

Research Article

Ligand Synthesis Catalyst and Complex Metal Ion: Multicomponent Synthesis of 1,3-Bis(4-phenyl-[1,2,3]triazol-1-yl)-propan-2-ol Copper(I) Complex and Application in Copper-Catalyzed Alkyne-Azide Cycloaddition

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A new bistriazole copper complex was synthesized by direct treatment of an alkyne, an azide, and CuI as copper salt through *in situ* ligand formation under a multicomponent reaction process. This complex was analyzed by XPS, TGA, DSC, and SEM techniques and revealed a triangular-shaped morphology, high thermal stability, and catalytic power in CuAAC reactions, requiring only 2.5% mol catalyst to afford 1,2,3-triazoles in good yields which can be reused at least for 4 cycles.

1. Introduction

Multicomponent reactions (MCRs) represent one of the growing synthetic approaches due to the fact that they provide useful products through the expeditious creation of multiple bonds in a one-pot reaction [1]. Under this concept, many reagents are added in only one step and they selectively react to give only one reaction product [2]. This approach has been successfully applied in the organic chemistry field [3, 4]; however, few examples of this synthetic strategy are found in the preparation of metal complexes. A relevant case was described by the group of Xiong and Abrahams to prepare tetrazole metal complexes from nitriles, sodium azide, and diverse metal salts [5].

On the other hand, Click Chemistry through copper-catalyzed alkyne-azide cycloaddition (CuAAC) has been recognized as the most important method developed in this century for creating new molecules and chemical libraries as well as macromolecular diversified architectures with high efficiency in terms of yield and atom economy [6]. In spite of

all these advantages, the potential of Click Chemistry could be further increased by combining with multicomponent reactions towards synthesis of sophisticated materials, particularly metal catalysts.

In connection with other synthetic studies, we prepared an array of bistriazoles derived from diazidopropanol using CuAAC reaction. During the reaction work-up, we noticed that copper catalyst was difficult to remove in these compounds, probably owing to complex formation between product and catalyst. This feature encouraged us to explore this process in order to devise a simple method for the preparation of a sort of novel bistriazole copper(I) complexes from the *in situ* ligand synthesis into a multicomponent reactions concept. Herein is described our recent endeavors in this area.

2. Experimental Section

The starting materials were purchased from Aldrich Chemical Co. and were used without further purification. Solvents

were distilled before use. Silica plates of 0.20 mm thickness were used for thin layer chromatography. Melting points were determined with a Fisher-Johns melting point apparatus and they are uncorrected. ^1H and ^{13}C NMR spectra were recorded using Varian 500; the chemical shifts (δ) are given in ppm relative to TMS as internal standard (0.00). For analytical purposes, the mass spectra were recorded on Shimadzu GCMS-QP2010 Plus in the EI mode, 70 eV, 200°C via direct inlet probe. Only the molecular and parent ions (m/z) are reported. IR spectra were recorded on Bruker Tensor 27 equipment. The XPS wide and narrow spectra were acquired using JEOL JPS-9200, equipped with a Mg X-ray source (1253.6 eV) at 300 W, the area of analysis was 3 mm², and the vacuum was in the order of 7.5×10^{-9} Torr for all samples. The spectra were analyzed using the SpecSurf™ software included with the instrument; all spectra were charge-corrected by means of the adventitious carbon signal (C1s) at 284.5 eV. The Shirley method was used for the background subtraction, whereas for the curve fitting the Gauss-Lorentz method was used. TGA/DSC studies were carried out in thermal analyzer Netzsch STA 449 F3 Jupiter with a heating ramp of 10°C/min, in a nitrogen atmosphere at a flow rate of 20 mL/min. Samples were heated from room temperature to 560°C; aluminum crucibles of 5 mm diameter were used. Savitzky-Golay smoothing algorithm was employed for TGA curves. 1,3-Diazido-propan-2-ol (**13**) was synthesized according to a previous report [7].

