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An efficient heterogeneous gold(I)-catalyzed hydration of haloalkynes leading to α-halomethyl ketones

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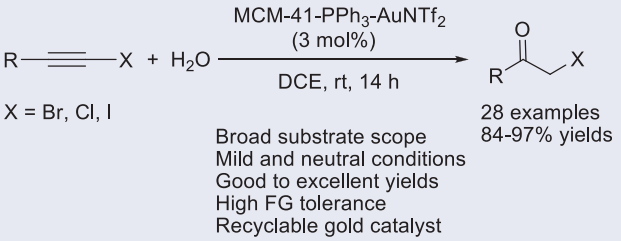
ABSTRACT

A highly efficient heterogeneous gold(I)-catalyzed hydration of haloalkynes has been developed that proceeds smoothly under mild and neutral conditions and provides a general and practical route for the synthesis of a variety of α-halomethyl ketones with high atom-economy, excellent yield, and recyclability of the gold(I) catalyst. The presented method delivers an attractive alternative to classical α-halogenation of ketones.

GRAPHICAL ABSTRACT



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KEYWORDS
Gold; hydration; haloalkyne; MCM-41; heterogeneous catalysis

Introduction

α-Halomethyl ketones are important intermediates in organic synthesis[1] and have been broadly applied in various fields including fine chemicals, pharmaceuticals, agrochemicals, and materials.[2] Besides, some α-halomethyl ketones exhibit various biological activities and have found their uses in medicine as drugs or diagnostic aids.[3] Traditional methods for the synthesis of α-halomethyl ketones involve the halogenation of olefins[4] or ketones and their derivatives (enol silyl ethers[5] and *β*-keto esters[6]) using an excess of halogenating reagents such as molecular halogen,[7] metal halides,[8] *N*-halosuccinimides,[9] and other related reagents.[10] However, most of these known methods suffer from some disadvantages, such as non-regiospecific reactions, over-halogenation, relatively harsh reaction conditions, and generation of undesirable by-products and halide waste. Therefore, the

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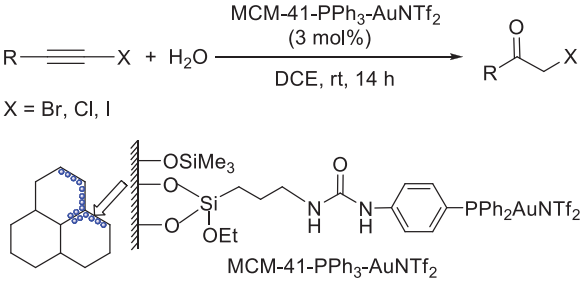
Supplemental data (full experimental detail, characterization data, and copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds) can be accessed on the publisher's website.



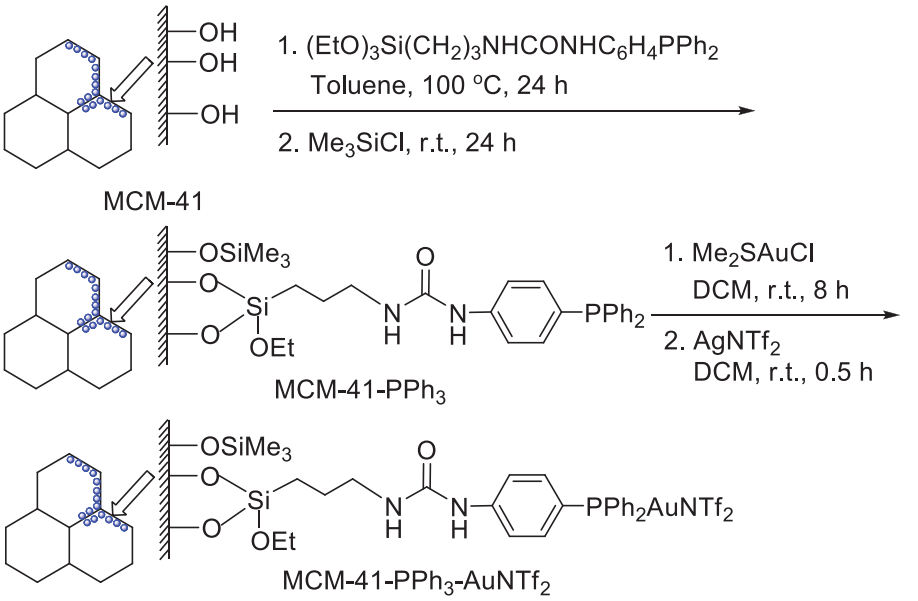
Scheme 1. Heterogeneous gold(I)-catalyzed synthesis of α-halomethyl ketones.

