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Copper complexes bearing C-scorpionate ligands: Synthesis, characterization and catalytic activity for azide-alkyne cycloaddition in aqueous medium

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A R T I C L E   I N F O

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A B S T R A C T

Reactions of CuX (X = Br or I) and $[Cu(MeCN)_4][BF_4]$ with the neutral C-scorpionates $HC(3,5\text{-}Me_2pz)_3$ and $HC(3\text{-}Phpz)_3$ (Tpm^* and Tpm^{Ph}, respectively) proceed readily at room temperature to give the neutral copper(I) complexes $[CuBr(Tpm^{Ph})]$ (**1**), $[CuI(Tpm^{Ph})]$ (**2**), $[CuBr(Tpm^*)]$ (**3**), $[CuI(Tpm^*)]$ (**4**) and the cationic $[Cu(Tpm^{Ph})(NCMe)][BF_4]$ (**5**), $[Cu(Tpm^*)(NCMe)][BF_4]$ (**6**) and $[Cu(Tpm^*)_2][BF_4]_2$ (**7**), the latter also obtained from **6** after some time in air. Compounds **1**–**7** act as homogeneous catalysts for the low-power microwave-assisted three component (alkyne, bromobenzyl, sodium azide) cycloaddition reaction (CuAAC) to afford 1,4-disubstituted-1,2,3-triazoles, with **7** as the best catalyst. The catalytic reaction evolves well in ROH/H_2O solution, depends on the R group and proceeds better when R = Me, here achieving yields up to 94%. The alcohol plays a role in the Cu(II)-to-Cu(I) Glaser-type induction period, therefore avoiding a reducing agent in the system.

1. Introduction

Copper species play a very essential role in several enzymes and catalytic systems, which leads to a significant interest to develop new copper models for catalysis [1–4]. Among the most interesting copper species applications in catalysis is the copper catalyzed azide-alkyne cycloaddition reaction (CuAAC, Scheme 1). Since its discovery [5,6], this reaction has become the most genuine example of "click chemistry" [7] and constituted a powerful tool for the synthesis of 1,2,3-triazoles with growing applications in materials science, molecular biology, polymer and medicinal chemistry [8–10].

Due to the explosive nature of organic azides, their isolation and purification can be problematic [11,12]. Therefore, intensive attention has been devoted to a new one-pot procedure of three components reaction (alkyne, organic halide and sodium azide) [13–16], which involves *in-situ* generation of organo azides followed by addition to an alkyne to produce the corresponding 1,2,3-triazole (Scheme 2).

The most common procedure for CuAAC is the *in situ* generation of Cu(I) from a mixture of Cu(II) salt (*e.g.*, $CuSO_4$) and sodium ascorbate as reducing agent in aqueous medium [6,17,18]. Other catalytic systems have been developed including the use of (a) Cu(I) salts with addition of a ligand [16,19], (b) electrochemically generated Cu(I) species [20], (c) supported Cu(I) on an immobilized phase [21,22], (d) Cu-containing nanoparticles [23] and, to a lower extent, (e) well-defined Cu(I) complexes [15,24–31] where the main role of the ligand is to stabilize the Cu(I) centres. In this respect, tris(triazoles) [15,24], phosphines [25–28], tetramines [29], and *N*-heterocyclic carbenes [30,31] are successfully used ligands under different conditions.

In 2006 [32], Kantam et al. reported the first example of using solely a Cu(II) salt (*i.e.*, $Cu(OAc)_2$, OAc = acetate) without reducing agents or additional bases for the CuAAC reaction, in aqueous medium, and postulated a direct participation of Cu(II) in the catalytic process. Considering the extremely high efficiency of Cu(I) for the CuAAC reaction at less than 0.01 equiv., as well as many studies providing the essentiality of the presence of Cu(I) for the catalysis process [5,6,25,26,29–31,17–24], it is more persuasive to ascribe catalysis to small amounts of Cu(I) present or somehow generated in the reaction mixture. Brotherton et al. [33] suggested that, in the presence of Cu(II), Cu(I) may be generated during an oxidative homocoupling of terminal alkynes (Eq. (1)), the process then pursuing as Glaser reaction [34]. This assumption has been confirmed by several spectroscopic, mechanistic and computational studies on different Cu(II) salts and

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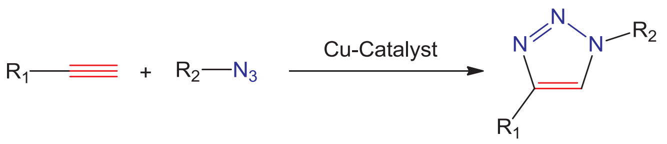
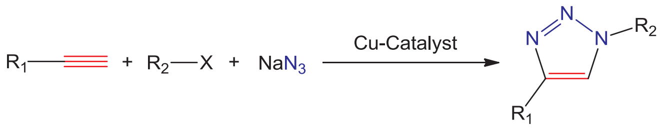


Scheme 1. Copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction.



Scheme 2. Three components catalyzed CuAAC reaction.

complexes, clearly revealing that Cu(I) species are generated in a short induction period from alkyne-alkyne homocoupling [33,35,36]. Thereafter, Cu(II) salts [37] or complexes [35,38,39] and immobilized Cu(II) species [36,40] have been successfully applied for reducing agents free ACC reaction.

in a few hours, a colour which is typical of a Cu(II) derivative. Complexes **1**–**4** are soluble in MeCN, CH_2Cl_2 and DMSO, **3** and **4** also having good solubilities in MeOH. They present a half-sandwich structure with one κN^3-coordinated Tpm^{Ph} (**1**, **2**) or Tpm^* (**3**, **4**) ligand, their formulations being confirmed by spectroscopic and analytical data (see below). The structures of **1** and **4** have also been established by single crystal X-ray diffraction. However, since the structure of the former is of very low quality (see Supplementary Information) and the structure of **4** has already been reported [46], none will be discussed.

The coordination of Tpm^{Ph} and Tpm^* ligands to the Cu(I) centre in **1**–**4** was confirmed by the downfield shift of resonances for the pyrazolyl ring protons of the ligands in their ^1H NMR spectra (see the Experimental Section, and Figs. S1 and S2). Both their ^1H NMR and ^{13}C NMR spectra show the equivalence of the three pyrazolyl rings by exhibiting a single resonance for each type of protons or carbons, according to the *N,N,N*– coordination mode to the Cu(I) centre. The IR spectra of the compounds exhibit a set of bands with diverse intensities typical of Tpm^{Ph} and Tpm^* ligands [42,48], in particular the C=N stretching vibrations at 1532, 1524, 1562 and 1557 cm^{-1}. The coordination of the halide (Br^- or I^-) was confirmed by the typical bands in the 213–224 cm^{-1} range.

$$2\,R{-}{\equiv}{-}H + 2\,\mathbf{Cu(II)} \xrightarrow[-2H^+]{} R{-}{\equiv}{-}{\equiv}{-}R + 2\,\mathbf{Cu(I)} \qquad (1)$$

Since the discovery of tris(pyrazol-1-yl)methane (Tpm) compounds (C-scorpionates) [41] and the improvement of their synthetic procedures [42,43], a significant number of copper complexes bearing these ligands have been synthesized, used as catalysts for several processes and, most notably, in C−H bond activation methods [44]. Due to the ability of Tpm ligands to form stable copper complexes [45–49], they would be promising candidates for CuAAC processes. However, to our knowledge, the reported CuAAC processes catalyzed by Cu-Tpm compounds is limited to just one Cu(I) example [50]. Herein we report the catalytic performance of well-defined Cu(I) and Cu(II) complexes with Tpm ligands, *viz* tris(3,5-dimethyl-1-pyrazolyl)methane, $HC(3,5\text{-}Me_2pz)_3$ or Tpm^*, and tris(3-phenylpyrazolyl)methane, $HC(3\text{-}Phpz)_3$ or Tpm^{Ph}, (pz = pyrazol-1-yl; Fig. 1) for three-components CuAAC process. The microwave assisted efficiency of such catalytic systems was also investigated, confirming the already proven [14,15] great increase of the CuAAC reaction rate under such experimental conditions.

