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Silver supramolecule catalyzed multicomponent reactions under mild conditions[†]

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A novel supramolecular complex [Ag(L)(NO₃)] (1) was synthesized by reaction of the oxazolinecontaining ligand 1,4-bis(4,5-dihydro-2-oxazolyl)benzene (L) with silver(1) nitrate and its structure was determined by single-crystal X-ray diffraction. Structurally speaking, the one-dimensional (1D) zigzag chains of 1, in which the Ag(1) is three-coordinated with distorted trigonal-planar coordination geometry, are linked together by the hydrogen bonding interactions to form a three-dimensional (3D) supramolecular structure. It was found that the silver supramolecule 1 catalyzes the three-component coupling reactions of aldehyde, alkyne, and amine in the air at room temperature to generate propargylic amines with high efficiency. No additional co-catalyst or activator is required. A variety of aldehydes and amines were used to demonstrate the versatility of the reaction.

Introduction

Multi-component reactions have been attractive to chemists in recent years,^{1,2} not only because they are well-suited for the easy preparation of complicated compounds, but also due to their ability to provide platforms for generation of complexity in a collection of compounds with predefined functionality, e.g. compounds for catalysis.³ Coordination polymers have also been of widespread concern for their remarkable catalytic properties.⁴ Functionalized coordination polymers bearing specific interaction sites have been designed for useful catalytic applications in organic and polymer syntheses, which show several advantages: (1) changing the reaction rate; (2) regulating and controlling reactions; (3) substrate specificity.⁵ Because of the factors mentioned above, we focused our attention on multi-component reactions with coordination polymers as catalysts. The threecomponent reaction of aldehyde, alkyne and amine gives propargylamines, which are important synthetic intermediates for functional amino derivatives.⁶ However, the majority of such reactions are carried out by using metal salts or molecular metal complexes in harsh conditions such as high temperature.^{7,8} Thus, the development of mild, highly efficient as well as environmentally benign method for constructing propargylamines is

desirable. Herein, we report such reactions catalyzed by a silver(1) complex, namely $[Ag(L)(NO_3)]$ (1), obtained by reaction of the oxazoline-containing ligand 1,4-bis(4,5-dihydro-2-oxazolyl) benzene (L) with silver(1) nitrate under mild conditions.

Experimental

Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification unless otherwise noted. The ligand L was synthesized by the method reported for the preparation of oxazoline-containing compounds.⁹ Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer at the analysis center of Nanjing University. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX 500 spectrometer in CDCl₃. FT-IR spectra were obtained in the range of 400–4000 cm⁻¹ on a Bruker Vector22 FT-IR spectral measurements were carried out on an LCQ System (Finnegan MAT, USA) using a mixing solution of methanol and water (1:1) as the mobile phase. Column chromatography was performed with 300–400 mesh silica gel (Woelm).

Preparation of [Ag(L)(NO₃)] (1). Ligand L (6.5 mg, 0.03 mmol) was added to a methanol solution (5 ml) of AgNO₃ (5.1 mg, 0.03 mmol) with continuous stirring. The solution was filtered after 5 min. Colorless crystals were obtained by the slow diffusion of diethyl ether into the methanol solution for several days. Yield: 60%. Anal. Calcd for $C_{12}H_{12}AgN_3O_5$ (386.12): C, 37.33; H, 3.13; N, 10.88 (%). Found: C, 37.54; H, 2.91; N, 10.65 (%). IR (KBr pellet, cm⁻¹): 3098(w), 3050(w), 2981(w), 2918(w), 1720(w), 1635(vs), 1462(s), 1407(s), 1369(s), 1268

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(vs), 1093(s), 1006(m), 931(s), 854(m), 810(m), 729(w), 682(m).

General procedure for the catalytic reactions. All the experiments were carried out under air atmosphere. A mixture of complex 1 (14.8 mg, 0.038 mmol, 1.9 mmol%), phenylacetylene (2.4 mmol), aldehyde (2 mmol) and amine (2.2 mmol) in solvent (2 mL) was stirred at room temperature. When the reaction was stirred for a long enough time (monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography to afford the product.

