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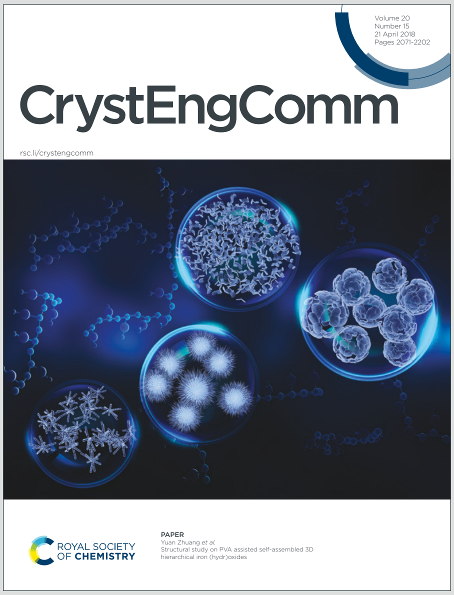

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ARTICLE

Two Inorganic-Organic Hybrid Silver-Polyoxometalates as Reusable Catalysts for One-Pot Synthesis of Propargylamines *via* Three-Component Coupling Reaction at Room Temperature

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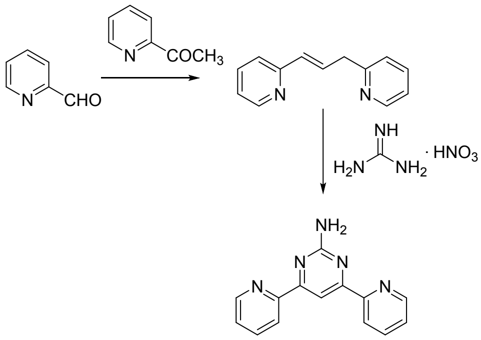
By the combination of Ag-complexes and Keggin POMs, two novel inorganic-organic silver-polyoxometalates hybrids, $[Ag_3L_2(DMSO)_2][PW_{12}O_{40}]\cdot 4DMSO$ (**1**) and $[(Ag_2L_2)_2][SiW_{12}O_{40}]\cdot 10DMSO\cdot 2H_2O$ (**2**) (L = 4-(2-pyridyl)-6-(4-pyridyl)-2-aminopyrimidine) were synthesized and characterizated. Interestingly, the silver atoms in compound **1** are three-coordinated with AgNO model, however, the Ag atoms of compound **2** were surrounded by four N atoms of the organic ligands and displayed the distorted tetrahedron configuration. Importantly, compound **1** shows high catalytic activities for the three-component coupling reaction of alkynes and secondary amines along with formaldehyde, and resulted in a series of propargylamine derivatives in higher yields (up to 99%). Furthermore, the Ag-POMs catalyst was easily is recovered by filtration and reused for three cycles without a significant loss in catalytic activity. A tentative mechanism is also proposed for this transformation.

Introduction

Inorganic-organic hybrid materials based on polyoxometalates (POMs) have attracted considerable attention in the field of materials chemistry owing to their potential widespread applications in catalysis, molecular electronics, magnetism and biomedicine.[1-3] Thus, design and assembly of POM-based inorganic-organic hybrid materials are still an appealing topic. To date, a number of POM-based inorganic-organic hybrid materials have been widely researched. For instance, Wu's group reported some inorganic-organic hybrid materials based on Anderson-Evans POMs, which exhibited interesting nanocage or extended structures.[4] Recently, Duan et al have designed a powerful tandem catalyst ZnW-PYIs for the efficient conversion of CO_2 into enantiomerically cyclic carbonates.[5] Additionally, 4,6-dipyridyl-2-aminopyrimidine (Scheme 1) as a kind of fascinating multi-functional ligands played an important role in generating the excellent inorganic-organic hybrid architectures because the five nitrogen donors in pyrimidine and pyridyl heterocycle system possessed potential coordina-tion sites. Up to date, although some 4,6-dipyridyl-2-aminopyrimidine complexes have been reported, however, few inorganic-organic POMs hybrids examples based on 4,6-dipyridyl-2-aminopyrimidine were described.[6-10] And it still remains a significant challenge to synthesize these Inorganic-organic POMs hybrids and develop their catalytic activities in some organic reactions.



Scheme 1. Synthetic route of ligand L.

On the other hand, Ag^+ ion, as the soft d^{10} metal cation, is a suitable candidate as good metal connector in the process of making Keggin-type POMs owing to its diverse coordination modes and valuable performance.[11–12] Taking all these into account, we chose Keggin-POMs, $AgNO_3$ and 4,6-dipyridyl-2-aminopyrimidine to make inorganic-organic POM-based hybrids. Here, two new Keggin-type POMs based inorganic-organic hybrids $[Ag_3L_2(DMSO)_2][PW_{12}O_{40}]\cdot 4DMSO$ (**1**) and $[(Ag_2L_2)_2][SiW_{12}O_{40}]\cdot 10\text{-}DMSO\cdot 2H_2O$ (**2**) were successfully made by using $AgNO_3$, $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$, and H_2L (L = 4,6-dipyridyl-2-aminopyrimidine) as starting materials. Furthermore, the one-pot three-component coupling reactions using compounds **1** and **2** as the catalysts have also been investigated.