2. Results and discussion

Reaction of Cu(I) bromide or iodide with Tpm^{Ph} or Tpm^* in an equimolar amount proceeds readily at room temperature to give the respective $[CuBr(Tpm^{Ph})]$ (**1**), $[CuI(Tpm^{Ph})]$ (**2**), $[CuBr(Tpm^*)]$ (**3**) and $[CuI(Tpm^*)]$ (**4**) colourless complexes in good yield (Scheme 3). Complexes **1**, **2** and **4** are air stable both in solid state and in solution, but **3** is stable in air only in the solid state since its solution changes to green

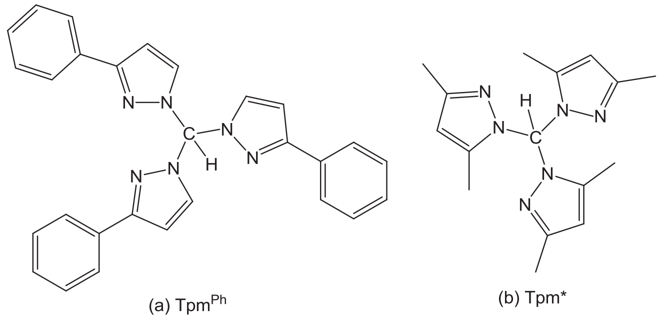
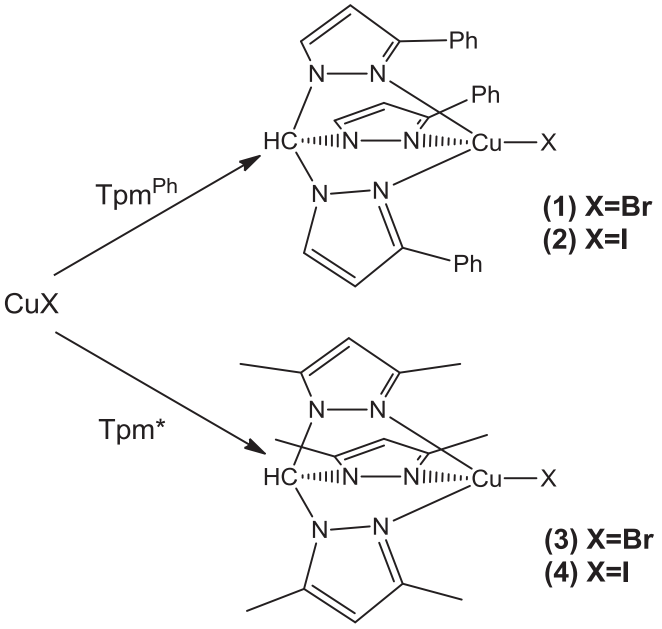


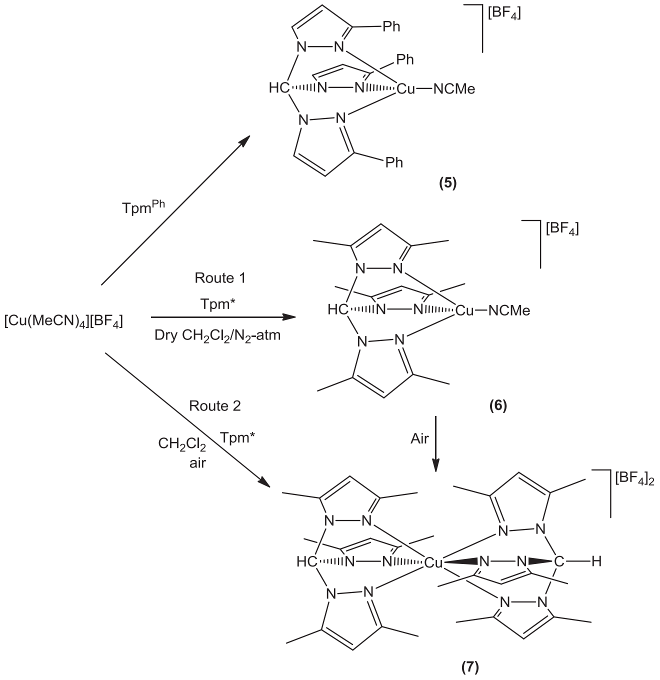
Fig. 1. Structures of C-scorpionate ligands employed in this work: (a) tris(3-phenylpyrazolyl)methane $HC(3\text{-}Phpz)_3$ (pz = pyrazol-1-yl), Tpm^{Ph}; (b) tris(3,5-dimethyl-1-pyrazolyl)methane $HC(3,5\text{-}Me_2pz)_3$, Tpm^*.

ESI(+)MS spectra for **1**–**4** were obtained in acetonitrile solution, showing in all cases the base peak corresponding to the $[M - X + MeCN]^+$ fragment.

Reaction of $[Cu(MeCN)_4][BF_4]$ with Tpm^{Ph} in air, under mild conditions, yields the Cu(I) complex $[Cu(Tpm^{Ph})(NCMe)][BF_4]$ (**5**) (Scheme 4). By mixing equimolar amounts of $[Cu(MeCN)_4][BF_4]$ and Tpm^* in degassed CH_2Cl_2, under inert N_2-atmosphere, $[Cu(Tpm^*)(NCMe)][BF_4]$ (**6**) was afforded as an off-white powder in high yield (Scheme 4, route 1). Compound **6** is stable as a solid in air, but is unstable in solution as it is oxidized to the green coloured Cu(II) complex $[Cu(Tpm^*)_2][BF_4]_2$ (**7**) in a few hours (Scheme 4). Compound **7** can also be obtained following the same procedure as for compound **6** synthesis, using CH_2Cl_2 solvent in open air (Scheme 4, route 2). This compound has already initially been obtained [51] following a 1:2 reaction of the



Scheme 3. Synthesis of Cu(I) complexes $[CuBr(Tpm^{Ph})]$ (**1**), $[CuI(Tpm^{Ph})]$ (**2**), $[CuBr(Tpm^*)]$ (**3**) and $[CuI(Tpm^*)]$ (**4**).



Scheme 4. Synthesis of compounds $[Cu(Tpm^{Ph})(NCMe)][BF_4]$ (**5**), $[Cu(Tpm^*)(NCMe)][BF_4]$ (**6**) and $[Cu(Tpm^*)_2][BF_4]_2$ (**7**).

$Cu(BF_4)_2$ hydrated salt and Tpm^*. Compounds **5–7** display a good solubility in MeOH, DMSO, MeCN, and chlorinated solvents such as CH_2Cl_2 and $CHCl_3$.

The cationic complexes **5–7** were characterized by ESI-MS spectrometry, elemental analysis, FT-IR and NMR (^1H and $^{13}C\{^1H\}$, except for **7**) spectroscopies, which support the proposed formulations (see experimental section) and the results are consistent with the data already reported when $[PF_6]^-$ is the counter anion (i.e., $[Cu(Tpm^{Ph})(NCMe)][PF_6]$ and $[Cu(Tpm^*)(NCMe)][PF_6]$) [47]. The crystal structure of **7** agreed with the already established one [51].