Synthesis of Copper(I) Complex of 1,3-Bis(4-phenyl-[1,2,3]triazol-1-yl)-propan-2-ol (4). To a solution of 1,3-diazido-propan-2-ol [7] (0.142 g, 1 mmol) in MeOH (15 mL) were added successively phenylacetylene (0.22 mL, 0.204 g, 2 mmol), 0.5 N aqueous solution of NaOH (0.2 mL), and CuI (0.189 g, 1 mmol). The resulting mixture was stirred for 24 hours at room temperature under a nitrogen atmosphere. The solid was filtered and washed with cold MeOH (20 mL) and diethyl ether (20 mL). The product was dried under reduced pressure. Yield: 0.335 g (97%), m.p. 180°C. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 3369, 3122, 1440, 1227, 1157. ^1H NMR: (500 MHz, DMSO- d_6) δ 8.59 (s, 2H), 7.89 (s, 4H), 7.44 (s, 4H), 7.34 (s, 2H), 5.85 (s, 1H), 4.67 (s, 2H), 4.45 (s, 2H), 3.15 (s, 1H). ^{13}C NMR: (125 MHz, DMSO- d_6) δ 146.1, 130.8, 128.9, 127.8, 125.1, 122.5, 68.3, 53.2. Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{CuIN}_6\text{O}$ (%): C, 42.51; H, 3.38; N, 15.65. Found: C, 72.05; H, 11.50; N, 7.67. HRMS: calcd. for $\text{C}_{19}\text{H}_{18}\text{CuIN}_6\text{O}$ [M]⁺: 535.9983, found: 535.9989.

Synthesis of 1,2,3-Triazoles Catalyzed by 1,3-Bis(4-phenyl-[1,2,3]triazol-1-yl)-propan-2-ol Copper(I) Complex: General Procedure. The copper complex **4** (0.0268 g, 0.025 mmol) was added to a stirred solution containing the corresponding alkyne (1.0 mmol) and the appropriate azide (1.05 mmol) in CH_2Cl_2 (10 mL). The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was filtered through celite-activated charcoal. The solvent was removed under reduced pressure and the final product was purified by crystallization.

1-Benzyl-4-phenyl-1,2,3-triazole (6). Phenylacetylene and benzyl azide afforded 1-benzyl-4-phenyl-1,2,3-triazole as

white solid. Yield: 132.8 mg (99%). m. p. 130°C (lit. 130–130.9°C) [8]. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 3140, 3028, 2974, 1606, 1579, 1489. ^1H NMR (300 MHz, CDCl_3) δ /ppm: 7.78–7.81 (m, 2H), 7.66 (s, 1H), 7.41–7.36 (m, 3H), 7.32–7.25 (m, 5H), 5.55 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ /ppm: 148.2, 134.7, 130.5, 129.1, 128.7, 128.1, 127.9, 125.6, 119.5, 54.1. MS (EI^+) m/z (%): 235 [M]⁺ (20), 206 [$\text{M}-\text{HN}_2$]⁺ (74), 116 [$\text{M}-\text{C}_6\text{H}_5\text{N}_3$]⁺ (100), 91 [$\text{C}_6\text{H}_5\text{CH}_2$]⁺ (85).

1-(1-Benzyl-[1,2,3]triazol-4-yl)-cyclohexanol (7). 1-Ethynyl-cyclohexanol and benzyl azide afforded 1-(1-benzyl-[1,2,3]triazol-4-yl)-cyclohexanol as white solid. Yield: 244.4 mg (95%). m. p. 150°C. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 3386, 3291, 2930, 2855, 1604. ^1H NMR (300 MHz, DMSO- d_6) δ /ppm: 7.98 (s, 1H), 7.39 (m, 5H), 5.60 (s, 1H), 4.92 (s, 1H), 1.92–1.46 (m, 10H). ^{13}C NMR (75 MHz, DMSO- d_6) δ /ppm: 136.2, 128.7, 128.5, 128.0, 121.1, 68.0, 52.7, 37.8, 25.224, 21.6. MS (EI^+) m/z (%): 257 [M]⁺ (20), 91 [$\text{C}_6\text{H}_5\text{CH}_2$]⁺ (100). HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}$: 257.1528; found: 257.1534.