Experimental section

Materials and reagents

$AgNO_3$, $H_3PW_{12}O_{40}\cdot xH_2O/H_4SiW_{12}O_{40}$ and other solvents/reagents purchased from Aladdin Co., Ltd. The 4-(2-pyridyl)-6-(4-pyridyl)-2-aminopyrimidine ligand was synthesized according to the reported literature.[10]

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Electronic Supplementary Information (ESI) available: CIF files of **1** and **2**. CCDC 1959945 and 1959951 contain the supplementary crystallographic data for this paper. See DOI: 10.1039/x0xx00000x.

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The FT-IR spectra of **1** and **2** were recorded on Nicolet 170 SXFT/IR spectrometer in the range 4000–400 cm^{-1}. PXRD data was obtained by using a Rigaku D/max-2550 diffractometer with Cu-Kα radiation. After each catalytic reaction was completed, the result of product was evaluated by GC (Shimadzu GC-2014C) and GC-MS (Agilent 7890A-5975C) using naphthalene as internal standard substrate. The elemental analyses measurements were done on Perkin-Elmer 240C elemental analyzer.

Single X-ray crystal diffraction data for **1** and **2** were performed on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298 K. All absorption corrections were applied using multi-scan technique. The crystal structures of **1** and **2** were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using SHELXTL 2018 crystallographic software package. The crystallographic data for **1** and **2** are summarized in Table 1.

Synthesis of compound 1

L ligand (0.025 g, 0.1 mmol), $AgNO_3$ (0.034 g, 0.2 mmol) and $H_3PW_{12}O_{40}\cdot xH_2O$ (0.288 g, 0.1 mmol) were successively dissolved in DMSO (10 mL) at room temperature and further stirred for 50 min in air. After the reaction was completed, the mixture was filtrated and the resulted solution stood for several weeks at ambient conditions. The light-yellow crystals of product were collected by filtration and washed with small amount of ice-cold water. Yield: 55% (based on L). Anal. Calcd. (%) (found) for $C_{40}H_{58}Ag_3N_{10}O_4PS_6W_{12}$: C, 13.74 (13.64); H, 1.67 (1.55); N 4.01 (3.89); IR (KBr, cm^{-1}): 3429 (s), 1645 (s), 1566 (m), 1476 (m), 1417 (m), 1366 (s), 1315 (s), 1236 (s), 1054 (s), 1020 (s), 951 (s), 871 (s), 799 (s), 657 (m), 528 (s).

Synthesis of compound 2

2 was synthesized according to the similar procedure of compound **1**, except that $H_3PW_{12}O_{40}\cdot xH_2O$ was replaced by $H_4SiW_{12}O_{40}\cdot xH_2O$ (0.144 g, 0.05 mmol). The yellow crystals were obtained by filtration and washed. Yield: 52% (based on L). Anal. Calcd. (%) (found) for $C_{76}H_{112}Ag_4N_{20}O_{54}S_{10}SiW_{12}$: C, 17.70 (17.58); H, 2.19 (2.05); N, 5.43 (5.30); IR (KBr, cm^{-1}): 3427 (s), 1646 (s), 1560 (s), 1473 (m), 1405 (m), 1356 (s), 1315 (s), 1224 (s), 1025 (s), 972 (s), 912 (s), 865 (s), 799 (s), 650 (m), 530 (s).

General procedure of catalytic three-component coupling reaction by organic-inorganic Ag-POMs

The catalytic reaction was conducted in a 25 mL reaction tube using arylacetylenes (0.25 mmol), piperidine or morpholine (0.7 mmol), formaldehyde (1.4 mmol) and catalyst (0.5 mol%). The reaction mixture was slowly stirred at room temperature in a Wattecs Parallel Reactor for proper time. When the reactions were finished, catalyst was simply retrieved by filtration, washed with methanol (ca. 3 * 5 mL), and the reaction mixtures were analyzed using a Shimadzu GC 2014C.