Azide-alkyne cycloaddition in aqueous-three component catalytic system

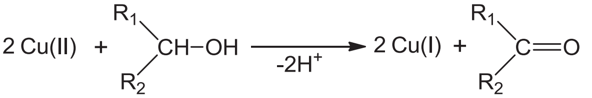
The catalytic performances of compounds **1–7** were investigated towards the three component CuAAC reaction. Under low power (10 W) microwave (MW) irradiation and in homogeneous conditions, taking the reaction between phenylacetylene, benzyl bromide and sodium azide to afford 1-benzyl-4-phenyl-1H-1,2,3-triazole as a model (see Table 1, inset reaction). The reaction product could be easily isolated by filtration and no byproducts were identified. In order to optimize the reaction conditions a series of experiments was performed to study the influence of variables such as type and amount of catalyst, solvent and reaction time (Table 1).

The catalytic reactivity of compounds **1–7** for the indicated CuAAC reaction was initially tested (Table 1, entries 1–7), using 1.5 mol% of catalyst, in water:MeCN (1:1) mixture, under MW irradiation (10 W) for 30 min, to produce 1-benzyl-4-phenyl-1H-1,2,3-triazole as unique product with yield in the 18–88% range. Compound **7** revealed the highest activity and was thus used for the optimization of the reaction conditions.

Increasing the catalyst loading from 0.5 mol% to 1.5 mol% raised the isolated yield sharply from 36% to 88% (Table 1, compare entries 7 and 8). However, a further increase in the amount of catalyst did not have a significant effect on the yield (Table 1, entries 9 and 10, Fig. 2-a). Extending the reaction time from 15 to 30 min increased the yield from 56% to 88%, and no significant change in yield was observed with further extending the reaction time up to 90 min (Table 1, compare entries 7, 11–13, Fig. 2-b).

The effect of temperature has also been studied (Table 1, entries 7 and 14–16). With 10 W of microwave power, raising the temperature from 75 °C up to 125 °C increased the yield from 78% to 88% (Table 1, entries 7, 14 and 15). Higher temperature of 150 °C resulted in diminished yield of 84% (Table 1, entry 16).

The reaction was also carried out in various solvents used individually (Table 1, entries 17–21) or as 1:1 mixtures with water (Table 1, entries 22–25), the former giving significant lower product yields than the latter. Since water is necessary to dissolve NaN_3 and the organic solvent is vital for solubilization of the other reactants as well as the catalyst, using mixtures of water and an organic solvent enhance the homogeneity of the reaction system and the efficiency of the catalysis. When mixtures of water with different alcohols were employed (Table 1, entries 22–25), the obtained yields using oxidizable alcohols (*i.e.*, ^{i}PrOH, EtOH or MeOH) are higher than that obtained using ^{t}BuOH. According to the literature [33,52], the presence of oxidizable alcohols may enhance the reduction of Cu(II) to Cu(I) species (the Glaser induction period), which is necessary for the catalytic CuAAC reaction to proceed (Eq. (2)).



$$2\,Cu(II) + R_1R_2CH{-}OH \xrightarrow[-2H^+]{} 2\,Cu(I) + R_1R_2C{=}O \qquad (2)$$

Consequently, the best experimental conditions for the three-component CuAAC reaction to afford 1,4-disubstituted-1,2,3-triazoles involve using 1.5 mol% of Cu(II)-compound **7** as pre-catalyst, in (1:1) H_2O:MeOH mixtures, under microwave irradiation at 125 °C in air for 30 min. Using these conditions, the scope of our catalytic system with **7** as pre-catalyst for one-pot three-component cycloaddition reaction was expanded to several other terminal alkynes (Table 2). In all cases, the reaction proceeded to afford the corresponding triazoles with yields ranging from 68 to 95%.

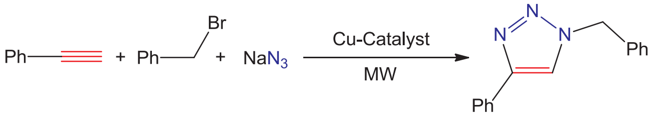
Complex **7** displays a relatively high activity for the CuAAC reaction as, *e. g.*, a yield up to 94% could be achieved in water:methanol medium under microwave irradiation (table 1, entry 25), which is similar to other reported catalytic systems [14,15]. However, our experimental conditions are comparatively milder since only 10 W MW radiation was used, in a relatively short reaction time (30 min.) and in the absence of reduction agents. In addition, our complex reveals a higher selectivity when compared to a reported system for catalytic AAC reaction between phenylacetylene and *N*-sulfonyl azide using a $Cu(I)$-Tpm^{*Br} complex [$Tpm^{*Br} = HC(4\text{-}Br\text{-}3,5\text{-}Me_2pz)_3$] [50]. Yet, in this case, chloroform was used as solvent and tosylamide was a byproduct the concentration of which increased considerably upon addition of water.

By analogy with previous reports [6,17], a plausible mechanism for the Cu(II)-catalyzed cycloaddition to the synthesis of 1,2,3-triazoles is depicted in Scheme 5. The reaction begins with Cu(II) promoted alkyne-alkyne homocoupling to generate the Cu(I) catalytic active species [34]. Then the reaction proceeds in a stepwise manner as described by Sharpless and coworkers [6], which involves the coordination of the alkyne to the Cu(I) species to form the Cu(I)-acetylenide complex, followed by its cyclization with the *in situ* generated organic azide to produce the Cu(I)-tryazolyl intermediate. Finally, the 1,4-disubstituted 1,2,3-triazole product is afforded by protonation of the the Cu(I)-tryazolyl intermediate to complete the catalytic cycle.

3. Conclusions

A set of well-defined scorpionate copper complexes **1–7** were prepared by direct reaction of commercially available Cu(I) salts with neutral $HC(3,5\text{-}Me_2pz)_3$ (Tpm^*) and $HC(3\text{-}Phpz)_3$ (Tpm^{Ph}) under mild conditions. The possibility of employing such complexes as catalyst precursors for the three-component (alkyne, organic halide and sodium azide) CuAAC in aqueous medium was investigated. The obtained copper complexes, in particular $[Cu(Tpm^*)_2][BF_4]_2$ (**7**), act as

Table 1
Three-component catalytic CuAAC reaction of phenylacetylene, benzyl bromide and sodium azide to produce 1-benzyl-4-phenyl-1H-1,2,3-triazole, under microwave irradiation, catalyzed by **1**–**7**.[a]



Entry	Catalyst	Cat. load[b] (mol%)	Solvent	Temperature (°C)	Time (min)	Yield[c] (%)	TON[d]
1	**1**	1.5	H_2O:MeCN	125	30	18	12
2	**2**	1.5	H_2O:MeCN	125	30	22	15
3	**3**	1.5	H_2O:MeCN	125	30	64	42
4	**4**	1.5	H_2O:MeCN	125	30	81	54
5	**5**	1.5	H_2O:MeCN	125	30	65	43
6	**6**	1.5	H_2O:MeCN	125	30	27	18
7	**7**	1.5	H_2O:MeCN	125	30	88	59
8	**7**	0.5	H_2O:MeCN	125	30	36	73
9	**7**	3	H_2O:MeCN	125	30	90	30
10	**7**	5	H_2O:MeCN	125	30	90	18
11	**7**	1.5	H_2O:MeCN	125	15	56	37
12	**7**	1.5	H_2O:MeCN	125	60	89	59
13	**7**	1.5	H_2O:MeCN	125	90	89	59
14	**7**	1.5	H_2O:MeCN	75	30	78	52
15	**7**	1.5	H_2O:MeCN	100	30	79	52
16	**7**	1.5	H_2O:MeCN	150	30	84	56
17	**7**	1.5	DMSO	125	30	14	9
18	**7**	1.5	DMF	125	30	17	11
19	**7**	1.5	MeCN	125	30	22	15
20	**7**	1.5	MeOH	125	30	27	18
21	**7**	1.5	H_2O	125	30	63	42
22	**7**	1.5	H_2O:^{t}BuOH	125	30	82	55
23	**7**	1.5	H_2O:^{i}PrOH	125	30	87	58
24	**7**	1.5	H_2O:EtOH	125	30	89	59
25	**7**	1.5	H_2O:MeOH	125	30	94	63

[a] Reaction conditions: phenylacetylene (0.33 mmol), benzyl bromide (0.3 mmol, limiting reactant), sodium azide (0.33 mmol), 1.5 mL of solvent (1:1 in case of solvent mixtures), MW irradiation (10 W), 125 °C.