1-Benzyl-4-(4-bromophenoxy)methyl)-[1,2,3]triazole (8). 1-Bromo-4-prop-2-ynyloxy-benzene and benzyl azide afforded 1-benzyl-4-(4-bromophenoxy)methyl)-[1,2,3]triazole as white solid. Yield: 116.6 mg (34%). 109–110°C. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 3040, 2954, 2926, 2873, 1581, 1487. ^1H NMR (300 MHz, CDCl_3) δ /ppm: 7.51 (s, 1H), 7.33–7.38 (m, 3H), 7.27–7.30 (m, 2H), 7.25–7.27 (d, 2H, $J = 8.3$ Hz), 6.81–6.85 (d, 2H, $J = 8.2$ Hz), 5.52 (s, 2H), 5.14 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ /ppm: 157.3, 144.2, 134.4, 132.3, 129.2, 128.9, 128.1, 122.7, 116.6, 113.5, 62.2, 54.3. MS (EI^+) m/z (%): 343 [M]⁺ (5), 172 [$\text{M}-\text{C}_6\text{H}_4\text{BrO}$]⁺ (15), 144 [$\text{M}-\text{C}_8\text{H}_8\text{BrO}$]⁺ (65), 91 [$\text{C}_6\text{H}_5\text{CH}_2$]⁺ (100).

1-Benzyl-4-(4-chlorophenoxy)methyl)-1,2,3-triazole (9). 1-Chloro-4-prop-2-ynyloxy-benzene and benzyl azide afforded 1-benzyl-4-(4-chlorophenoxy)methyl)-1,2,3-triazole as white solid. Yield: 140.5 mg (47%). 102°C (lit. 102–103°C) [9]. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 2945, 2873, 1582, 1488, 1458. ^1H NMR (300 MHz, CDCl_3) δ /ppm: 7.53 (s, 1H), 7.38–7.40 (m, 3H), 7.27–7.30 (m, 2H), 7.22–7.25 (d, 2H, $J = 8.5$ Hz), 6.89–6.92 (d, 2H, $J = 8.5$ Hz), 5.54 (s, 2H), 5.16 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ /ppm: 156.7, 144.1, 134.3, 129.7, 129.4, 128.8, 128.0, 122.6, 116.0, 62.2, 54.2. MS (EI^+) m/z (%): 299 [M]⁺ (15), 91 [$\text{C}_6\text{H}_5\text{CH}_2$]⁺ (100), 144 [$\text{C}_{10}\text{H}_{10}\text{N}$]⁺ (78), 172 [$\text{C}_{10}\text{H}_{10}\text{N}$]⁺ (25).

1-Benzyl-4-(4-methoxyphenoxy)methyl)-1,2,3-triazole (10). 1-Methoxy-4-prop-2-ynyloxy-benzene and benzyl azide afforded 1-benzyl-4-(4-methoxyphenoxy)methyl)-1,2,3-triazole as white solid. Yield: 280.0 mg (95%). m.p. 92.1°C (lit. 92–93°C) [10]. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 2946, 2831, 1505, 1286. ^1H NMR (300 MHz, CDCl_3) δ /ppm: 7.50 (s, 1H), 7.37–7.38 (m, 3H), 7.23–7.26 (m, 2H), 6.88–6.90 (d, 2H, $J = 8.2$ Hz), 6.78–6.87 (d, 2H, $J = 8.2$ Hz), 5.51 (s, 2H), 5.12 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ /ppm: 154.2, 152.3, 144.8, 134.5, 129.1, 128.8, 128.1, 122.6, 115.9, 114.7, 62.8, 54.2. MS (EI^+) m/z (%): 295 [M]⁺ (20), 144 [$\text{C}_{10}\text{H}_{10}\text{N}$]⁺ (35), 124 [$\text{C}_7\text{H}_8\text{O}_2$]⁺ (100), 91 [$\text{C}_6\text{H}_5\text{CH}_2$]⁺ (50).

1-Benzyl-4-p-toloxymethyl-[1,2,3]triazole (11). 1-Methyl-4-prop-2-ynyloxy-benzene and benzyl azide afforded 1-benzyl-4-p-toloxymethyl-[1,2,3]triazole as white solid. Yield: 273.2 mg (98%). m.p. 109–110°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 2954, 2919, 2869, 1607, 1287. ^1H NMR (300 MHz, CDCl_3) δ/ppm : 7.50 (s, 1H), 7.34–7.40 (m, 3H), 7.24–7.27 (m, 2H), 7.04–7.07 (d, 2H, $J = 8.2$ Hz), 6.83 (d, 2H, $J = 8.2$ Hz), 5.50 (s, 2H), 5.15 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 156.1, 144.9, 134.5, 130.1, 129.9, 129.1, 128.7, 128.1, 122.5, 114.7, 62.3, 54.2. MS (EI^+) m/z (%): 279 $[\text{M}]^+$ (20), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (100).