development of efficient and environmentally friendly approaches for the preparation of α-halomethyl ketones under mild conditions is highly desirable.

Haloalkynes are versatile and readily available building blocks and have been widely utilized in organic synthesis. Recently, transition-metal-catalyzed hydration of haloalkynes has provided a simple and straightforward route for the construction of α-halomethyl ketones, various metals such as gold,[11] silver,[12] copper,[13] iron,[14] indium,[15] and cerium[16] have proven their value in the hydration of haloalkynes, of which homogeneous cationic gold catalysis has attracted significant attention because of its excellent activity under neutral and mild reaction conditions. However, the non-recyclability of expensive gold catalysts and the decay of cationic gold greatly limit their application in organic synthesis. The heterogenization of the existing homogeneous catalysts appears to be a logical solution to this problem.[17] Moreover, heterogeneous catalysis can reduce waste derived from reaction workup, thereby contributing to development of green and sustainable chemical processes. However, to the best of our knowledge, no examples of heterogeneous gold complex-catalyzed hydration of haloalkynes for the construction of α-halomethyl ketones have been described until now despite the practical benefits of heterogeneous catalysis. Recently, we reported the first synthesis of an MCM-41-supported phosphine-gold(I) complex [MCM-41-PPh_3-$AuNTf_2$] and its successful application to the [2 + 2 + 1] annulation of terminal alkynes, nitriles, and oxygen atoms leading to 2,5-disubstituted oxazoles.[18] To further expand applications of this heterogeneous gold(I) catalyst, herein, we report the hydration reaction of haloalkynes catalyzed by MCM-41-PPh_3-$AuNTf_2$ leading to α-halomethyl ketones in good to excellent yields (Scheme 1).

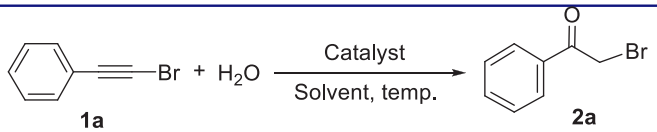
Results and discussion

The MCM-41-supported phosphine gold(I) complex [MCM-41-PPh_3-$AuNTf_2$] was easily prepared according to the procedure as shown in Scheme 2.[18] First, the mesoporous material MCM-41[19] was condensed with 1-(4-(diphenylphosphino)-phenyl)-3-(3-(triethoxysilyl)propyl)urea[20] in toluene at 100 °C for 24 h, followed by silylation with Me_3SiCl in toluene at room temperature for 24 h to give triphenylphosphine-functionalized MCM-41 (MCM-41-PPh_3). The MCM-41-PPh_3 was then reacted with Me_2SAuCl and $AgNTf_2$ in dichloromethane (DCM) at room temperature to afford the MCM-41-supported phosphine gold(I) complex [MCM-41-PPh_3-$AuNTf_2$] as a gray



Scheme 2. Preparation of the MCM-41-PPh_3-$AuNTf_2$ complex.

Table 1. Optimization of the reaction conditions[a].