[b] Calculated on the basis of benzyl bromide.

[c] Isolated yield; calculated on the basis of benzyl bromide.

[d] Number of moles of product (1-benzyl-4-phenyl-1H-1,2,3-triazole) per mol of catalyst.

homogeneous catalysts for the reaction under low power (10 W) microwave irradiation to afford, in 30 min., the 1,4-disubstituted-1,2,3-triazoles in pure form with yields up to 94%.

A comparison of our catalytic system with already reported similar ones proved that it was highly efficient under milder conditions and in the absence of added reducing agent. In addition, it also showed that the properties of the C-scorpionate compounds are easily tunable and their usage as ligands can contribute for the optimization of the catalytic behaviour of their metal complexes, a research route that deserves to be further explored.

4. Experimental

4.1. General procedures and instrumentation

All operations were carried out in open air, unless stated otherwise. All solvents and reagents were obtained from commercial sources and used without further purifications. Tris(3-phenylpyrazoyl)methane [42], tris(3,5-dimethyl-1-pyrazoyl)methane [48] and complex **4** [46] were prepared according to literature procedures. Synthesis under microwave irradiation were carried out in an Anton Paar (Monowave 300) apparatus. The reactions were performed in 10 mL cylindrical pyrex

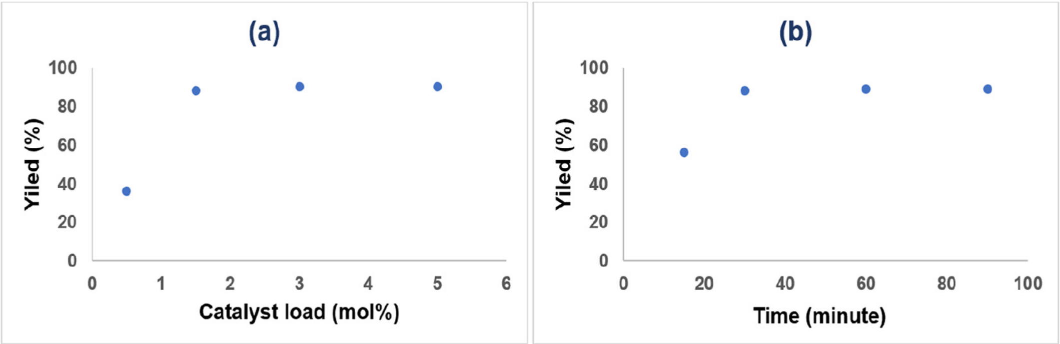
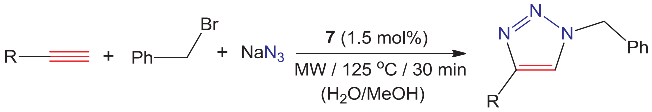
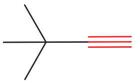
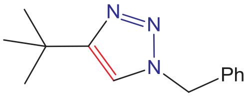
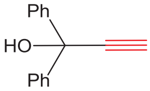
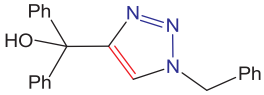
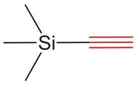
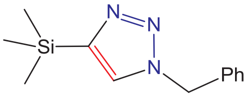
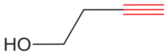
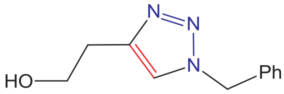
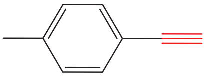
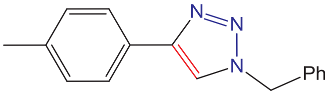
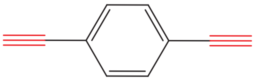
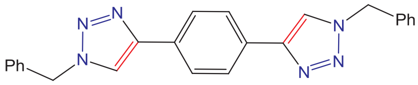


Fig. 2. Plots of yields of 1-benzyl-4-phenyl-1H-1,2,3-triazole *vs.* catalyst amount (a) and reaction time (b) for the CuAAC reaction in (1:1) water:MeCN mixtures using 1.5 mol% of catalyst **7** at 125 °C under microwave irradiation (10 W).

Table 2
One-pot multicomponent catalytic cycloaddition of benzyl bromide with several terminal alkynes and NaN_3 catalyzed by **7** under optimized reaction conditions.[a]



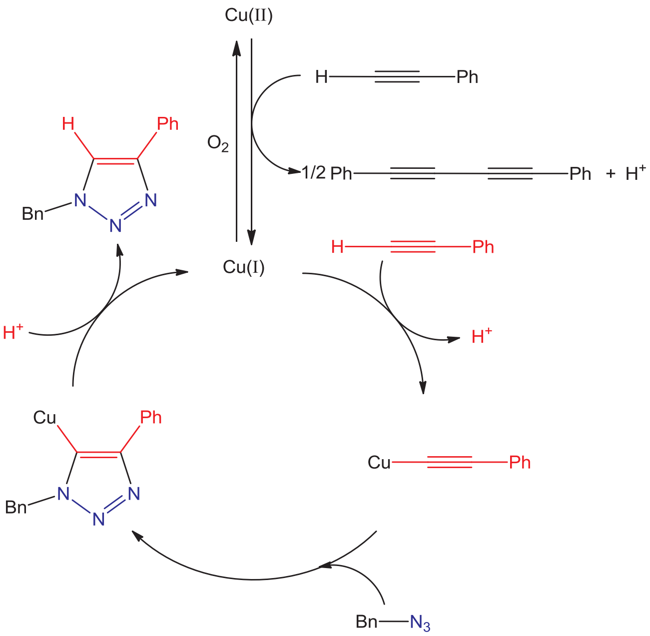
Entry	Alkyne	Product	Yield[b]	TON[c]
1			72	48
2			78	52
3			68	45
4			79	53
5			86	57
6[d]			95	63

[a] Reaction conditions: alkyne (0.33 mmol), benzyl bromide (0.3 mmol, limiting reactant), sodium azide (0.33 mmol), 1.5 mL of solvent (H_2O:MeOH, 1:1), under MW irradiation (10 W) at 125 °C, 30 min.

[b] Isolated yield; calculation based on benzyl bromide.

[c] Number of moles of the 1,2,3-triazole product per mol of catalyst.

[d] Benzyl bromide (0.6 mmol, limiting reactant), 1,4-diethynylbenzene (0.33 mmol) and sodium azide (0.62 mmol).



Scheme 5. Postulated mechanism of the Cu(II) catalyzed reaction. Bn = Benzyl.

tubes, sealed using a teflon crimp top. After the reaction, the vail was cooled rapidly to ambient temperature by gas jet cooling.

^{1}H and ^{13}C NMR spectra were obtained using a Bruker Advance 300 MHz spectrometer, at ambient temperature. All chemical shifts are reported in δ (ppm). All spectra were internally referenced to residual protio-solvent resonance and are reported relative to $SiMe_4$. Assignments of some ^{1}H and ^{13}C signals rely on g-COSY and g-HSQC experiments. Elemental analyses (C, H, and N) were obtained by the microanalytical services of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were obtained in a Cary 630 FTIR spectrometer; wavenumbers are in cm^{-1}; abbreviations: s, strong; m, medium; w, weak. Far infrared spectra (400–180 cm^{-1}) were recorded on a Vertex 70 spectrophotometer in CsI pellets. Electrospray mass spectra (ESI-Ms) were obtained on a Varian 500- MS LC Ion Trap Mass spectrometer equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate was optimized according to the particular sample with 35p.s.i. nebulizer pressure. The scanning was performed from *m/z* 100–1200 in acetonitrile solution. All compounds were observed in the positive mode (capillary voltage = 80–105 V).