1-Benzyl-4-phenoxyethyl-[1,2,3]triazole (12). Prop-2-ynyl-oxy-benzene and benzyl azide afforded 1-benzyl-4-phenoxyethyl-[1,2,3]triazole as white solid. Yield: 249.2 mg (94%). m.p. 119–120°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 2922, 2872, 1598, 1490. ^1H NMR (300 MHz, CDCl_3) δ/ppm : 7.52 (s, 1H), 7.24–7.37 (m, 7H), 6.73–6.97 (m, 3H), 5.52 (s, 2H), 5.17 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 158.2, 144.6, 134.4, 129.5, 129.1, 128.7, 128.0, 121.2, 114.7, 62.0, 54.1. MS (EI^+) m/z (%): 265 $[\text{M}]^+$ (5), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (100).

4-(1-Benzyl-1,2,3-triazol-4-ylmethoxy)-benzaldehyde (13). 4-Prop-2-ynyloxy-benzaldehyde and benzyl azide afforded 4-(1-benzyl-1,2,3-triazol-4-ylmethoxy)-benzaldehyde as white solid. Yield: 275.1 mg (94%). m.p. 79°C (lit. 79–80°C) [11]. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 2821, 2798, 2731, 1693, 1653, 1508 (m), 1261. ^1H NMR (300 MHz, CDCl_3) δ/ppm : 9.88 (s, 1H), 7.82–7.83 (dd, 2H, $J = 3, 9$ Hz), 7.54 (s, 1H), 7.36–7.38 (m, 3H), 7.26–7.29 (m, 2H), 7.07–7.09 (dd, 2H, $J = 3, 9$ Hz), 5.54 (s, 2H), 5.26 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 190.7, 163.3, 143.6, 134.3, 130.9, 130.3, 129.2, 128.9, 128.2, 123.1, 115.3, 62.2, 54.3. MS (EI^+) m/z (%): 293 $[\text{M}]^+$ (5), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (100).

Butyl-carbamic Acid 1-Benzyl-[1,2,3]triazol-4-ylmethyl Ester (14). Butyl-carbamic acid prop-2-enyl ester and benzyl azide afforded butyl-carbamic acid 1-benzyl-1H-[1,2,3]triazol-4-ylmethyl ester as white solid. Yield: 267.9 mg (93%). m.p. 99–100°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 2958, 2930, 2868, 1684, 1531. ^1H NMR (300 MHz, CDCl_3) δ/ppm : 7.54 (s, 1H), 7.28–7.41 (m, 3H), 7.26 (m, 2H), 5.54 (s, 2H), 5.15 (s, 2H), 4.81 (s, broad, 1H), 3.15 (m, 2H), 1.44 (m, 2H), 1.25 (m, 2H), 0.87 (t, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ/ppm : 156.1, 143.9, 134.5, 129.1, 128.7, 128.1, 123.5, 57.7, 54.1, 40.7, 31.9, 19.8, 13.6. MS (EI^+) m/z (%): 288 $[\text{M}]^+$ (10), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (100).

3. Results and Discussion

As mentioned above, the first observations were made on the reaction of 1,3-diazido-propan-2-ol **1** with phenylacetylene **2** in the presence of catalytic amounts of CuI to afford 1,3-bis(4-phenyl-[1,2,3]triazol-1-yl)-propan-2-ol, compound **3**. The difficulties found in the work-up process to separate the copper salt motivated us to change the copper salt ratio. Thus, when an equimolar amount of CuI was used in the reaction, an insoluble precipitate was formed after 24 h. A reexamination of these last conditions permitted us to establish a general procedure where the straightforward