1a **2a**

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Yield (%)[b]
1	MCM-41-PPh_3-$AuNTf_2$ (3)	DCM	Room temperature	71
2	MCM-41-PPh_3-$AuNTf_2$ (3)	MeCN	Room temperature	22
3	MCM-41-PPh_3-$AuNTf_2$ (3)	THF	Room temperature	20
4	MCM-41-PPh_3-$AuNTf_2$ (3)	DMF	Room temperature	14
5	MCM-41-PPh_3-$AuNTf_2$ (3)	DCE	Room temperature	92
6	MCM-41-PPh_3-$AuNTf_2$ (3)	MeOH	Room temperature	0
7	–	DCE	Room temperature	0
8	$AgNTf_2$ (10)	DCE	Room temperature	0
9	$AgNTf_2$ (10)	DCE	40	0
10	$AgNTf_2$ (10)	DCE	80	0
11	Ph3PAuNTf2 (3)	DCE	Room temperature	80
12	MCM-41-PPh_3-$AuNTf_2$ (3)	DCE	40	85
13[c]	MCM-41-PPh_3-$AuNTf_2$ (1.5)	DCE	Room temperature	64
14[d]	MCM-41-PPh_3-$AuNTf_2$ (5)	DCE	Room temperature	93
15[e]	MCM-41-PPh_3-$AuNTf_2$ (100)	DCE	Room temperature	83

[a]Reaction conditions: **1a** (0.3 mmol), H_2O (0.9 mmol), solvent (3 mL), 14 h under air.
[b]Isolated yield.
[c]For 24 h.
[d]For 10 h.
[e]For 2 h. DCM: dichloromethane. DCE: 1,2-dichloroethane.

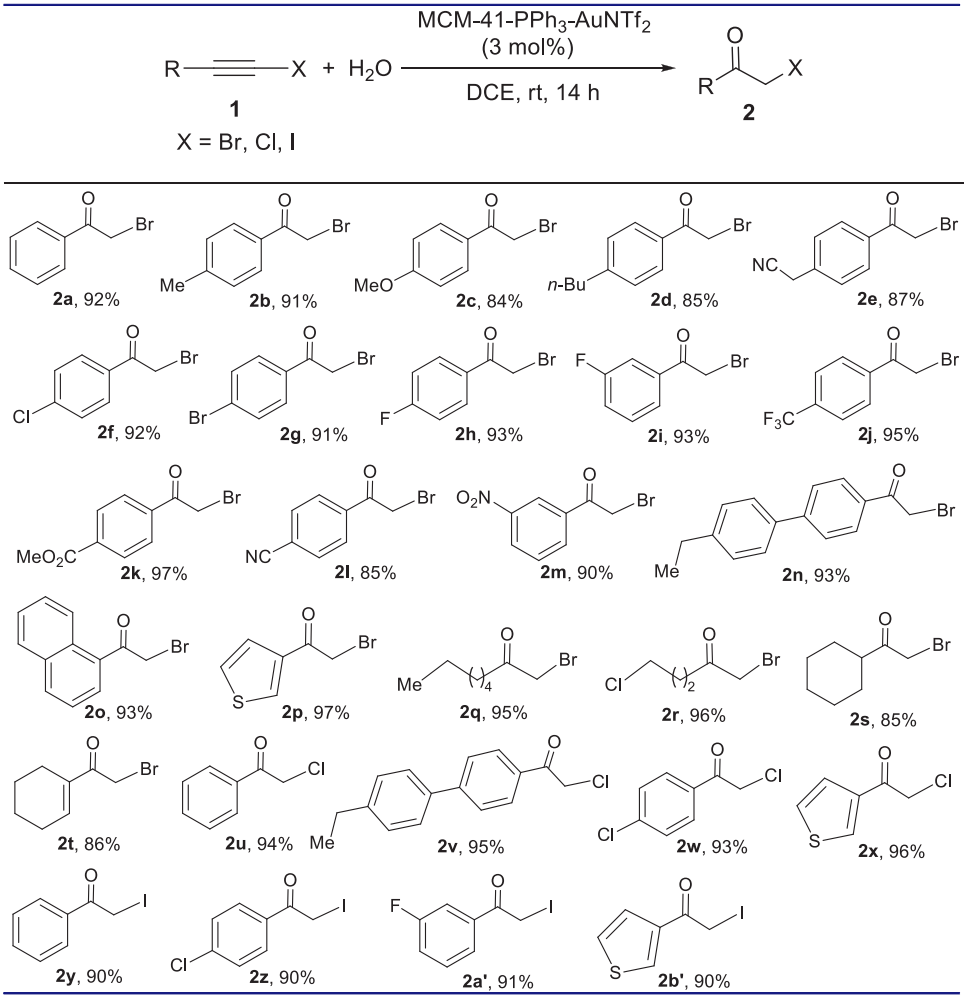
powder. The gold content of the complex was found to be 0.26 mmol g^{-1} according to the ICP-AES measurements.