4.2. Synthesis of complexes 1 and 2

In a round bottom flask, copper(I) halide (0.1 mmol, CuBr for **1** or CuI for **2**) was dissolved in 2 mL of MeCN. Under continuous stirring, a 5 mL MeCN:EtOH (3:2) solution of $HC(3\text{-}PhPz)_3$ (0.11 mmol, 50 mg) was added dropwise. The produced light brown solution was stirred at room temperature for 3 h, then its volume was reduced by evaporation to *ca.* 2 mL. Hexane (10 mL) was added and the obtained precipitate was filtered off, recrystallized from a mixture of CH_2Cl_2 and hexane (1:1) to afford complexes **1** or **2** as colourless crystals.

[CuBr(Tpm^{Ph})] (**1**): Yield (45.9 mg) 78%. Elemental analysis calcd (%) for $C_{28}H_{22}BrCuN_6{\cdot}CH_2Cl_2$: C 51.92, H 3.61, N 12.53; found: C 51.51, H 3.70, N 12.64. FTIR (KBr): ν (cm^{-1}) = 1532 m, 1491 w, 1442 m, 1391 w, 1342 w, 1324 w, 1299 w, 1268 w, 1242 m, 1209 m, 1095 m, 1077 m, 1038 m, 798 m, 756 s, 688 s. Far IR (CsI): ν (cm^{-1}) = 221 m ν(Cu-Br). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.10 (s, 1H, *H*C(3-PhPz)$_3$), 8.11 (br, 3H, 5-*H*-pz), 7.85 (br, 6H, *o*-*H*-Ph), 7.42 (br, 9H, *m,p*-*H*-Ph), 6.95 (br, 3H, 4-*H*-pz). ^{13}C{^{1}H} NMR (300 MHz, DMSO-d_6, δ): 152.14 (3-C-pz), 132.20 (*C*$_{\text{quat}}$-Ph), 131.82 (5-*C*-pz)), 128.76 (*m*-*C*-Ph), 128.32 (*p*-*C*-Ph), 125.53 (*o*-*C*-Ph), 104.57 (4-*C*-pz), 82.09 (H*C*(3-Phpz)$_3$). ESI(+)MS in MeCN (*m/z* assignment, % intensity): 546 ({[HC(3-Phpz)$_3$]Cu + MeCN}$^+$, 100), 505 ({[HC(3-Phpz)$_3$]Cu}$^+$, 23).

[CuI(Tpm$^{\text{Ph}}$)] (**2**). Yield (51.7 mg) 82%. Elemental analysis calcd (%) for $C_{28}H_{22}CuIN_6$: C 53.13, H 3.50, N 13.28; found: C 52.84, H 3.62, N 12.78. FTIR (KBr): ν (cm^{-1}) = 1525 m, 1496 w, 1450 m, 1398 w, 1352 w, 1323 w, 1302 w, 1277 w, 1239 m, 1202 m, 1098 m, 1072 m, 1046 m, 796 m, 752 s, 692 s. Far IR (CsI): ν (cm^{-1}) = 224 m ν(Cu-I). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.10 (s, 1H, *H*C(3-Phpz)$_3$), 8.12 (d, J_{HH} = 3 Hz, 3H, 5-*H*-pz), 7.86 (m, 6H, *o*-*H*-Ph), 7.43 (m, 6H, *m*-*H*-Ph), 7.34 (m, 3H, *p*-*H*-Ph), 6.96 (d, 3H, J_{HH} = 3 Hz, 4-*H*-pz). ^{13}C{^{1}H} NMR (300 MHz, DMSO-d_6, δ): 152.13 (3-*C*-pz), 132.19 (*C*$_{\text{quat}}$-ph), 132.07 (5-*C*-pz), 128.75 (*m*-*C*-Ph), 128.32 (*p*-*C*-Ph), 125.52 (*o*-*C*-Ph), 104.56 (4-*C*-pz), 82.09 (H*C*(3-Phpz)$_3$). ESI(+)MS in MeCN (*m/z* assignment, % intensity): 546 ({[HC(3-Phpz)$_3$]Cu + MeCN}$^+$, 100), 505 ({[HC(3-Phpz)$_3$]Cu}$^+$, 10).

4.3. Synthesis of complex 3

In a round bottom flask, copper(I) bromide (0.3 mmol, 0.043 g) was dissolved in 5 mL of degassed MeCN. Under continuous stirring and in a N_2-atmosphere, a 2 mL degassed NCMe solution of HC(3,5-Me$_2$pz)$_3$ (0.33 mmol, 0.1 g) was added dropwise. The mixture was stirred at room temperature for 3 h, then its volume was reduced to *ca.* 2 mL by evaporation. Hexane (10 mL) was added, and the obtained precipitate was filtered off and recrystallized from a mixture if CH_2Cl_2 and hexane (1:1) to afford complexes **3** as off-white powder.

[CuBr(Tpm*)] (**3**): Yield (108.9 mg) 82%. Elemental analysis calcd (%) for $C_{16}H_{22}BrCuN_6$: C 43.49, H 5.02, N 19.02; found: C 43.45, H 5.51, N 19.62. FTIR (KBr): ν (cm^{-1}) = 3397 m, 2962 m, 2925 m, 1562 s, 1455 s, 1412 s, 1383 s, 1303 s, 1239 s, 1153 w, 1112 w, 1035 m, 980 m, 905 m, 845 s, 824 m, 796 m, 695 s. Far IR (CsI): ν (cm^{-1}) = 216 m ν(Cu-Br). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.83 (s, 1H, *H*C(3,5-Me$_2$pz)$_3$), 6.04 (s, 3H, 4-*H*-pz), 2.40, 2.22 (s, s, 9H, 9H, 3,5-Me). ^{13}C{^{1}H} NMR (300 MHz, DMSO-d_6, δ): 149.12 (3-*C*$_{\text{quat}}$-pz), 140.28 (5-*C*$_{\text{quat}}$-pz), 106.44 (4-*C*-pz), 70.67 (H*C*(3,5-Me$_2$pz)$_3$), 13.48,10.37 (3,5-Me). ESI(+)MS in MeCN (*m/z* assignment, % intensity): 204 ({[HC(3,5-Me$_2$pz)$_3$]Cu + MeCN}$^+$, 100), 361 ({[HC(3,5-Me$_2$pz)$_3$]Cu}$^+$, 26).

4.4. Synthesis of compound 5

A round bottom flask was charged with [Cu(MeCN)$_4$][BF$_4$] (0.12 mmol, 0.038 g), HC(3-PhPz)$_3$ (0.11 mmol, 50 mg) and 2 mL of CH_2Cl_2. The produced yellow solution was stirred at room temperature for 1 h, then 10 mL of hexane were added and the obtained precipitate was filtered off and recrystallized from a mixture of CH_2Cl_2 and hexane (1:1) to afford **5** as an off-white powder.