Results and discussion

Crystal structure of compounds 1 and 2

Crystal structure analysis reveals that **1** crystallizes in the triclinic *P*-1 space group, and the asymmetric unit of **1** consists of one and a half crystallographically independent Ag$^+$ cations, half α-Keggin $PW_{12}O_{40}^{3-}$ polyanion (abbreviated to PW_{12}), one organic L ligand and two DMSO molecules (one coordinated with Ag cations and one free) (Figure 1). Obviously, three crystallographic independent Ag$^+$ cations in **1** have two different coordination environments. More specifically, the Ag1 is surrounded by one Ag2 ion, two N atoms (N1, N4) from 2-pyridyl group and one pyrimidyl N atom (N2) from another L ligand. The Ag2 adopts a distorted "T-shape" geometry and coordinated by one pyrimidyl N atom (N3) from L ligand, one O atom (O24) from DMSO and Ag1 atoms. Interestingly, the argentophilic $\{Ag_2\}^{2+}$ dimers were constructed by the bond of Ag1 and Ag2 (2.810(13) Å), which is shorter than the sum of the Van der Waals radii of two silver atoms (3.44 Å). The $\{Ag_2\}^{2+}$ dimer is further linked by four nitrogen atoms (N1, N2, N3, and N4) into $[Ag_2]^{2+}$ ten-membered ring unit (Figure 2). All of Ag-N bond distances fall in the range of 2.37(2)–3.07(3) Å, while the Ag-O bond distance is 2.39(2) Å, which are similar with those of reported Ag/1,2,4-triazole/POMs.[13] In addition, these highly disordered atoms in **1** were omitted by using of SQUEEZE program, and the disordered atom sets were Ag1/Ag1#, Ag2/Ag2#, S1/S1#, C15/C15# and C16/ C16#, respectively. The corresponding occupancies were 0.836/0.164, 0.319/0.181, 0.64/0.36, 0.64/0.36 and 0.64/0.36, respectively.

Additionally, the structure of PW_{12} polyanion in **1** is the classical saturated α-isomer consisting of a central PO_4 tetrahedron and four trimetallic W_3O_{13} subunits, the distance of P-O bonds and W-O bonds are in normal range.

Table 1. The crystallographic data and structure refinement for **1** and **2**.

	1	2
Formula	$C_{40}H_{58}Ag_3N_{10}O_4PS_6W_{12}$	$C_{76}H_{112}Ag_4N_{20}O_{54}S_{10}SiW_{12}$
M_r	4168.10	5156.23
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
T(K)	298(2) K	298(2) K
a (Å)	11.6301(11)	14.1080(13)
b (Å)	13.3660(12)	15.0509(14)
c (Å)	15.5869(13)	16.3421(15)
α (deg)	98.1610(10)	97.1360(10)
β (deg)	101.089(2) deg	108.793(2)
γ (deg)	101.148(2)	104.501(2)
V (Å^3)	2292.1(4)	3099.9(5)
Z	1	1
$D_{calc.}$(g/cm^{-3})	3.020	2.762
F(000)	1876	2390
$R_1[I>2\sigma(I)]$	0.0815	0.0789
$wR_2[I>2\sigma(I)]$	0.2058	0.1943
R_1(all data)	0.1331	0.1372
wR_2(all data)	0.2284	0.2223

In order to explore whether the different POMs have an effect on the Ag-POMs structure, one homologue's analog $H_4SiW_{12}O_{40}$ was also tested instead of $H_3PW_{12}O_{40}$ during the synthesis of Ag-POMs. Single crystal X-ray diffraction analysis revealed that compound **2** consists of four Ag$^+$ cations, one Keggin $SiW_{12}O_{40}^{4-}$ polyanion (similar to in **1**), ten free DMSO molecules and two free water molecules (Figure 3). For **2**, it is noteworthy that each Ag$^+$ cations are surrounded by two N atoms (N1, N4 for Ag1 or N6, N9 for Ag2) from two 2-pyridyl groups and two pyrimidyl N atoms (N2, N3 for Ag1 or N7, N8 for Ag2) and presented distorted tetrahedron configuration. Interestingly, two eight-member-ed $[Ag_2L_2]^{2+}$ unit different from compound **1**

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(Ag1/N2/C9/N3/Ag1′/ N2′/C9′/N3′ and Ag2/N7/C23/N8/ Ag2′/N7′/C23′/N 8′) was formed by two Ag ions and two L ligands (Figures 3 and 4).

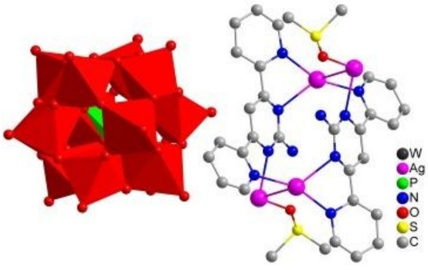

Figure 1. The crystal structure of compound **1**. Ag, lavender; C, gray; O, red; N, blue; S, yellow. All lattice solvent molecules and hydrogen atoms are omitted for clarity.

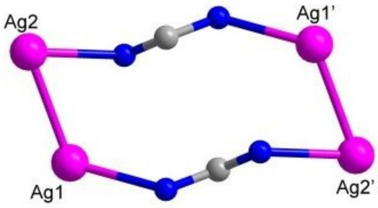

Figure 2. The ten-membered ring structure of compound **1.** Ag, lavender; C, gray; N, blue.