In our initial screening experiments, the hydration reaction of 1-bromo-2-phenylacetylene (**1a**) was investigated to optimize the reaction conditions, and the results are

summarized in Table 1. The reactions were performed under neutral conditions to achieve high functional group tolerance. First, the effect of solvent on the hydration reaction was examined in the presence of 3 mol% of MCM-41-PPh_3-$AuNTf_2$ at room temperature and a significant solvent effect was observed (Table 1, Entries 1–6). The reaction run in DCM at room temperature produced the desired product **2a** in 71% yield (Entry 1). Replacement of DCM with other common solvents such as MeCN, THF, DMF, and MeOH resulted in low yields or no product (Entries 2–4 and 6). To our delight, when DCE was used as the solvent, the yield of **2a** could be improved to 92% (Entry 5); so, DCE as solvent was the best choice. The reaction did not occur under the same reaction conditions in the absence of any catalyst and the starting material **1a** was recovered in 95% yield (Entry 7). The special catalytic role of gold in this reaction was demonstrated by the inability of $AgNTf_2$ to catalyze this hydration reaction under neutral conditions at different temperatures (Entries 8–10). When a homogeneous $Ph_3PAuNTf_2$ was used as catalyst under the same conditions, the desired **2a** was isolated in 80% yield, which indicating that MCM-41-PPh_3-$AuNTf_2$ exhibited higher catalytic activity than $Ph_3PAuNTf_2$ (Entry 11). The higher catalytic activity of MCM-41-PPh_3-$AuNTf_2$ should result from the efficient site isolation and the optimal dispersion of the active sites on the inner channel walls of MCM-41. Raising the reaction temperature to 40 °C resulted in a slightly decreased yield (Entry 12). Finally, the amount of the gold catalyst was also screened. Reducing the amount of the gold catalyst to 1.5 mol% afforded the target product **2a** in only 64% yield and a longer reaction time was required (Entry 13), while increasing the amount of the gold catalyst to 5 mol% could shorten the reaction time, but did not improve the yield significantly (Entry 14). When a stoichiometric amount of MCM-41-PPh_3-$AuNTf_2$ was used, although the reaction time was shortened to 2 h, the desired **2a** was obtained in only 83% yield due to high solid content (Entry 15). Thus, the optimized reaction conditions for this transformation are the use of 3 mol% of MCM-41-PPh_3-$AuNTf_2$ in DCE as solvent at room temperature for 14 h (Table 1, Entry 5).

With the optimized reaction conditions in hand, the generality of this heterogeneous gold-catalyzed hydration reaction was examined using a variety of haloalkynes as substrates and the results are listed in Table 2. The reaction was highly efficient with a variety of bromoalkynes, and the yields were all above 84%. For examples, various substituted phenylethynyl bromides **1b–1m** bearing either electron-donating or electron-withdrawing groups could undergo the heterogeneous gold(I)-catalyzed hydration reaction smoothly to give the corresponding substituted α-bromoaceto-phenones **2b–2m** in 84–97% yields. These results indicate that the electronic nature of the substituents on the benzene ring has limited influence on the heterogeneous gold(I)-catalyzed hydration reaction. 4-(Bromoethynyl)-4'-ethylbiphenyl **1n** and bulky 1-(bromoethynyl)naphthalene **1o** displayed good reactivity in this transformation and afforded the desired α-bromomethyl ketones **2n** and **2o**, respectively, in excellent yields. Notably, 3-bromoethynylthiophene **1p** proved to be a suitable substrate and gave the target product **2p** in 97% yield. In addition, aliphatic bromoalkynes were also compatible with the standard conditions. For instance, 1-bromooct-1-yne **1q** and 1-bromo-5-chloropent-1-yne **1r** could provide the expected α-bromomethyl ketones **2q** and **2r**, respectively, in excellent yields. Reactions with substrates bearing a bulky group such as a cyclohexyl group (**1s**) and a

Table 2. Synthesis of α-halomethyl ketones by heterogeneous gold(I)-catalyzed hydration of haloalkynes[a,b].



