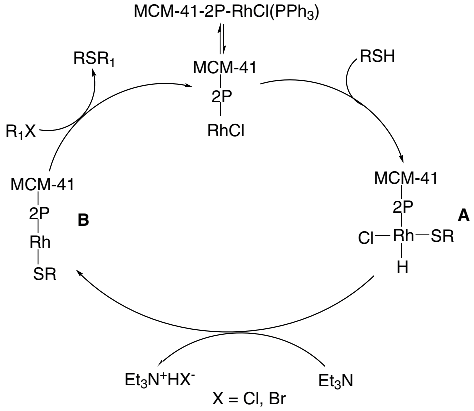
Entry	R^{1}SH	R^{2}X	Product	Yield[b] (%)
1	PhSH	PhCH$_2$Cl	PhSCH$_2$Ph (**3r**)[25]	91
2	4-ClPhSH	PhCH$_2$Cl	4-ClPhSCH$_2$Ph (**3 s**)[28]	82
3	*p*-TolSH	PhCH$_2$Cl	*p*-TolSCH$_2$Ph (**3 t**)[29]	87
4	4-FPhSH	PhCH$_2$Cl	4-FPhSCH$_2$Ph (**3u**)[30]	86
5	PhCH$_2$SH	PhCH$_2$Cl	PhCH$_2$SCH$_2$Ph (**3v**)[31]	85
6	*n*-BuSH	PhCH$_2$Cl	*n*-BuSCH$_2$Ph (**3w**)[32]	78
7	PhCH$_2$SH	CH$_3$(CH$_2$)$_4$Br	CH$_3$(CH$_2$)$_4$SCH$_2$Ph (**3x**)[32]	83

[a] Reaction was performed using MCM-41-2P-RhCl(PPh$_3$) (0.025 mmol), thiol (0.5 mmol), alkyl halide (0.5 mmol), Et$_3$N (0.5 ml) at 80 °C for 24 h under argon.

[b] Isolated yield.

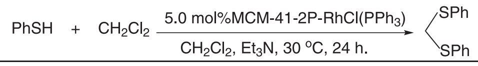
To verify whether the observed catalysis is due to the heterogeneous catalyst MCM-41-2P-RhCl(PPh$_3$) or to a leached rhodium species in solution, we performed the hot filtration test.[33] We focused on the reaction of thiophenol with CH$_2$ClCH$_2$Cl. We filtered off the MCM-41-2P-RhCl(PPh$_3$) complex after 10 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (80 °C) in order to avoid possible re-coordination or precipitation of soluble rhodium upon cooling. After this hot filtration, no further reaction is observed, indicating that leached rhodium species from the catalyst (if any) are not responsible for the observed activity. It is confirmed from inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis that no rhodium is detected in the hot filtered solution. This result suggests that the rhodium catalyst remains on the support at elevated temperatures during the reaction. The heterogeneous C–S coupling reaction of thiols with alkyl halides may proceed through a catalytic cycle analogous to that proposed for homogeneous rhodium catalysts (Scheme 3).[12] Oxidative addition of thiol S–H bond to the MCM-41-2P-RhCl(PPh$_3$) complex provides an MCM-41-bound rhodium(III) complex (A), which is followed by elimination of HX with Et$_3$N giving an MCM-41-bound rhodium(I) thiolate (B). The latter reacts with alkyl halides in an S$_N$2 fashion, thereby producing thioethers and regenerating the MCM-41-2P-Rh(I) complex.

For a heterogeneous transition metal catalyst, it is important to examine its ease of separation, recoverability and reusability. This heterogeneous rhodium catalyst can be easily recovered by a simple filtration of the reaction solution. We also investigated the possibility of reuse of the catalyst by using the reaction of thiophenol with CH$_2$Cl$_2$. After carrying out the reaction, the catalyst was separated by simple filtration and washed with ethyl acetate and diethyl ether. After being air-dried, it can be reused directly without further purification. The recovered rhodium catalyst was



Scheme 3. Plausible mechanism of reaction catalyzed by heterogeneous rhodium.

Table 4. Reaction of thiophenol with CH_2Cl_2 catalyzed by recycled catalyst[a]



Cycle	Yield[b] (%)	Cycle	Yield[b] (%)
1	95	2	95
3	94	4	94
5	94	6	93
7	94	8	93
9	93	10	92

[a] Reaction was carried out with thiophenol (0.5 mmol), CH_2Cl_2 (2.0 ml), Et_3N (0.5 ml) and 5.0 mol% rhodium catalyst at 30 °C for 24 h under argon.