1-Cyclopentyl-*NN***-diethyl-3-phenylprop-2-yn-1-amine.** Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.10 (t, *J* = 6.8 Hz, 6H), 1.44–1.51 (m, 2H), 1.55–1.60 (m, 2H), 1.61–1.68 (m, 2H), 1.79–1.81 (m, 1H), 1.90–1.96 (m, 1H), 2.18–2.25 (m, 1H), 2.45–2.49 (m, 2H), 2.72–2.76 (m, 2H), 3.37 (d, *J* = 10.0 Hz, 1H), 7.30–7.33 (m, 3H), 7.42–7.44 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 13.84, 25.20, 25.38, 30.60, 31.02, 43.22, 44.95, 58.72, 84.45, 89.06, 123.94, 127.57, 128.18, 131.69. IR (KBr pellet, cm⁻¹): 3080(w), 3056(w), 2962(vs), 2868(s), 2816 (s), 1598(s), 1489(s), 1470(s), 1444(s), 1380(s), 1295(m), 1255 (s), 1196(s), 1115(s), 1068(s), 985(m), 911(w), 754(vs), 690(s). ESI-MS: calcd for C₁₈H₂₅N (M + 1) 256.20, found: 256.25.

1-(1-Cyclopentyl-3-phenylprop-2-ynyl)pyrrolidine. Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.91 (t, J = 6.5 Hz, 1H), 1.28 (s, 2H), 1.52–1.61 (m, 3H), 1.67–1.68 (m, 2H), 1.83 (s, 3H), 1.90–1.93 (m, 1H), 2.22–2.24 (m, 1H), 2.74 (s, 2H), 2.81 (s, 2H), 3.58 (s, 1H), 7.31–7.34 (m, 3H), 7.44–7.46 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 23.64, 25.46, 25.59, 30.34, 30.54, 44.07, 49.96, 60.09, 85.33, 88.13, 123.77, 127.67, 128.18, 131.74. IR (KBr pellet, cm⁻¹): 2955(vs), 2868(s), 2805 (s), 1598(m), 1489(s), 1444(s), 1346(m), 1312(m), 1254(w), 1138(m), 1029(m), 754(vs), 690(vs). ESI-MS: calcd for C₁₈H₂₃N (M + 1) 254.18, found: 254.33.

1-(1-Cyclohexyl-3-phenylprop-2-ynyl)pyrrolidine. Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.13–1.31 (m, 6H), 1.70 (d, J = 11.0 Hz, 1H), 1.78–1.83 (m, 6H), 1.98 (d, J = 12.5 Hz, 1H), 2.11 (d, J = 13.0 Hz, 1H), 2.71 (s, 2H), 2.78 (s, 2H), 3.41 (s, 1H), 7.31–7.34 (m, 3H), 7.45–7.47 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 23.61, 26.26, 26.75, 30.37, 30.73, 41.40, 50.03, 61.24, 85.86, 87.86, 123.71, 127.71, 128.90, 131.73. IR (KBr pellet, cm⁻¹): 3080(w), 3056(w), 2923(vs), 2874(s), 2851 (vs), 2806(s), 1598(m), 1489(s), 1448(s), 1348(m), 1308(m), 1217(m), 1196(m), 1129(m), 1112(s), 1069(m), 984(m), 911(m), 755(vs), 690(vs). ESI-MS: calcd for C₁₉H₂₅N (M + 1) 268.20, found: 268.25.

1-(1-Cyclohexyl-3-phenylprop-2-ynyl)piperidine. Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.89–1.09 (m, 2H), 1.16–1.34 (m, 4H), 1.46 (d, J = 4.5 Hz, 2H), 1.58–1.63 (m, 4H), 1.69–1.71 (m, 1H), 1.77–1.80 (m, 2H), 2.06 (d, J = 13.0 Hz, 1H), 2.12 (d, J = 12.5 Hz, 1H), 2.42 (s, 2H), 2.65 (s, 2H), 3.12 (d, J = 9.5 Hz, 1H), 7.31–7.32 (m, 3H), 7.46–7.47 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 24.75, 26.14, 26.30, 26.84, 30.49, 31.36, 39.65, 64.42, 86.23, 87.73, 123.84, 127.61, 128.18, 131.73. IR (KBr pellet, cm⁻¹): 3056(w), 2929(vs), 2850(vs), 2801(s), 2749(m), 1598(m), 1489(s), 1444(s), 1348(m), 1317

(m), 1261(m), 1228(m), 1156(m), 1103(s), 1112(s), 1028(m), 910(w), 754(vs), 690(vs). ESI-MS: calcd for $C_{20}H_{27}N$ (M + 1) 282.21, found: 282.33.