[Cu(Tpm$^{\text{Ph}}$)(NCMe)] [BF$_4$] (**5**): Yield (61 mg) 80%. Elemental analysis calcd (%) for $C_{30}H_{25}BCuF_4N_7$: C 56.84, H 3.98, N 15.47; found: C 55.91, H 4.14, N 14.97. FTIR (KBr): ν (cm^{-1}) = 1531 m, 1496 m, 1462 m, 1430 m, 1367 m, 1341 m, 1300 w, 1280 w, 1237 s, 1070 s, 1012 s, 856 m, 796 s, 752 s, 686 s. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.18 (s, 1H, *H*C(3-Phpz)$_3$), 8.16 (s, 3H, 5-*H*-pz), 7.86 (m, 6H, *o*-*H*-Ph), 7.43 (m, 9H, *m,p*-*H*-Ph), 6.95 (s, 3H, 4-*H*-pz), 2.06 (s, 3H, NCC*H*$_3$). ^{13}C{^{1}H} NMR (300 MHz, DMSO-d_6, δ): 151.89 (3-*C*-pz), 132.04 (*C*$_{\text{quat}}$-ph), 131.41 (5-C-pz), 128.26 (*m*-*C*-Ph), 128.01 (*p*-*C*-Ph), 125.23 (*o*-*C*-Ph), 115.05 (N*C*CH$_3$), 104.20 (4-*C*-pz), 80.88 (H*C*(3-Phpz)$_3$), 1.44 (NC*C*H$_3$). ESI(+)MS in MeCN (*m/z* assignment, % intensity): 546 ({[HC(3-Phpz)$_3$]Cu(MeCN)}$^+$, 100), 505 ({[HC(3-Phpz)$_3$]Cu}$^+$, 10).

4.5. Synthesis of compound 6

Under a N_2-atmosphere, a round bottom flask was charged with [Cu(MeCN)$_4$][BF$_4$] (0.33 mmol, 0.1 g), HC(3,5-Me$_2$Pz)$_3$ (0.33 mmol, 0.1 g) and 2 mL of degassed CH_2Cl_2. The produced yellow solution was stirred under N_2 at room temperature for 3 h, then 10 mL of hexane were added, and the obtained precipitate was filtered off and washed repeatedly with hexane to afford **6** as an off-white powder.

[Cu(Tpm*)(NCMe)] [BF$_4$] (6): Yield (140.1 mg) 87%. Elemental analysis calcd (%) for $C_{18}H_{25}BCuF_4N_7$: C 44.14, H 5.14, N 20.02; found: C 44.63, H 5.41, N 19.86. FTIR (KBr): ν (cm^{-1}) = 3582 m, 2962 m, 2928 m, 1559 m, 1450 m, 1412 m, 1389 m, 1300 s, 1245 s, 1032 s, 894 m, 847 s, 802 m, 698 s. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.84 (s, 1H, *H*C(3,5-Me$_2$pz)$_3$), 6.14 (s, 3H, 4-*H*-pz), 2.43, 2.24 (s, s, 9H, 9H, 3,5-Me), 2.09 (s, 3H, NCC*H*$_3$). ^{13}C{^{1}H} NMR (300 MHz, DMSO-d_6, δ): 149.62 (3-*C*$_{\text{quat}}$-pz), 140.71 (5-*C*$_{\text{quat}}$-pz), 115.31 (N*C*CH$_3$), 106.37 (4-*C*-pz), 70.24 (H*C*(3,5-Me$_2$pz)$_3$), 14.20,10.74 (3,5-Me), 1.27 (NC*C*H$_3$). ESI(+)MS in MeCN (*m/z* assignment, % intensity): 402 ({[HC(3,5-Me$_2$pz)$_3$]Cu(MeCN)}$^+$, 100), 361 ({[HC(3,5-Me$_2$pz)$_3$]Cu}$^+$, 31).

4.6. Synthesis of compound 7

A round bottom flask was charged with [Cu(MeCN)$_4$][BF$_4$] (0.33 mmol, 0.1 g), HC(3,5-Me$_2$Pz)$_3$ (0.33 mmol, 0.1 g) and 2 mL CH_2Cl_2 and stirred in open air, at room temperature, overnight. 2 mL of MeOH were then added to the produced green solution and left for slow evaporation in open air. Green crystals of **7** suitable for single crystal X-ray diffraction analysis were obtained after 2 days.

[Cu(Tpm*)$_2$] [BF$_4$]$_2$ (7): Yield (103.4 mg) 38%. Elemental analysis calcd (%) for $C_{32}H_{44}B_2CuF_8N_{12}$: C 46.09, H 5.32, N 20.16; found: C 45.90, H 5.16, N 19.75. FTIR (KBr): ν (cm^{-1}) = 3141 w, 2923 w, 2966 w, 1561 m, 1460 m, 1444 m, 1413 m, 1386 m, 1312 m, 1257 m, 1027 s, 906 m, 855 s, 816 m, 699 s. ESI(+)MS in MeCN (*m/z* assignment, % intensity): 745 ({[HC(3,5-Me$_2$pz)$_3$]$_2$Cu[BF$_4$]}$^+$, 100). The crystal structure of the compound agrees with the already reported one [51].

4.7. General procedure for three-component azide alkyne cycloaddition reaction

A mixture of benzyl bromide (0.3 mmol, 1 equiv.), acetylene derivative (0.33 mmol, 1.1 equiv.), NaN$_3$ (0.33 mmol, 1.1 equiv.) and 1.5 mL of solvent was charged to a 10 mL pyrex vial equipped with a magnetic stirring bar. The catalyst (0.5–5 mol%) was then added, the vial tightly sealed, placed in the microwave reactor and irradiated (10 W) at 125 °C for the periods of time indicated in Tables 1 and 2. A precipitate was formed, the reaction mixture was cooled to ambient temperature and 5 mL of water were added to force a complete precipitation of the triazole product. The product was filtered off, washed repeatedly with petroleum ether and dried in vacuum.

1,4-bis(1-benzyl-1H-1,2,3-triazol-4-yl)benzene (Table 2, entry 6) was prepared according to the general procedure described above except 0.6 mmol of benzyl bromide, 0.33 mmol of 1,4-diethynylbenzene and 0.62 mmol of sodium azide were used.

The ^{1}H and ^{13}C NMR spectroscopic data of all 1,2,3-triazol products are in agreement with those already reported [14,25,29,53–56].

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Appendix A. Supplementary data

Proton NMR spectra (selected region) of **1**-**6** and triazole products are presented, as well as the crystal structure (low quality) of complex **1**.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2018.08.052.

References

[1] M.C. Linder, M. Hazegh-Azam, Copper biochemistry and molecular biology, Am. J. Clin. Nutr. 63 (1996) 797S–811S, https://doi.org/10.1093/ajcn/63.5.797.

[2] I.P. Beletskaya, A.V. Cheprakov, Copper in cross-coupling reactions: The post-Ullmann chemistry, Coord. Chem. Rev. 248 (2004) 2337–2364, https://doi.org/10.1016/J.CCR.2004.09.014.

[3] S.E. Allen, R.R. Walvoord, R. Padilla-Salinas, M.C. Kozlowski, Aerobic copper-catalyzed organic reactions, Chem. Rev. 113 (2013) 6234–6458, https://doi.org/10.1021/cr300527g.

[4] J. Moegling, A. Hoffmann, S. Herres-Pawlis, Insights into copper-poly(pyrazolyl) methane-catalyzed reactions for organic transformations, Synthesis (Stuttg). 49 (2017) 225–236, https://doi.org/10.1055/s-0036-1588892.

[5] C.W. Tornøe, C. Christensen, M. Meldal, Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides, J. Org. Chem. 67 (2002) 3057–3064, https://doi.org/10.1021/JO011148J.

[6] V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes, Angew. Chemie. 114 (2002) 2708–2711, https://doi.org/10.1002/1521-3757(20020715)114:14<2708::AID-ANGE2708>3.0.CO;2-0.