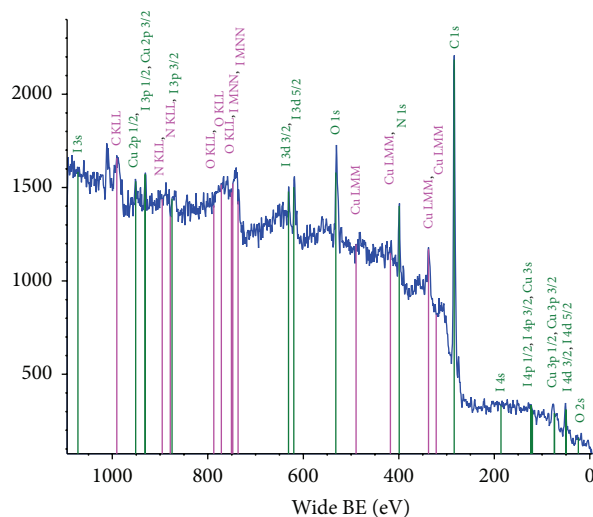


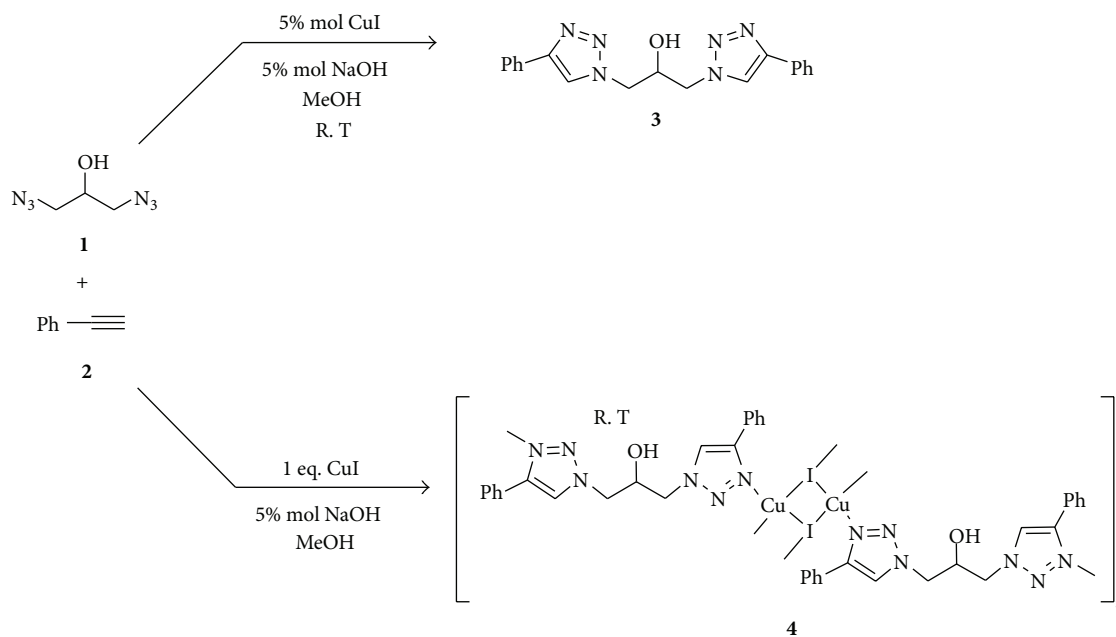
FIGURE 1: Survey spectra of the reaction product **4**.

mixing of CuI, alkyne **1**, and azide **2** generated the polymeric copper complex **4** whose structure is proposed in Scheme 1. The formation of analogous coordination polymers has been reported by Reiser [12] and Zink [13] groups, with a halogen-bridged Cu_2X_2 -type structure for this kind of compounds [14–16].

In order to determine the chemical environment surrounding copper ion and evaluate a possible interaction I-Cu-N in the complex, XPS analysis was performed on product **4**. Figure 1 shows that the survey spectra of the product, the usual signals of Cu 2p 3/2 (934.424 eV), N 1s (402 eV), C 1s (284.5 eV), and I 3d 5/2 (618.88 eV), are easily identified.

In addition, this study confirms the presence of the cited elements involved in the product, which is proposed as a complex between CuI and the bistriazole system. A narrow spectra focused on the Cu 2p 3/2 region (Figure 2) obtained to analyze the possible interactions of copper; the signal of copper appears with a center of 934.424 eV. A noteworthy characteristic is the existence of 2 satellite peaks at 941 eV and 944.9 eV; these satellites are well known to appear when copper is forming complexes especially with nitrogen, characteristic of Cu^{+2} species surrounded by electron donor nitrogen atoms [17]. However, the HWFM of the copper signal exhibits at least 2 signals, so a curve fit was performed and it resolved 2 signals at 934.366 eV and 932.734 eV, close to other Cu^{+1} signals observed at 931.7 eV [18]. The chemical shift observed in the study confirms the interaction in the proposed copper complex **4** bearing both Cu-N and Cu-I interactions [17, 19]; this was further supported with the analysis of the iodine and nitrogen regions as shown in Figures 1 and 2.