The $[Ag_2L_2]^{2+}$ units are connected with SiW_{12} polyanions to form 1D chains via N-H…O intermolecular weak interactions (N(5)-H(5)A… O23 3.138Å, N(5)-H(5)B…O24 2.906 Å, N(5)-H(5)B…O24 2.906 Å N(10)-H(10)A…O25 3.029 Å and N(10)-H(10)B…O14 2.937 Å). Furthermore, the 1D chains are further connected by intermolecular O-H…O hydrogen bonds into a 2D supramolecular network.

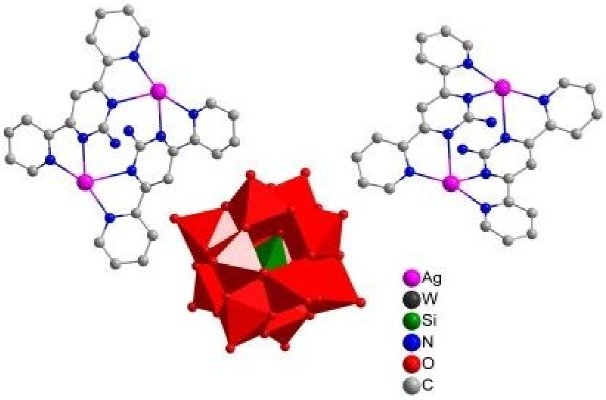

Figure 3. The crystal structure of compound **2**. Ag, lavender; C, gray; O, red; N, blue; S, yellow. All lattice solvent molecules and hydrogen atoms are omitted for clarity.

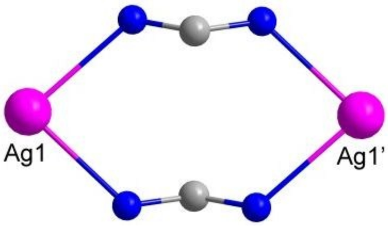

Figure 4. The ring structure of compound **2**. Ag, lavender; C, gray; N, blue.

Catalytic property

The three-component coupling (alkynes, aldehydes and amines) reaction is one of the most widely used tools for the synthesis of various propargylamines *via* the activation of C–H and N-H bonds. The obtained propargylamines are frequently used as synthetically adaptable key intermediates for the production of many N-containing biologically active organic compounds, such as conformationally restricted peptides, oxotremorine analogues, β-lactams, isosteres and some therapeutic drug molecules.[14-15] In the present, this three-component coupling reaction of alkynes, aldehydes along with amines has been catalyzed by various different kinds of metal catalysts, such as Ag,[16–18] Au,[19,20] Cu,[21–29] Ir,[30–32] Zr.[33,34] However, these catalytic systems suffer from some disadvantages, such as, required elevated temperature and longer time or the catalysts can't be reused. Hence, we reported a highly efficient heterogeneous Ag-POMs catalyst for three-component coupling strategy to make a series of propargylamines at room temperature.

Initially, we investigated the model reaction by utilizing phenylacetylene (**1a**), piperidine (**2a**) and formaldehyde (**3a**) as three-component substrates in the presence of different catalysts in acetonitrile at room temperature for 4 h (Scheme 2). As expected, preliminary studies showed that almost no desired product **4a** was obtained when the reaction was performed in the absence of any catalyst (Table 2, entry 1). When $AgNO_3$ (1.5 mol %) was employed as homogeneous catalyst in the reaction (Table 2, entry 2), the reactions proceeded and afforded the corresponding propargylamine **4a** in 65% yield. The similar compounds AgCl, $Ag_3PW_{12}O_{40}$ and $Ag_4SiW_{12}O_{40}$ were employed as heterogeneous catalysts, respectively, the yields of **4a** were from 7% to 70% (Table 2, entries 3-5). It was not until compound **1** was introduced as a heterogeneous catalyst that the yield of product **4a** was remarkably increased up to 99% (Table 2, entry 4). Strikingly, yield of compound **1** outperform compound **2** and some Ag-grafted covalent imine network material in the reactions.[35]

In contrast, the use of $H_3PW_{12}O_{40}$, compound **2** as catalysts, as well as the mixture of $AgNO_3$ and $H_3PW_{12}O_{40}$ only gave rise to the anticipated product **4a** in 8−72% yields (Table 2, entries 2, 6 and 7). For compound **2**, lower catalytic activity (45%) can be detected due to more saturated coordination of Ag centres than that of compound **1**. Moreover, catalyst loading was also further optimized and the results revealed that the yield of propargylamines **4a** decreased obviously when 0.25 mol% of compound **1** was used, but 99% yield can be obtained by using 0.5 mol% catalyst **1**. As a result, 0.5 mol% catalyst was performed in the following experiments. Additionally, some other solvents were also screened. The employment of other solvents (methyl benzene, water and solvent-free) resulted in markedly decreased product yields (Table 2, entries 8, 10-12). In addition, the reaction time also have been investigated from 2h to 6h at room temperature, and found the reaction can be completed in 4 h in 99% yield. Hence, we concluded that the optimum conditions for catalytic three-component coupling reaction are as follows: phenylacetylene (0.25 mmol), piperidine (0.7 mmol), aqueous formaldehyde (1.4 mmol), acetonitrile (2 mL), 0.5 mol% of compound **1** at room temperature for 4 h (Table 2, entry 4)