1-Cyclohexyl-*NN***-diethyl-3-phenylprop-2-yn-1-amine.** Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.89–0.94 (m, 1H), 1.08 (t, *J* = 7.0 Hz, 6H), 1.18–1.32 (m, 4H), 1.58–1.60 (m, 1H), 1.70–1.71 (m, 1H), 1.75–1.80 (m, 3H), 2.12–2.14 (m, 2H), 2.43–2.47 (m, 2H), 2.65–2.72 (m, 2H), 3.32 (d, *J* = 10.0 Hz, 1H), 7.29–7.34 (m, 3H), 7.43–7.45 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 13.77, 26.05, 26.29, 26.83, 30.70, 31.40, 40.31, 44.85, 59.38, 85.28, 88.39, 123.90, 127.55, 128.16, 131.66. IR (KBr pellet, cm⁻¹): 3080(w), 3057(w), 2968(vs), 2924(vs), 2851(vs), 1598(m), 1489(s), 1468(m), 1448(s), 1381 (s), 1293(m), 1260(m), 1197(m), 1169(s), 1111(m), 1068(s), 1045(s), 981(m), 911(w), 754(vs), 691(s). ESI-MS: calcd for C₁₉H₂₇N (M + 1) 270.21, found: 270.33.

2-(1-Cyclohexyl-3-phenylprop-2-ynyl)isoindoline. Brown solid, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.12–1.36 (m, 6H), 1.67–1.74 (m, 1H), 1.79–1.84 (m, 2H), 2.11 (d, *J* = 12.5 Hz, 1H), 2.20 (d, *J* = 12.5 Hz, 1H), 3.60 (d, *J* = 7.0 Hz, 1H), 4.16 (s, 4H), 7.21–7.25 (m, 4H), 7.28–7.29 (m, 3H), 7.40–7.41 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 26.19, 26.25, 26.75, 30.56, 30.72, 41.36, 55.37, 60.91, 87.42, 87.89, 122.41, 123.42, 126.61, 127.89, 128.22, 131.76, 140.03. IR (KBr pellet, cm⁻¹): 3424(vs), 2916(vs), 2892(s), 2847(s), 2791(s), 1652(m), 1488 (m), 1462(m), 1443(m), 1345(w), 1302(w), 1260(m), 1126(s), 1062(m), 1026(w), 978(w), 917(w), 858(w), 747(vs), 692(s). ESI-MS: calcd for C₂₃H₂₅N (M + 1) 316.20, found: 316.33.

1-(1-Cyclohexyl-3-phenylprop-2-ynyl)indoline. Brown oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.98–1.08 (m, 1H), 1.17–1.37 (m, 4H), 1.75–1.87 (m, 4H), 2.12 (d, J = 12.5 Hz, 1H), 2.23 (d, J = 12.0 Hz, 1H), 3.00–3.06 (m, 2H), 3.48–3.54 (m, 2H), 4.17 (d, J = 10.0 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 7.0 Hz, 1H), 7.11 (t, J = 6.5 Hz, 2H), 7.27 (m, 3H), 7.34–7.35 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 26.06, 26.19, 26.68, 28.46, 30.28, 31.06, 41.15, 48.32, 55.41, 85.31, 87.11, 107.76, 117.98, 123.33, 124.47, 127.24, 127.95, 128.20, 130.16, 131.86, 151.72. IR (KBr pellet, cm⁻¹): 3420(m), 3049(w), 2924(vs), 2850(s), 1606(s), 1487(vs), 1460(m), 1449(m), 1379(w), 1316 (w), 1252(s), 1157(m), 754(vs), 715(m), 691(s). ESI-MS: calcd for C₂₃H₂₅N (M + 1) 316.20, found: 316.17.