Moreover, the iodine 3d5/2 region shows a signal at 618.88 eV coincident to 619 eV signal reported for a Cu-I interaction [17, 19], which allows us to conclude that this interaction is still present, confirming that compound **4** has not undergone a chemical change. The N 1s region was also analyzed and a curve fit was performed (Figure 3); 3 signals were obtained as expected, since the complex structure



SCHEME 1: Cycloaddition between azide 2 and alkyne 1 using catalytic and equimolar amounts of CuI.

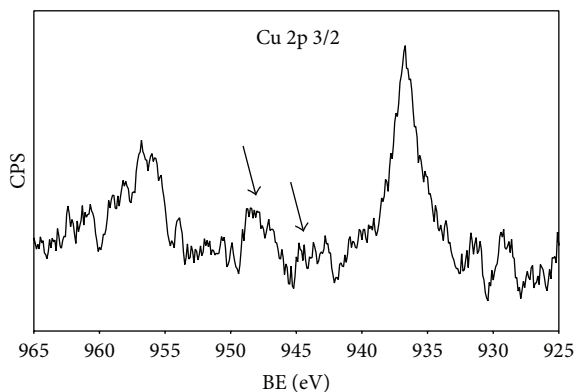


FIGURE 2: Narrow spectra of Cu 2p 3/2 region showing the characteristic copper signal and 2 satellites attributed to the Cu-N interaction of the formed complex 4.

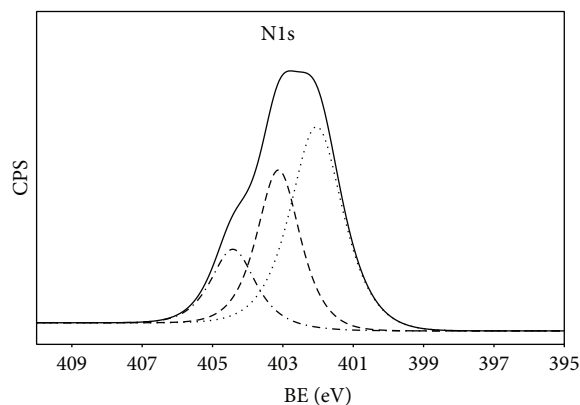


FIGURE 3: XPS curve fit spectra of the N 1s region in compound 4.

proposed would consist of nitrogen with 3 different chemical environments, a first N-Cu-I interaction and 2 additional nitrogen signals which form part of the triazole molecule but without any interaction with Cu, confirming the formation of the complex proposed.

Other outstanding property observed in compound 4 is the high thermal stability. This behavior was determined by TG curves analysis for complex 4 which displays an important weight loss around 320–400°C, associated with the compound degradation and similar to that described by Cavalheiro and coworkers [20]. In contrast, the TGA curve for copper-free bistriazole 3 indicates only a slight loss presumably due to volatile solvents and humidity (Figure 4).

DSC studies were determined on copper complex 4 and copper-free bistriazole 3 and the corresponding DSC curves

are plotted in Figure 5. For compound 3, DSC profile denotes an endothermic process at 243°C assigned to the product melting point and an exotherm at 369°C, showing decomposition thereof. In the case of complex 4, an exotherm observed at 320°C shows the compound decomposition, followed by two endothermic processes, 379 and 397°C associated copper loss and degradation; a third point of decomposition can be found at 598°C corresponding to the decomposition of the compound. This decomposition pattern is analogous to a copper(II) coordination polymer containing tetrazole ligands [21]. Hence, DSC results support TGA studies and suggest stability for bistriazole copper complex 4.