[7] A set of fundamental requirements has to be fulfilled for a reaction procedure to be applicable in this context: i) it must be wide in scope, ii) evince no sensitivity towards oxygen or moisture, iii) proceed in absence of solvent or using a benign one, iv) afford products in high yields and easily isolable, and v) be stereospecific.

[8] H.C. Kolb, K.B. Sharpless, The growing impact of click chemistry on drug discovery, Drug Discov. Today. 8 (2003) 1128–1137, https://doi.org/10.1016/S1359-6446(03)02933-7.

[9] J.E. Moses, A.D. Moorhouse, The growing applications of click chemistry, Chem. Soc. Rev. 36 (2007) 1249–1262, https://doi.org/10.1039/B613014N.

[10] W.H. Binder, R. Sachsenhofer, 'Click' chemistry in polymer and materials science, Macromol. Rapid Commun. 28 (2007) 15–54, https://doi.org/10.1002/marc.200600625.

[11] E.F.V. Scriven, K. Turnbull, Azides: their preparation and synthetic uses, Chem. Rev. 88 (1988) 297–368, https://doi.org/10.1021/cr00084a001.

[12] S. Bräse, C. Gil, K. Knepper, V. Zimmermann, Organic azides: an exploding diversity of a unique class of compounds, Angew. Chemie Int. Ed. 44 (2005) 5188–5240, https://doi.org/10.1002/anie.200400657.

[13] A.K. Feldman, B. Colasson, V.V. Fokin, One-pot synthesis of 1,4-disubstituted 1,2,3-triazoles from in situ generated azides, Org. Lett. 6 (2004) 3897–3899, https://doi.org/10.1021/ol048859z.

[14] P. Appukkuttan, W. Dehaen, V.V. Fokin, E. Van der Eycken, A Microwave-Assisted Click Chemistry Synthesis of 1,4-Disubstituted 1,2,3-Triazoles via a Copper(I)-Catalyzed Three-Component Reaction, Org. Lett. 6 (2004) 4223–4225, https://doi.org/10.1021/OL048341V.

[15] S. Özçubukçu, E. Ozkal, C. Jimeno, M.A. Pericàs, A Highly Active Catalyst for Huisgen 1,3-Dipolar Cycloadditions Based on the Tris(triazolyl)methanol − Cu(I) Structure, Org. Lett. 11 (2009) 4680–4683, https://doi.org/10.1021/ol9018776.

[16] F. Li, T.S.A. Hor, Facile Synthesis of Nitrogen Tetradentate Ligands and Their Applications in Cu ^{I} -Catalyzed N-Arylation and Azide-Alkyne Cycloaddition, Chem. – A Eur. J. 15 (2009) 10585–10592, https://doi.org/10.1002/chem.200901014.

[17] F. Himo, T. Lovell, R. Hilgraf, V.V. Rostovtsev, L. Noodleman, K.B. Sharpless, V.V. Fokin, Copper(I)-catalyzed synthesis of azoles. DFT study predicts unprecedented reactivity and intermediates, J. Am. Chem. Soc. 127 (2005) 210–216, https://doi.org/10.1021/ja0471525.

[18] X. Zhang, H. Li, L. You, Y. Tang, R.P. Hsung, Copper salt-catalyzed azide-[3 + 2] cycloadditions of ynamides and bis-ynamides, Adv. Synth. Catal. 348 (2006) 2437–2442, https://doi.org/10.1002/adsc.200600404.

[19] J.E. Hein, J.C. Tripp, L.B. Krasnova, K.B. Sharpless, V.V. Fokin, Copper(I)-Catalyzed Cycloaddition of Organic Azides and 1-Iodoalkynes, Angew. Chemie Int. Ed. 48 (2009) 8018–8021, https://doi.org/10.1002/anie.200903558.

[20] V. Hong, A.K. Udit, R.A. Evans, M.G. Finn, Electrochemically protected copper(I)-catalyzed azide-alkyne cycloaddition, ChemBioChem. 9 (2008) 1481–1486, https://doi.org/10.1002/cbic.200700768.

[21] C. Girard, E. Önen, M. Aufort, S. Beauvière, E. Samson, J. Herscovici, Reusable polymer-supported catalyst for the [3 + 2] Huisgen cycloaddition in automation protocols, Org. Lett. 8 (2006) 1689–1692, https://doi.org/10.1021/ol060283l.

[22] M. Chtchigrovsky, A. Primo, P. Gonzalez, K. Molvinger, M. Robitzer, F. Quignard, F. Taran, Functionalized chitosan as a green, recyclable, biopolymer-supported catalyst for the [3 + 2] huisgen cycloaddition, Angew. Chemie – Int. Ed. 48 (2009) 5916–5920, https://doi.org/10.1002/anie.200901309.

[23] G. Molteni, C.L. Bianchi, G. Marinoni, N. Santo, A. Ponti, Cu/Cu-oxide nanoparticles as catalyst in the "click" azide–alkyne cycloaddition, New J. Chem. 30 (2006) 1137–1139, https://doi.org/10.1039/B604297J.

[24] E. Ozkal, S. Özçubukçu, C. Jimeno, M.A. Pericàs, Covalently immobilized tris (triazolyl)methanol–Cu(i) complexes: highly active and recyclable catalysts for CuAAC reactions, Catal. Sci. Technol. 2 (2012) 195–200, https://doi.org/10.1039/C1CY00297J.

[25] J. García-Álvarez, J. Díez, J. Gimeno, A highly efficient copper(i) catalyst for the 1,3-dipolar cycloaddition of azides with terminal and 1-iodoalkynes in water: regioselective synthesis of 1,4-disubstituted and 1,4,5-trisubstituted 1,2,3-triazoles, Green Chem. 12 (2010) 2127–2130, https://doi.org/10.1039/c0gc00342e.

[26] S. Lal, S. Díez-González, [CuBr(PPh $_3$) 3] for Azide − Alkyne Cycloaddition Reactions under Strict Click Conditions, J. Org. Chem. 76 (2011) 2367–2373, https://doi.org/10.1021/jo200085j.

[27] J. García-Álvarez, J. Díez, J. Gimeno, F.J. Suárez, C. Vincent, (Iminophosphorane) copper(I) complexes as highly efficient catalysts for 1,3-dipolar cycloaddition of azides with terminal and 1-iodoalkynes in water: One-pot multi-component reaction from alkynes and in situ generated azides, Eur. J. Inorg. Chem. (2012) 5854–5863, https://doi.org/10.1002/ejic.201200789.

[28] A.G. Mahmoud, M.F.C. Guedes da Silva, J. Sokolnicki, P. Smoleński, A.J.L. Pombeiro, Hydrosoluble Cu(i)-DAPTA complexes: synthesis, characterization, luminescence thermochromism and catalytic activity for microwave-assisted three-component azide–alkyne cycloaddition click reaction, Dalt. Trans. 47 (2018) 7290–7299, https://doi.org/10.1039/C8DT01232F.

[29] N. Candelon, D. Lastécouères, A.K. Diallo, J. Ruiz Aranzaes, A highly active and reusable copper(i)-tren catalyst for the "click" 1,3-dipolar cycloaddition of azides and alkynes, Chem. Commun. 41 (2008) 741–743, https://doi.org/10.1039/B716306A.

[30] S. Díez-González, S.P. Nolan, [(NHC) $_2$ Cu]X Complexes as Efficient Catalysts for Azide-Alkyne Click Chemistry at Low Catalyst Loadings, Angew. Chemie. 120 (2008) 9013–9016, https://doi.org/10.1002/ange.200803289.

[31] A. Makarem, R. Berg, F. Rominger, B.F. Straub, A Fluxional Copper Acetylide Cluster in CuAAC Catalysis, Angew. Chemie Int. Ed. 54 (2015) 7431–7435, https://doi.org/10.1002/anie.201502368.