2-(1-Cyclohexyl-3-phenylprop-2-ynyl)-1,2,3,4-tetrahydroisoquinoline. Yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.89–1.00 (m, 2H), 1.10–1.14 (m, 1H), 1.21–1.28 (m, 3H), 1.31–1.41 (m, 1H), 1.73–1.84 (m, 3H), 2.11 (d, J = 13.0 Hz, 1H), 2.21 (d, J = 12.0 Hz, 1H), 2.74 (d, J = 3.0 Hz, 1H), 2.95–3.00 (m, 2H), 3.40 (d, J = 7.5 Hz, 1H), 3.76 (d, J = 15.0Hz, 1H), 3.93 (d, J = 14.5 Hz, 1H), 7.09–7.14 (m, 4H), 7.30 (s, 3H), 7.44 (d, J = 4.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 26.10, 26.34, 26.85, 29.82, 30.52, 31.45, 39.88, 47.35, 52.49, 63.81, 86.74, 86.96, 123.58, 125.55, 125.92, 126.78, 127.85, 128.27, 128.72, 131.80, 134.75, 135.72. IR (KBr pellet, cm⁻¹): 3421(vs), 3021(w), 2922(vs), 2850(s), 1639(m), 1598(m), 1489 (s), 1446(s), 1384(w), 1318(w), 1267(m), 1130(m), 1099(m), 1038(w), 981(w), 936(w), 890(w), 754(vs), 743(vs), 690(s). ESI-MS: calcd for C₂₄H₂₇N (M + 1) 330.21, found: 330.33. **1-(5-Methyl-1-phenylhex-1-yn-3-yl)pyrrolidine.** Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.97–1.01 (m, 6H), 1.54–1.60 (m, 1H), 1.68–1.74 (m, 1H), 1.83 (t, *J* = 6.2 Hz, 4H), 1.92–1.99 (m, 1H), 2.71–2.73 (m, 2H), 2.78–2.80 (m, 2H), 3.81–3.84 (m, 1H), 7.30–7.32 (m, 3H), 7.44–7.46 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 22.00, 23.30, 23.56, 25.41, 44.09, 49.46, 53.05, 85.40, 88.18, 123.59, 127.73, 128.86, 131.71. IR (KBr pellet, cm⁻¹): 3421(m), 2956(vs), 2931(s), 2869(m), 2807 (m), 1598(w), 1489(s), 1466(m), 1384(m), 1365(w), 1313(m), 1138(m), 1110(w), 1070(w), 1028(w), 911(w), 755(vs), 743(vs), 691(s). ESI-MS: calcd for C₁₇H₂₃N (M + 1) 242.18, found: 242.25.

1-(1-PhenyInon-1-yn-3-yl)pyrrolidine. Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.91 (t, J = 6.8 Hz, 3H), 1.28–1.37 (m, 6H), 1.44–1.54 (m, 1H), 1.56–1.64 (m, 1H), 1.73–1.79 (m, 2H), 1.84 (m, 4H), 2.73 (d, J = 5.5 Hz, 2H), 2.80 (d, J = 6.5 Hz, 2H), 3.70–3.73 (m, 1H), 7.31–7.33 (m, 3H), 7.44–7.46 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 14.07, 22.64, 23.54, 26.69, 29.12, 31.78, 35.11, 49.72, 55.13, 85.29, 88.31, 123.56, 127.75, 128.16, 131.71. IR (KBr pellet, cm⁻¹): 3424(m), 2956(vs), 2927(vs), 2857(s), 2808(m), 1728(w), 1598 (w), 1489(m), 1460(m), 1348(w), 1319(w), 1290(w), 1136(m), 1070(w), 1028(w), 912(w), 755(vs), 743(vs), 691(s). ESI-MS: calcd for C₁₉H₂₇N (M + 1) 270.21, found: 270.33.