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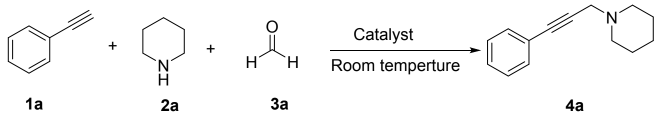


Scheme 2. Transformation of phenylacetylene, piperidine and formaldehyde to propargylamine using Ag-POMs as catalysts

Table 2. A three-component coupling reaction of phenylacetylene, piperidine and aqueous formaldehyde.^{a}

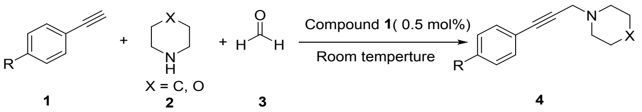
Entry	Catalysts	catalyst loading (mol%)	t[h]	solvent	Yields[%]^{b}
1	No		4	CH_3CN	Trace
2	$AgNO_3$	1.5	4	CH_3CN	65
3	AgCl	1.5	4	CH_3CN	7
4	$Ag_3PW_{12}O_{40}$	0.5	4	CH_3CN	70
5	$Ag_4SiW_{12}O_{40}$	0.375	4	CH_3CN	61
6	$H_3PW_{12}O_{40}$	0.5	4	CH_3CN	8
7	$AgNO_3$ and $H_3PW_{12}O_{40}$	1.5 and 0.5	4	CH_3CN	72
8	**1**	0.5	4	CH_3CN	99
9	**2**	0.5	4	CH_3CN	45
10	**1**	0.5	4	toluene	75
11	**1**	0.5	4	neat	55
12	**1**	0.5	4	H_2O	5
13	**1**	0.25	4	CH_3CN	78
14	**1**	0.5	2	CH_3CN	69
15	**1**	0.5	6	CH_3CN	99

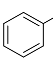
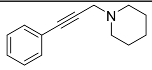
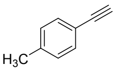
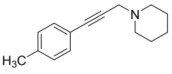
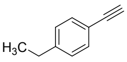
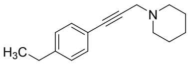
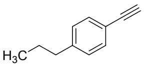
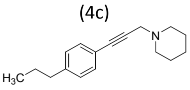
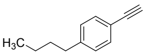
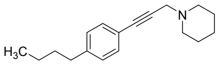
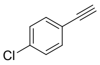
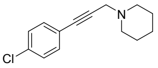
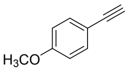
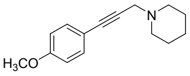
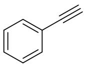
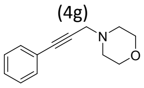
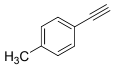
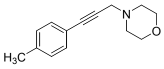
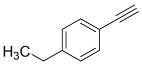
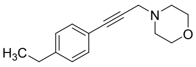
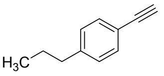
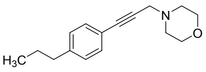
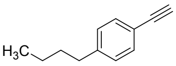
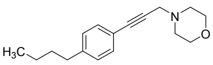
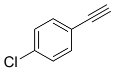
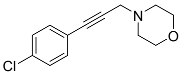
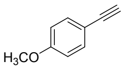
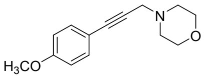
^{a} Reaction conditions: phenylacetylene (0.25 mmol), piperidine (0.7 mmol), aqueous formaldehyde (1.4 mmol) catalyst, solvent (2 mL), room temperature. ^{b}The yields were determined by GC/GC-MS.

Encouraged by the optimized reaction conditions obtained above, we subsequently evaluated the substrate cope of the three-component coupling reaction by employing a wide array of structurally varied substituted phenylacetylenes as substrates. As shown in Table 3, in all cases, the phenylacetylene bearing either electron-withdrawing (e.g., -Cl) or electron-donating (e.g., Me-, OMe-) groups in the phenyl ring were proven to be suitable starting materials for the transformation and achieved the responding propargylamines. It should be mentioned that substituted phenylacetylenes with longer linear chain, such as, 1-eth-1-ynyl-4-propylbenzene and 1-butyl-4-eth-1-ynylbenzene, also gave excellent yields in the reaction (Table 3, entries 4-5).

To expand the scope of three-component coupling, the substrates of the reaction was further surveyed by using morpholine as starting materials. As illustrated in Table 3, compound **1** mediated three-component coupling reactions involving morpholine as secondary amine proceeded smoothly under the optimized reaction conditions and produced the corresponding products in good to excellent yields (Table 3, entries 8-14). In addition, compared with the piperidine as secondary amine, less reactive 4-chlorophenylacetylene worked equally well, leading to the anticipated product in 87% yield (Table 3, entry 13). These preliminary results suggested that compound **1** can effectively promote the three-component coupling reaction at room temperature.