[a]Reaction conditions: **1** (0.5 mmol), H_2O (1.5 mmol), MCM-41-PPh_3-$AuNTf_2$ (0.015 mmol) and DCE (5 mL) at room temperature for 14 h under air.
[b]Isolated yield.

cyclohexenyl group (**1t**) also worked well, thus affording the corresponding α-bromomethyl ketones **2s** and **2t** in high yields. A wide range of functional groups such as alkyl, methoxy, cyanomethyl, chloro, bromo, fluoro, trifluoromethyl, ester, cyano, nitro, and alkyl chloride were tolerated well in this reaction. By employing chloroalkynes and iodoalkynes as the substrates, this heterogeneous gold(I)-catalyzed alkyne hydration strategy could be extended to prepare the corresponding α-chloromethyl ketones and α-iodomethyl ketones. For example, chloroalkynes **1u–1w** could undergo the hydration reaction smoothly to give the corresponding α-chloromethyl ketones **2u–2w** in 93–95% yields. 3-Chloroethynylthiophene **1x** also reacted well in this transformation and furnished the target product **2x** in 96% yield. Besides, aryl or heteroaryl iodoalkynes **1y–1b'** were also compatible with the standard conditions and produced the desired α-iodomethyl ketones **2y–2b'** in excellent yields. It should be mentioned that in the

presence of 3 mol% of homogeneous XPhosAuNTf$_2$ the hydration of 1-iodo-2-phenylacetylene **1y** afforded the corresponding α-iodomethyl ketone **2y** in less than 20% NMR yield.[11a] The present method provides a quite general and practical procedure for the synthesis of a wide variety of α-halomethyl ketones.

To determine whether the observed catalysis was due to the heterogeneous catalyst MCM-41-PPh$_3$-AuNTf$_2$ or to a leached gold species in solution, we focused on the hydration reaction of 1-bromo-2-phenylacetylene (**1a**). We filtered off the catalyst after 5 h of reaction time and allowed the filtrate to react further at room temperature for 12 h. We found that, after removal of the gold catalyst, no further reaction was observed, indicating that leached gold species from the catalyst (if any) are not responsible for the observed activity. It was also confirmed by ICP-AES analysis that no gold species could be detected in the filtrate. These results suggest that the gold(I) complex was stable during the hydration and the observed catalysis was intrinsically heterogeneous.

For a heterogeneous precious metal catalyst, it is important to examine its ease of separation, stability, and reusability. The MCM-41-PPh$_3$-AuNTf$_2$ complex can be easily separated and recovered by a simple filtration of the reaction solution. We next investigated the recycling of the catalyst using the hydration reaction of methyl 4-bromoethynylbenzoate (**1k**). After completion of the reaction, the catalyst was recovered by simple filtration and washed with acetone. After being air-dried, it can be reused directly without further purification. The recovered gold catalyst was used in the next run, and almost the same yield of **2k** was observed for eight consecutive cycles (97%, 96%, 97%, 95%, 96%, 95%, 96%, and 95%, respectively). In addition, gold leaching in the heterogeneous catalyst was also determined using ICP-AES analysis on the recovered catalyst after eight consecutive runs, which revealing almost the same gold content as the fresh one. Although XPhosAuNTf$_2$ was highly efficient for the hydration of alkynyl bromides and chlorides, this homogeneous Au(I) catalyst showed low activity for the hydration of alkynyl iodides presumably due to steric hindrance.[11a] Furthermore, non-recyclability of expensive XPhosAuNTf$_2$ complex and the decay of cationic gold greatly restrict its application in large-scale syntheses. Compared with XPhosAuNTf$_2$, MCM-41-PPh$_3$-AuNTf$_2$ is stable to air and moisture owing to its heterogeneous nature and exhibited high catalytic activity for the hydration of not only alkynyl bromides and chlorides but also alkynyl iodides. Importantly, MCM-41-PPh$_3$-AuNTf$_2$ can be recovered from the reaction mixture by a simple filtration and recycled up to eight times without significant loss of activity.