Although crystallization of copper complex 4 was not possible, we realized that this compound produces an aggregate with a specific supramolecular structure. In the SEM micrographs obtained from compound 4 (Figure 6), a triangular-shaped morphology is presented, which could

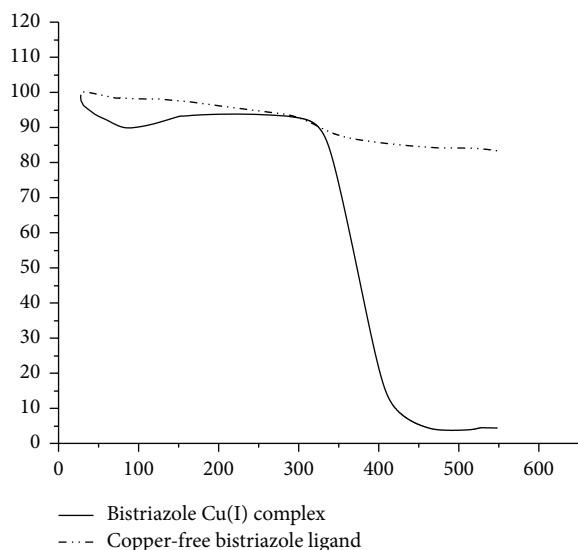


FIGURE 4: TG thermograms of copper-free bistriazole **3** and complex **4**.

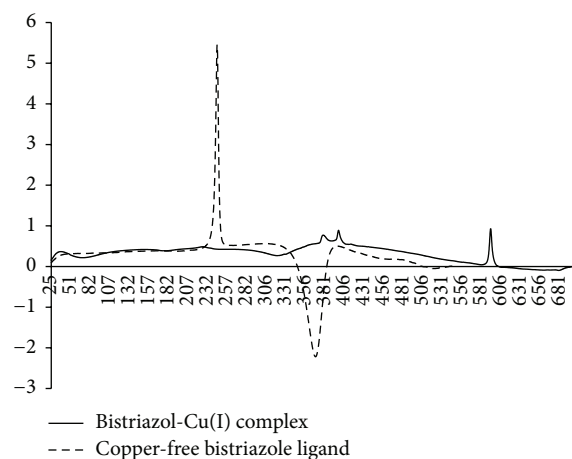


FIGURE 5: DSC curves for copper-free bistriazole **3** and complex **4**.

be generated by metamorphic transformations during the synthesis. This well-defined architecture is consequence of metal-ligand interactions and suggests a kind of self-organization [22].

The catalytic activity of copper complex **4** was tested in the reaction between phenylacetylene **2** and benzyl azide **5** which were treated with varying catalyst quantities (Scheme 2). In all cases, the formation of triazole **6** was registered as only reaction product, and the results, summarized in Table 1, demonstrate that complex **4** efficiently catalyzes the CuAAC reaction on a wide range of solvents. Even though the reaction proceeded with 0.5% mol catalyst, the optimal conditions were obtained using a 2.5% mol catalyst ratio. From these results, we selected CH_2Cl_2 as reaction solvent for subsequent experiments.

The breadth of this process was also studied. Examples in Table 2 and Scheme 3 proved that compound **4** works with

TABLE 1: Synthesis of triazole **6** catalyzed by copper complex **4**.

Entry	Catalyst ratio (% mol)	Solvent	% yield
1	0.5	CH_2Cl_2	80
2	1.0	CH_2Cl_2	89
3	2.5	CH_2Cl_2	100
4	5.0	CH_2Cl_2	100
5	0.5	H_2O	35
6	1.0	H_2O	43
7	2.5	H_2O	100
8	5.0	H_2O	100
9	0.5	Acetone	40
10	1.0	Acetone	60
11	2.5	Acetone	100
12	5.0	Acetone	100
13	0.5	THF	45
14	1.0	THF	70
15	2.5	THF	95
16	5.0	THF	100
17	0.5	DMF	46
18	1.0	DMF	69
19	2.5	DMF	96
20	5.0	DMF	100
21	0.5	AcOEt	30
22	1.0	AcOEt	60
23	2.5	AcOEt	93
24	5.0	AcOEt	96
25	0.5	MeOH	40
26	1.0	MeOH	50
27	2.5	MeOH	96
28	5.0	MeOH	100
29	2.5	EtOH	96
30	5.0	EtOH	100
31	2.5	<i>n</i> PrOH	94
32	5.0	<i>n</i> PrOH	100
33	2.5	CHCl_3	94
34	5.0	CHCl_3	100
35	2.5	CH_3CN	93
36	5.0	CH_3CN	100
37	2.5	Et_2O	94
38	5.0	Et_2O	100

different alkynes to afford the respective benzyl triazoles in high yields.