Table 3. Substrate Scope of the three-component coupling reaction under optimized conditions.^{a}



Entry	Substrates	Products	Yields (%)^{b}
1	 (1a)	 (4a)	99
2	 (1b)	 (4b)	99
3	 (1c)	 (4c)	99
4	 (1d)	 (4d)	99
5	 (1e)	 (4e)	99
6	 (1f)	 (4f)	99
7	 (1g)	 (4g)	99
8	 (1h)	 (4h)	95^{c}
9	 (1i)	 (4i)	98^{c}
10	 (1j)	 (4j)	93^{c}
11	 (1k)	 (4k)	96^{c}
12	 (1l)	 (4l)	97^{c}
13	 (1m)	 (4m)	87^{c}
14	 (1n)	 (4n)	98^{c}

^{a}Reaction conditions: arylacetylenes (0.25 mmol), secondary amines (0.7 mmol), aqueous formaldehyde (1.4 mmol), compound **1** (0.5 mol%), CH_3CN (2 mL), room temperature, 4h; ^{b}The yields were determined by GC/GC-MS; ^{c}The reaction time is 8 h.

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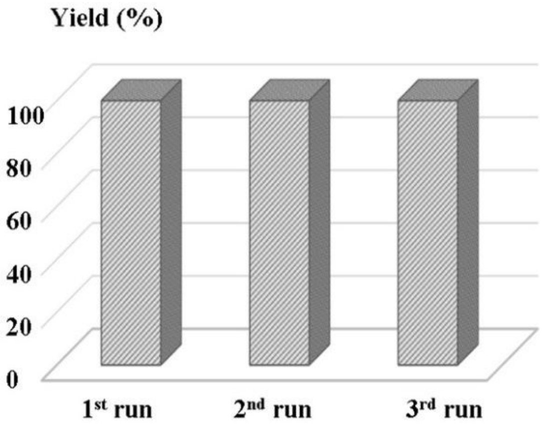
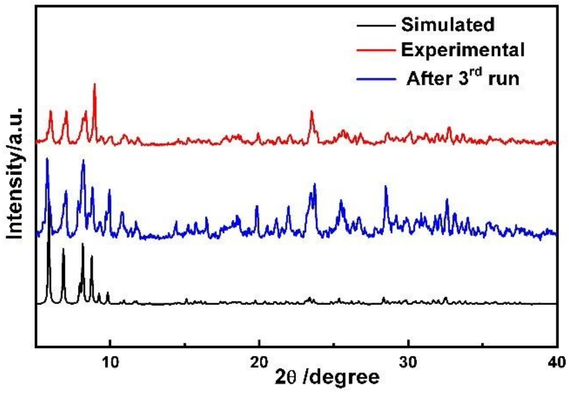


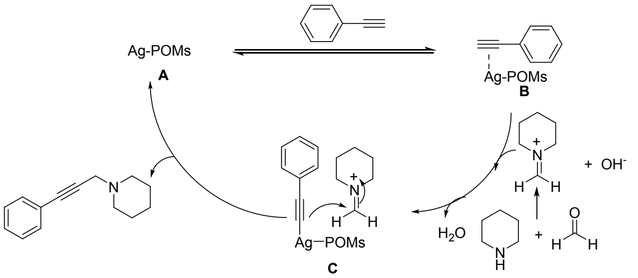
Figure 5. The results of three-component coupling reaction catalyzed by compound **1** in reused experiments. Reaction conditions: phenylacetylene (0.25 mmol), piperidine (0.7 mmol), formaldehyde (1.4 mmol) compound **1** (0.5 mol%), CH_3CN (2 mL), room temperature, 4 h.

Reusability of catalysts is very important for their industrial applications. As the excellent heterogeneous catalytic performance, compound **1** is designated to test the long-term stability in three-component heterogeneous system. After completion of the first run catalytic reaction, the catalyst can easily be separated from the reaction mixture by filtration. The recovered catalyst was washed with methanol and further reused directly in the subsequent catalytic reactions. The experiment results displayed that after three runs no obvious loss of activity was observed (yields. 99% (1st), 99% (2nd), 98% (3rd)) (Figure 5). The PXRD patterns (Figure 6) and IR spectrum (Figure S5) that after being reused for three cycles of compound **1** indicated that the structural integrity of **1** was well preserved.



Figures 6. The PXRD of compound **1** before and after the catalytic three-component coupling reaction.