Conclusions

In conclusion, we have developed a general, atom-economical, and practical approach for the synthesis of α-halomethyl ketones by the heterogeneous gold(I)-catalyzed hydration reaction of haloalkynes. The present method provides an attractive alternative to classical procedures because of some important advantages such as the easy availability of starting haloalkynes, broad substrate scope, mild and neutral conditions, high functional group tolerance, and excellent yields. Moreover, this heterogeneous gold(I) catalyst can be easily recovered by a simple filtration of the reaction solution and recycled

up to eight times without any loss of activity, thus making this procedure economically and environmentally more acceptable.

Experimental

All reagents and solvents were used as received without further purification. 1-Haloalkynes were prepared using DBU-mediated reaction of terminal alkynes with *N*-haloimides under mild conditions according to a literature method.[21] The MCM-41-PPh_3-$AuNTf_2$ complex was prepared according to our previous procedure.[18] ^1H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer using $CDCl_3$ as the solvent. HRMS spectra were recorded on a Q-Tof spectrometer with micromass MS software using electrospray ionization (ESI). Gold content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation).

Preparation of MCM-41-PPh_3-$AuNTf_2$ complex

1-(4-(Diphenylphosphino)phenyl)-3-(3-(triethoxysilyl)propyl)urea (0.525 g, 1 mmol) was added to a suspension of 2.0 g of the MCM-41 in 100 mL of dry toluene. The mixture was stirred at 100 °C for 24 h under Ar. Then, the solid was filtered, washed with $CHCl_3$ (20 mL), and dried in vacuum at 140 °C for 5 h. The dried white solid was then soaked in a solution of 2.8 g of Me_3SiCl in 80 mL of dry toluene at room temperature under stirring for 24 h. The solid product was filtered, washed with acetone (3 × 20 mL), and dried in vacuum at 100 °C for 5 h to obtain 2.364 g of hybrid material MCM-41-PPh_3. The phosphine content was found to be 0.37 mmol g^{-1} by elemental analysis.

In a small Schlenk tube, 1.00 g of MCM-41-PPh_3 was mixed with Me_2SAuCl (83 mg, 0.28 mmol) in 30 mL of dry CH_2Cl_2. The mixture was stirred at room temperature for 8 h under an argon atmosphere. The precipitate was filtered off, washed with CH_2Cl_2 and then treated with $AgNTf_2$ (107 mg, 0.28 mmol) in CH_2Cl_2 (30 mL) at room temperature for 0.5 h. The solid product was filtered, washed with $NH_3{\cdot}H_2O$ (2 × 10 mL), distilled water, and EtOH, and dried under vacuum to give 1.039 g of a gray gold complex (MCM-41-PPh_3-$AuNTf_2$). The gold content was found to be 0.26 mmol g^{-1} by ICP-AES.

General procedure for the synthesis of α-halomethyl ketones

To a solution of haloalkyne (0.5 mmol) in DCE (5 mL) were added H_2O (27 mg, 1.5 mmol) and MCM-41-PPh_3-$AuNTf_2$ (58 mg, 0.015 mmol). The reaction mixture was stirred at room temperature and the progress of the reaction was monitored using TLC. The reaction typically took 14 h. After completion of the reaction, the catalyst was separated by a simple filtration of the reaction solution, washed with acetone (2 × 5 mL), and reused in the next run. The filtrate was concentrated under reduced pressure and the residue was purified using chromatography on silica gel (eluent: light petroleum ether/ethyl acetate =25: 1) to afford the desired product **2a–2b'**.

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