[b] Isolated yield.

used in the next run, and almost consistent activity is observed for ten consecutive cycles (Table 4). In addition, rhodium leaching in the supported catalyst was also determined. The rhodium content of the catalyst is found from ICP-AES analysis to be 0.39 mmol g^{-1} after ten consecutive runs: no rhodium had been lost from the MCM-41 support. The high stability and excellent reusability of the catalyst should result from the chelating action of bidentate phosphine ligand on rhodium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and easy accessibility of the MCM-41-2P-RhCl(PPh_3) complex make it a highly attractive heterogeneous rhodium catalyst for the parallel solution-phase synthesis of diverse libraries of compounds.

Conclusions

In summary, we have developed a novel, practical, economic and environmentally friendly catalyst system for the C–S coupling reactions of thiols with polychloroalkanes or alkyl halides by using an MCM-41-immobilized bidentate phosphine rhodium complex (MCM-41-2P-RhCl(PPh_3)) as catalyst under mild reaction conditions. The reactions generated a variety of formaldehyde dithioacetals, ethylenedithioethers and unsymmetric thioethers in good to excellent yields. This heterogeneous rhodium catalyst could be easily recovered and recycled by a simple filtration of the reaction solution and reused for 10 cycles without significant loss of activity, thus making this procedure environmentally more acceptable.

Experimental

The diphosphino-functionalized mesoporous material MCM-41-2P was prepared according to our previous procedure, the phosphine content being 1.44 mmol g^{-1}.[34] Other chemicals were of reagent grade and used as purchased. All reactions were performed under an inert atmosphere of dry argon using distilled and dried solvents. All products were characterized by comparison of their spectra and physical data with authentic samples.

^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance 400 instrument (400 MHz for ^1H and 100 MHz for ^{13}C). Unless otherwise noted, $CDCl_3$ was used as the solvent. Chemical shift values for ^1H and ^{13}C are referenced to Me_4Si (0 ppm). Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer.

Preparation of MCM-41-2P-RhCl(PPh_3)[20]

To a solution of RhCl(PPh_3)$_3$ (1.109 g, 1.2 mmol) in benzene (50 ml) was added MCM-41-2P (2.04 g). The mixture was stirred under an argon atmosphere at 25 °C for 48 h. The solid product was filtered by suction, washed with benzene (5 × 10 ml) and dried at 70 °C/26.7 Pa under an argon atmosphere for 3 h to give 2.34 g of the light-yellow rhodium complex MCM-41-2P-RhCl(PPh_3). The phosphine and rhodium contents were 1.74 and 0.39 mmol g^{-1}, respectively.

General Procedure for Reaction of Thiols with Polychloroalkanes

A mixture of thiol (0.5 mmol), polychloroalkane (2.0 ml), Et_3N (0.5 ml) and the MCM-41-2P-RhCl(PPh_3) complex (64 mg, 0.025 mmol of Rh) was stirred under argon in an oil bath at 30 or 80 °C for 24 h. The mixture was cooled, diluted with EtOAc (20 ml) and filtered. The MCM-41-2P-RhCl(PPh_3) complex was washed with EtOAc (2 × 5 ml) and Et_2O (2 × 5 ml) and reused in the next run. The filtrate was washed with water (2 × 5 ml) and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel.

General Procedure for Reaction of Thiols with Alkyl Halides

A mixture of thiol (0.5 mmol), alkyl halide (0.5 mmol), Et_3N (0.5 ml) and the MCM-41-2P-RhCl(PPh_3) complex (64 mg, 0.025 mmol of Rh) was stirred under argon in an oil bath at 80 °C for 24 h. The mixture was cooled, diluted with EtOAc (20 ml) and filtered. The MCM-41-2P-RhCl(PPh_3) complex was washed with EtOAc (2 × 5 ml) and Et_2O (2 × 5 ml) and reused in the next run. The filtrate was washed with water (2 × 5 ml) and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel.

Compounds **3a–3 m** and **3r–3x** are known compounds and were characterized by comparing their ^1H NMR, ^{13}C NMR and IR spectra with those found in the literature.

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