Although the detailed mechanism of this three-component coupling reaction catalyzed by Ag-POMs remains to be elucidated, a tentative plausible catalytic mechanism is illustrated as shown in Scheme 3 on the basis of the above experimental results and previous literature reports. [36-40] Initially, the silver center of Ag-POMs (A) interacted with phenylacetylene and generated an initial silver(I)-acetylide intermediate (B) under the reaction conditions. Next, intermediate (B) underwent a subsequent hydrogen transfer and then reacted with iminium ion in situ generated by the reaction of aldehydes and secondary amines, and achieved the reactive silver(I)-acetylide intermediate (C). Further, the intermediate (C) added to the iminium ion and gave the corresponding propargylamine product and regenerated the Ag–POMs (A) catalyst for a further sequence of reactions.[41-43]



Scheme 3. The proposed mechanism for three-component coupling reaction using Ag-POMs as catalyst

Conclusions

In summary, we have reported two inorganic-organic silver-POM hybrids **1-2** with effective catalytic performance for three-component coupling reaction at room temperature. Especially, we found compound **1** can effectively catalyse three-component coupling reaction of alkynes and secondary amines along with formaldehyde in heterogeneous system with excellent yields and its activity is basically maintained after three cycles under room temperature. The investigations on using these Ag-POMs catalysts for other catalytic reactions are in progress.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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Notes and references

1 (a) S.-S. Wang and G.-Y. Yang, *Chem. Rev.*, 2015, **115**, 4893-4962;(b) I. A. Weinstock, R. E. Schreiber and R. Neumann, *Chem. Rev.*, 2018, **118**, 2680–2717; (c) C. Li, D. Zhong, X. Huang, G. Shen, Q. Li,J. Du, Q. Li, S. Wang, J. Li and J. Dou, *New J. Chem.*, 2019, **43**, 5813-5819.
2 M. Jeganathan, A. Dhakshinamoorthy and K. Pitchumani, *ACS Sustain. Chem. Eng.*, 2014, **2**, 781-787.
3 X. Huang, J. Li, G. Shen, N. Xin, Z. Lin, Y. Chi, J. Dou, D. Li and C. Hu, *Dalton Trans.*, 2018, **47**, 726–733.
4 Y. Wang, X. P. Kong, W. Xu, F. R. Jiang, B. Li and L. X. Wu, *Inorg. Chem.*, 2018, **57**, 3731–3741.
5 Q. Han, B. Qi, W. Ren, C. He, J. Niu and C. Duan, *Nat. Commun.*, 2015, **6: 10007**, 1-8
6 M. Trivedi, G. Singh, A. Kumar and N. P. Rath, *Inorg. Chim. Acta*, 2015, **438**, 255-263.
7 X. X. Lu, Y. H. Luo, C. Lu, X. Chen and H. Zhang, *J. Solid State Chem.*, 2015, **232**, 123-130.
8 L. C. Wieland, E. M. Vieira, M. L. Snapper and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2009, **131**, 570-576.
9 M. X. Yang, S. Lin, L. J. Chen, X. H. Chen, X. H. Yang and J. Guo, *Polyhedron*,

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2015, **87**, 329‑337.

10 Y. N. Chi, K. L. Huang, F. Y. Cui, Y. Q. Xu and C. W. Hu, *Inorg. Chem*., 2006, **45**, 10605-10612.

11 P. Mandal and A. P. Chattopadhyay, *Dalton Trans.*, 2015, **44**, 11444–11456.

12 A. M. Munshi, M. W. Shi, S. P. Thomas, M. Saunders, M. A. Spackman, K. S. Iyer and N. M. Smith, *Dalton Trans.*, 2017, **46**, 5133–5137.

13 Q. G. Zhai, X. Y. Wu, S. M. Chen, Z. G. Zhao and C. Z. Lu, *Inorg. Chem.*, 2007, **46**, 5046-5058

14 Z. Li, C. Wei, L. Chen, R. S. Varma and C.-J. Li, *Tetrahedron Lett.,* 2004, **45**, 2443−2446.

15 K. M. Reddy, N. S. Babu, I. Suryanarayana, P.S. S. Prasad and N. Lingaiah, *Tetrahedron Lett.*, 2006, **47**, 7563−7566.