The insoluble nature of copper complex **4** prompted us to explore the possibility of use like heterogeneous catalyst. In this regard, the recycling experiments were carried out by simple filtration of insoluble catalyst which was reincorporated to the next cycle. The results in Table 3 suggest that comparatively good yields can be obtained after 5 cycles in spite of the progressive loss of efficiency. This peculiarity allows copper complex **4** to be used without other additives in similar way to other available catalytic systems designed for CuAAC reactions [23].

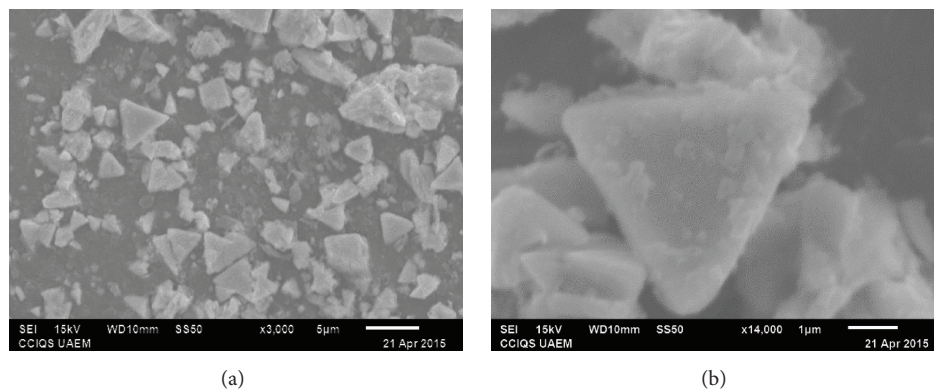


FIGURE 6: SEM micrographs complex 4. (a) $\times 3000$, $5 \mu\text{m}$ and (b) $\times 14000$, $1 \mu\text{m}$.

TABLE 2: Synthesis of triazoles catalyzed by copper complex 4 (see Scheme 3).

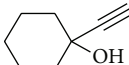
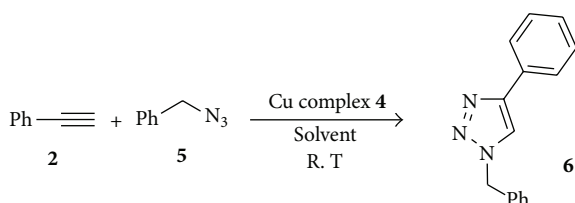
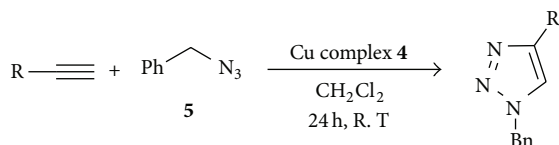
Compound	R	% yield
6	Ph	100
7		95
8	$\text{CH}_2\text{O}(4\text{-Br})\text{C}_6\text{H}_4$	34
9	$\text{CH}_2\text{O}(4\text{-Cl})\text{C}_6\text{H}_4$	47
10	$\text{CH}_2\text{O}(4\text{-OCH}_3)\text{C}_6\text{H}_4$	95
11	$\text{CH}_2\text{O}(4\text{-CH}_3)\text{C}_6\text{H}_4$	98
12	$\text{CH}_2\text{OC}_6\text{H}_5$	94
13	$\text{CH}_2\text{O}(4\text{-CHO})\text{C}_6\text{H}_4$	94
14	$\text{CH}_2\text{OCONH}(\text{CH}_2)_3\text{CH}_3$	93

TABLE 3: Recycling of copper complex 4 in the synthesis of triazole 6.

Cycle	% yield
1	100
2	99
3	98
4	95
5	91
6	85
7	76
8	57



SCHEME 2: Cycloaddition between azide 5 and alkyne 2 using copper complex 4.



SCHEME 3

4. Conclusions

A simple synthetic protocol which involves the direct combination of three reagents (“components”) was developed to provide a new bistriazole copper complex which shows catalytic activity for CuAAC reactions and can be recycled at

least for 4 times maintaining its catalytic ability; in addition, this complex exhibits a precise morphology, product of a self-organization, besides a high thermal stability which opens wide perspectives of promising applications in the future. The multicomponent reaction strategy for the synthesis of this copper complex represents a departure point for the preparation of similar compounds from nonexpensive starting materials in a one-pot process; these elements suggest that this approach will enjoy widespread use.

Competing Interests

The authors declare that they have no competing interests.

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