1-(1,3-Diphenylprop-2-ynyl)pyrrolidine. Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.84 (s, 4H), 2.74 (s, 4H), 4.93 (s, 1H), 7.32–7.35 (m, 4H), 7.39 (t, J = 7.5 Hz, 2H), 7.51–7.53 (m, 2H), 7.64 (s, 1H), 765 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ 23.55, 50.30, 59.16, 86.77, 86.95, 123.31, 127.58, 128.09, 128.28, 128.30, 131.82, 139.60. IR (KBr pellet, cm⁻¹): 3060(m), 3030(m), 2964(s), 2926(s), 2874(m), 2807(s), 1598 (m), 1490(vs), 1450(s), 1345(m), 1303(m), 1270(m), 1128(s), 1070(m), 1028(m), 971(m), 755(vs), 691(vs). ESI-MS: calcd for C₁₉H₁₉N (M + 1) 262.15, found: 262.17.

1-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)pyrrolidine. Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): *δ* 1.83 (m, 4H), 2.70 (m, 4H), 4.91 (s, 1H), 7.35–7.36 (m, 5H), 7.50–7.52 (m, 2H), 7.57–7.59 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): *δ* 23.59, 50.14, 58.39, 86.11, 87.38, 123.08, 128.25, 128.33, 128.40, 129.59, 131.83, 133.31, 138.26. IR (KBr pellet, cm⁻¹): 3056(w), 2964(s), 2927(s), 2874(m), 2853(m), 2810(s), 1687 (w), 1597(m), 1488(vs), 1442(m), 1345(m), 1303(m), 1267(m), 1128(w), 1089(s), 1070(w), 1016(s), 974(m), 852(m), 827(m), 756(vs), 690(vs). ESI-MS: calcd for C₁₉H₁₈CIN (M + 1) 296.11, found: 296.08.

1-(1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl)pyrrolidine. Pale yellow oil, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.83 (m, 4H), 2.72 (m, 4H), 3.84 (s, 3H), 4.87 (s, 1H), 6.92 (d, J = 9.0 Hz, 2H), 7.34 (m, 3H), 7.50–7.52 (m, 2H), 7.54–7.56 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 23.52, 50.27, 55.27, 58.55, 86.71, 87.11, 113.62, 123.35, 128.04, 128.26, 129.39, 131.79, 131.82, 159.09. IR (KBr pellet, cm⁻¹): 2959(s), 2927(s), 2874(m), 2833 (m), 2807(m), 1610(s), 1509(vs), 1489(s), 1461(s), 1441(m), 1343(m), 1247(vs), 1171(s), 1106(m), 1036(s), 973(w), 833(m), 756(vs), 691(s). ESI-MS: calcd for C₂₀H₂₁NO (M + 1) 292.16, found: 292.08.

 Table 1
 Crystal data and structure refinements for complex 1

Compound	1			
Empirical formula	C ₁₂ H ₁₂ AgN ₃ O ₅			
Formula weight	386.12			
Crystal system	Triclinic			
Space group	$P\overline{1}$			
<i>a</i> (Å)	7.100(4)			
b (Å)	8.900(5)			
<i>c</i> (Å)	11.174(5)			
α (°)	71.12(2)			
β (°)	88.459(17)			
γ (°)	75.42(2)			
$T(\mathbf{K})$	200			
$V(Å^3)$	645.4(6)			
Z	2			
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.987			
$\mu (\text{mm}^{-1})$	1.589			
F(000)	384			
Reflections collected	6145			
Unique reflections	2936			
R _{int}	0.0395			
Parameters refined	190			
GOF	1.092			
$R_1 \left[I > 2\sigma(I) \right]$	0.0280			
$wR_2 [I > 2\sigma(I)]$	0.0664			
R_1 (all data) ^a	0.0319			
wR_2 (all data) ^b	0.0677			
${}^{a}R_{1} = \Sigma F_{o} - F_{c} /\Sigma F_{o} . {}^{b}wR_{2} = \Sigma w(F_{o} ^{2} - F_{c} ^{2}) /\Sigma w(F_{o})^{2} ^{1/2}, \text{ where } w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP]. P = (F_{o}^{2} + 2F_{c}^{2})/3.$				