16 P. Li, L. Wang, Y. Zhang and M. Wang, *Tetrahedron Lett.*, 2008, **49**, 6650−6654.

17 R. Maggi, A. Bello, C. Oro, G. Sartori and L. Soldi, *Tetrahedron*, 2008, **64**, 1435−1439.

18 C. Wei, Z. Li and C.-J. Li, *Org. Lett.*, 2003, **5**, 4473−4475.

19 C. Wei and C.-J. Li, *J. Am. Chem. Soc.*, 2003, **125**, 9584−9585.

20 V. K.-Y. Lo, Y. Liu, M.-K. Wong and C.-M. Che, *Org. Lett.*, 2006, **8**, 1529−1532.

21 C. Wei, Z. Li and C.-J. Li, *J. Am. Chem. Soc.*, 2002, **124**, 5638−5639.

22 H.Z.S. Huma, R. Halder, S.S. Kalra, J. Das and J. Iqbal, *Tetrahedron Lett.*, 2002, **43**, 6485−6488.

23 N. Gommermann, C. Koradin, K. Polborn and P. Knochel, *Angew. Chem. Int. Ed.*, 2003, **42**, 5763−5766.

24 L. Shi, Y.-Q. Tu, M. Wang, F.-M. Zhang and C.-A. Fan, *Org. Lett.*, 2004, **6**, 1001−1003.

25 B.M. Choudary, C. Sridhar, M.L. Kantam and B. Sreedhar, *Tetrahedron Lett.*,2004, **45**, 7319−7321.

26 S. B. Park and H. Alper, *Chem. Commun.*, 2005, **10**, 1315−1317.

27 B. Sreedhar, P. S. Reddy, B. V. Prakash and A. Ravindra, *Tetrahedron Lett.*, 2005, **46**, 7019−7022.

28 P. R. Likhar, S. Roy, M. Roy, M. S. Subhas, M. L. Kantam and R. L. De, *Synlett*, 2007, 2301−2303.

29 M. K. Patil, M. Keller, B. M. Reddy, P. Pale and J. Sommer, *Eur. J. Org. Chem.,* 2008, **26**, 4440−4445.

30 C. Fischer and E. M. Carreira, *Org. Lett.*, 2001, **3**, 4319−4321.

31 S. Sakaguchi, T. Kubo and Y. Ishii, *Angew. Chem. Int. Ed.*, 2001, **40**, 2534−2536.

32 S. Sakaguchi, T. Mizuta, M. Furuwan, T. Kubo and Y. Ishii, *Chem. Commun.*, 2004, **22**, 1638−1639.

33 J. F. Traverse, A. H. Hoveyda and M. L. Snapper, *Org. Lett.*, 2003, **5**, 3273−3275.

34 L. C. Akullian, M. L. Snappe and. A. H. Hoveyda, *Angew. Chem. Int. Ed.*, 2003, **42**, 4244−4247.

35 N. Salam, S. K. Kundu, R. A. Molla, P. Mondal, A. Bhaumik and S. M. Islam, *RSC Adv.*, 2014, **4**, 47593-47604.

36 Y. Zhao, X. Zhou, T. Okamur, M. Chen, Y. Lu, W.-Y. Sun and J.-Q. Yu, *Dalton Trans.*, 2012, **41**, 5889-5896.

37 A. Grirrane, E. Álvarez, H. Garćia, and A. Cora, *Chem. Eur. J.*, 2016, **22**, 340 - 354.

38 G. Li, R. Long, S. Yang and L. Zhang, *Kinet. Catal,* 2011, **52**, 559–563.

39 C. Boglio, K. Micoine, P. Rémy, B. Hasenknopf, S. Thorimbert, E. Lacôe, M. Malacria, C. Afonso and J.-C. Tabet, *Chem. Eur. J.,* 2007, **13**, 5426-5432.

40 S. Sadjadi, M. M. Heravi, M. Malmir, *Appl. Organometal. Chem.*, 2018, **32:e4029,** 1-14.

41 A. M. Munshi, M. Shi, S. P. Thomas, M. Saunders, M. A. Spackman, K. Swaminathan Iyer and N. M. Smith, *Dalton Trans.*, 2017, **46**, 5133–5137.

42 S. Anvar, I. Mohammadpoor-Baltork, S. Tangestaninejad, M. Moghadam, V.Mirkhani, A. R. Khosropour and R. Kia, *RSC Adv.*, 2012,**2**, 8713-8720.

43 S. Naidoo and V. Jeena, *Synthesis*, 2017, **49**, 2621-2631.

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Two Inorganic-Organic Hybrid Silver-Polyoxometalates as Reusable Catalyst for One-Pot Synthesis of Propargylamines via Three-Component Coupling Reaction at Room Temperature

Ming-Yu Dou,[a] Xian-Qiang Huang*[b] and Guo-Yu Yang,*[a]

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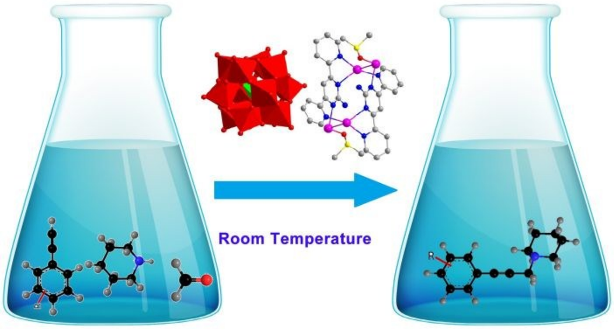

23 examples up to 96% yields

Two new inorganic-organic hybrid silver-polyoxometalates $[Ag_3L_2(DMSO)_2]$-$[PW_{12}O_{40}]\cdot 4DMSO$ (**1**) and $[(Ag_2L_2)_2][SiW_{12}O_{40}]\cdot 10DMSO\cdot 2H_2O$ (**2**) has been made and compound **1** shows good catalytic activities for three-component coupling reaction at room temperature.

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