X-ray crystallography

A colorless single crystal of **1** with approximate dimensions of $0.12 \times 0.08 \times 0.02$ mm was mounted on a MicroMountTM 200 µm, and the crystallographic data were collected on a Rigaku RAXIS-RAPID II imaging plate area detector with Mo-K α radiation (0.71075 Å) using MicroMax-007HF microfocus rotating anode X-ray generator and VariMax-Mo optics at 200 K. The structure of the complex was solved by direct methods using SIR92¹⁰ and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique.¹¹ All the hydrogen atoms were generated geometrically and refined using the riding model. All calculations were performed using the Crystal-Structure crystallographic software package except for refinement, which was performed using SHELXL-97.^{12,13} The details of the crystal parameters, data collection, and refinements for the complex are summarized in Table 1.

Results and discussion

Description of the crystal structure of complex 1

The results of crystallographic analysis revealed that the asymmetric unit of complex **1** consists of one Ag(i) ion, one ligand L and one nitrate anion. As shown in Fig. 1a, each Ag(i) atom is coordinated by two nitrogen atoms from two different L ligands, and an oxygen atom from a nitrate anion with Ag–N, Ag–O bond distances of 2.245(2), 2.308(2) and 2.347(2) Å, respectively. The coordination angles around the Ag(i) are in the range of 106.34(8)–127.27(7)°. Thus, the three-coordinated Ag(i) center in **1** has a distorted trigonal-planar coordination geometry. Each L ligand in turn uses its oxazoline groups to connect two metal centers, giving an infinite one-dimensional (1D) zigzag



(c)

Fig. 1 (a) Coordination environment of the Ag(1) atom in 1 with ellipsoids drawn at the 30% probability level, hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag(1)–O(21) 2.347(2), Ag(1)–N(1) 2.245(2), Ag(1)–N(4) 2.308(2), O(21)–Ag(1)–N (1) 125.82(7), O(21)–Ag(1)–N(4) 127.27(7), N(1)–Ag(1)–N(4) 106.34 (8). (b) 1D chain formed by Ag(1) atoms and L ligands. (c) 3D framework of 1 linked by hydrogen bonds indicated by dashed lines and the Ag atoms shown as balls.

chain structure (Fig. 1b). Such 1D chains are further held together *via* hydrogen bonds to generate a three-dimensional (3D) supramolecular structure (Fig. 1c). The hydrogen bonding data are summarized in Table S1. \dagger

The coupling reaction of aldehyde, amine and phenylacetylene catalyzed by complex 1

Silver(1) complexes are interesting not only for their diverse structures but also for their useful properties including catalysis.¹⁴ It was found that the silver supramolecular complex 1 can catalyze the three-component coupling of aldehydes, amines and alkynes to generate propargylamines without requirements of inert gas atmosphere and/or high temperature (Scheme 1). Various solvents were screened in the three-component reaction of cyclopentanecarbaldehyde, diethylamine and phenylacetylene at room temperature in the air and the results are summarized in Table 2. Dimethyl sulfoxide (DMSO) and chloroform provided excellent yields and proved to be the solvent of choice, while acetonitrile, dichloromethane and N,N-dimethylformamide (DMF) afforded low yields. The reactions in alcohol afforded quite poor yields. Further, the optimum ratio of aldehyde, amine and alkyne was found to be 1:1.1:1.2 after extensive screening. The controlled three-component reaction conducted under the same conditions with AgNO₃ in CHCl₃ afforded 68% yield (Table 2, entry 9). We also controlled the reaction temperature at 100 °C in DMSO, however the yield of the three-component reaction did not obviously change (Table 2, entry 8), which shows that the temperature has little effect on the reaction catalyzed by the supramolecular complex.

To examine the scope of this three-component coupling reaction, different amines and aldehydes were used to react with phenylacetylene, and the results are listed in Table 3. At the beginning, phenylacetylene and cyclohexylcarboxaldehyde were used as model substrates reacting with different amines (Table 3, entries 1-11). The results indicate that cyclic and acyclic secondary aliphatic amines gave excellent yields of the desired products at room temperature in short times (Table 3, entries 1-3). However, the silver supramolecule catalyzed the reaction of cyclohexanecarbaldehyde, heterocyclic secondary amines and phenylacetylene with low conversion (ca. 0-60%), despite of prolonged reaction times (Table 3, entries 4-8, 10). What is more, the primary amine and imidazole hardly reacted with the aldehyde and phenylacetylene (Table 3, entries 9 and 11). Subsequently, various aldehydes coupled with pyrrolidine and phenylacetylene had been tried. Both aromatic and aliphatic aldehydes are able to undergo the reaction to afford the corresponding propargylic amines effectively. The aliphatic aldehydes display high reactivity (Table 3, entries 12-14), while the aryl



Scheme 1 Silver supramolecule catalyzed three-component coupling of phenylacetylene, amine and aldehyde.





^{*a*} Cyclopentanecarbaldehyde (2 mmol), diethylamine (2.2 mmol), phenylacetylene (2.4 mmol), catalyst (1.9% mmol), rt, 8 h. ^{*b*} Isolated yields based on aldehyde. ^{*c*} The reaction was carried out at 100 °C. ^{*d*} The reaction was carried out using 1.9% mmol AgNO₃.

Table 3 Coupling of aldehyde, alkyne, and amine catalyzed by silver supramolecule in CHCl3^a



 Table 3 (Contd.)

Table 3 (C	R ¹ -CHO +	• R ² R ³ NH +	−H Catalyst R ¹ CHCl ₃ , air, rt	up2p3	
Entry	Aldehyde	Amine (R^2, R^3)	Product	Time	Yield ^b (%)
6	СНО		N	24 h	18 ^c
7	С	L		24 h	NR
8	СНО	NH		24 h	36
9	СНО	MH ₂		24 h	NR
10	СНО			24 h	NR
11	СНО	HN N		24 h	NR
12	С	NH		3 h	96
13	СНО	NH	N N	8 h	90
14	СНО	NH		12 h	62
15	СНО	NH		12 h	68



^{*a*} Aldehyde (2 mmol), amine (2.2 mmol), phenylacetylene (2.4 mmol), catalyst (1.9% mmol), rt. ^{*b*} Isolated yields based on aldehyde. ^{*c*} Yield determined by ¹H NMR analysis of the crude product using CH_2Br_2 as an internal standard. ^{*d*} The catalyst was filtrated after 0.5 h and the reaction solution was further stirred for 2.5 h. ^{*e*} Yield after the fourth cycle of reuse of the catalyst.

aldehydes decreased the reactivity of the reaction, required longer reaction times for reaction completion, and gave lower yields, which is effected by the electron-donating and electronwithdrawing functionalities in the aryl aldehyde (Table 3, entries 15-18). The cinnamaldehyde, as an unsaturated aldehyde, reacted with the pyrrolidine and phenylacetylene hardly giving any of the corresponding propargylic amines (Table 3, entry 19). Noticeably, the removal of complex 1 by filtration after only 0.5 h completely shut down the reaction, affording only 2% additional product upon stirring for another 2.5 h (Table 3, entry 20). The results unambiguously demonstrate that complex 1 is the true heterogeneous catalyst and has no dissolution in the reaction solution. The solids of complex 1 can be easily isolated from the reaction suspension by simple filtration and can be reused at least four times with a slight decrease in the catalytic activity (Table 3, entry 21).

Regarding the reaction mechanism, it has been reported that in the reactions catalyzed by silver iodide, a silver acetylide is proposed to be the intermediate, and reacts with the iminium ion formed from the aldehyde and amine to give the product.⁸ Such a simple silver acetylide may not be so stable in the air and thus the reactions need to be carried out under a nitrogen atmosphere.^{8a} However, in our reactions, we estimate that silver supramolecule used as catalyst may stabilize the intermediate of silver supramolecule–acetylide, which reacts with aldehydes and amines to give the products, and as a result the reactions can be performed in the air. Therefore, the formation and the stability of the metal–acetylide intermediate are important in such catalytic reactions.^{8,15}

Conclusions

In summary, the silver supramolecule successfully catalyzed the three-component reaction of aldehydes, amines and phenylacetylene to give propargylamines in one-pot under mild conditions. As the reaction is simple and the yields are satisfactory, we believe that this method may be widely useful in the preparation of propargylamines.

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