[32] K.R. Reddy, K. Rajgopal, M.L. Kantam, Copper(II)-Promoted Regioselective Synthesis of 1,4-Disubstituted 1,2,3-Triazoles in Water, Synlett. (2006) 957–959, https://doi.org/10.1055/s-2006-933134.

[33] W.S. Brotherton, H.A. Michaels, J.T. Simmons, R.J. Clark, N.S. Dalal, L. Zhu, Apparent Copper(II)-Accelerated Azide − Alkyne Cycloaddition, Org. Lett. 11 (2009) 4954–4957, https://doi.org/10.1021/ol9021113.

[34] P. Siemsen, R.C. Livingston, F. Diederich, Acetylenic coupling: a powerful tool in molecular construction, Angew. Chemie Int. Ed. 39 (2000) 2632–2657, https://doi.org/10.1002/1521-3773(20000804)39:15<2632::AID-ANIE2632>3.0.CO;2-F.

[35] K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, 1,3-Dipolar cycloaddition of organic azides to alkynes by a dicopper-substituted silicotungstate, J. Am. Chem. Soc. 130 (2008) 15304–15310, https://doi.org/10.1021/ja806249n.

[36] K. Yamaguchi, T. Oishi, T. Katayama, N. Mizuno, A supported copper hydroxide on titanium oxide as an efficient reusable heterogeneous catalyst for 1,3-dipolar cycloaddition of organic azides to terminal alkynes, Chem. – A Eur. J. 15 (2009) 10464–10472, https://doi.org/10.1002/chem.200901444.

[37] M. Vashist, K. Kushwaha, R. Kaushik, S.C. Jain, Synthesis of medicinally important quinazolines decorated with 1,4-disubstituted-1,2,3-triazoles using CuSO $_4$ ·5H $_2$ O-Et $_3$ N catalytic system, RSC Adv. 4 (2014) 23679–23684, https://doi.org/10.1039/C4RA02123A.

[38] C. Zhou, J. Zhang, P. Liu, J. Xie, B. Dai, 2-Pyrrolecarbaldiminato–Cu(ii) complex catalyzed three-component 1,3-dipolar cycloaddition for 1,4-disubstituted 1,2,3-triazoles synthesis in water at room temperature, RSC Adv. 5 (2015) 6661–6665, https://doi.org/10.1039/C4RA13423K.

[39] M. Bagherzadeh, A. Bayrami, R. Kia, M. Amini, L.J.K. Cook, P.R. Raithby, Two new copper(II) complexes with chelating N, O-type bidentate ligands: Synthesis, characterization, crystal structure and catalytic activity in azide–alkyne cycloaddition reaction, Inorganica Chim. Acta. 466 (2017) 398–404, https://doi.org/10.1016/J.ICA.2017.06.046.

[40] R.K. Reddy, K. Rajgopal, M.L. Kantam, Copper-alginates: a biopolymer supported Cu(II) catalyst for 1,3-dipolar cycloaddition of alkynes with azides and oxidative coupling of 2-naphthols and phenols in water, Catal. Letters. 114 (2007) 36–40, https://doi.org/10.1007/s10562-007-9032-x.

[41] S. Trofimenko, Geminal poly(1-pyrazolyl)alkanes and their coordination chemistry, J. Am. Chem. Soc. 92 (1970) 5118–5126, https://doi.org/10.1021/ja00720a021.

[42] D.L. Reger, T.C. Grattan, K.J. Brown, C.A. Little, J.J.S. Lamba, A.L. Rheingold, R.D. Sommer, Syntheses of tris(pyrazolyl)methane ligands and {[tris(pyrazolyl) methane]Mn(CO)3}SO3CF3 complexes: comparison of ligand donor properties, J. Organomet. Chem. 607 (2000) 120–128, https://doi.org/10.1016/S0022-328X(00)00290-4.

[43] D.L. Reger, T.C. Grattan, Synthesis of modified tris(pyrazolyl)methane ligands: backbone functionalization, Synthesis (Stuttg). 2003 (2003) 350–356, https://doi.org/10.1055/s-2003-37339.

[44] L.M.D.R.S. Martins, A.J.L. Pombeiro, Tris(pyrazol-1-yl)methane metal complexes for catalytic mild oxidative functionalizations of alkanes, alkenes and ketones, Coord. Chem. Rev. 265 (2014) 74–88, https://doi.org/10.1016/J.CCR.2014.01.013.

[45] A.M. Kirillov, P. Smoleński, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Unprecedented Metal-Free C(sp 3) − C(sp 3) Bond Cleavage: Switching from N -Alkyl- to N -Methyl-1,3,5-triaza-7-phosphaadamantane, Organometallics 28 (2009) 1683–1687, https://doi.org/10.1021/om801026a.

[46] E. Haldón, E. Álvarez, M.C. Nicasio, P.J. Pérez, Copper(I) complexes with trispyrazolylmethane ligands: synthesis, characterization, and catalytic activity in cross-coupling reactions, Inorg. Chem. 51 (2012) 8298–8306, https://doi.org/10.1021/ic300843a.

[47] D.L. Reger, J.E. Collins, A.L. Rheingold, L.M. Liable-Sands, Synthesis and Characterization of Cationic [Tris(pyrazolyl)methane]copper(I) Carbonyl and

Acetonitrile Complexes, Organometallics. 15 (1996) 2029–2032, https://doi.org/10.1021/OM960026S.

[48] R. Wanke, P. Smolenski, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, A.J.L. Pombeiro, Cu(I) Complexes Bearing the New Sterically Demanding and Coordination Flexible Tris(3-phenyl-1-pyrazolyl)methanesulfonate Ligand and the Water-Soluble Phosphine 1,3,5-Triaza-7-phosphaadamantane or Related Ligands, Inorg. Chem. 47 (2008) 10158–10168, https://doi.org/10.1021/ic801254b.

[49] M. Cvetkovic, S.R. Batten, B. Moubaraki, K.S. Murray, L. Spiccia, Copper(I) tris(pyrazolyl)methane complexes and their reactivity towards dioxygen, Inorganica Chim. Acta. 324 (2001) 131–140, https://doi.org/10.1016/S0020-1693(01)00565-5.

[50] I. Cano, M.C. Nicasio, P.J. Pérez, Copper(i) complexes as catalysts for the synthesis of N-sulfonyl-1,2,3-triazoles from N-sulfonylazides and alkynes, Org. Biomol. Chem. 8 (2010) 536–538, https://doi.org/10.1039/B912835B.

[51] D.L. Reger, C.A. Little, M.D. Smith, G.J. Long, Solid-State Structural and Magnetic Investigations of {M[HC(3,5-Me2pz)3]2}(BF4)2 (M = Fe Co, Ni, Cu): Observation of a Thermally Induced Solid-State Phase Change Controlling an Iron(II) Spin-State Crossover, Inorg. Chem. 41 (2002) 4453–4460, https://doi.org/10.1021/IC0112645.

[52] N. Kirai, Y. Yamamoto, Homocoupling of arylboronic acids catalyzed by 1,10-phenanthroline-ligated copper complexes in air, European J. Org. Chem. 2009 (2009) 1864–1867, https://doi.org/10.1002/ejoc.200900173.

[53] M.S. Raghavendra, Y. Lam, Regiospecific solid-phase synthesis of substituted 1,2,3-triazoles, Tetrahedron Lett. 45 (2004) 6129–6132, https://doi.org/10.1016/j.tetlet.2004.06.055.

[54] M.S.R. Murty, M.R. Katiki, D. Kommula, Multicomponent Click Synthesis of β-Hydroxy/Benzyl 1,2,3- Triazoles Catalyzed by Magnetically Recyclable Nano Iron Oxide in Water, Can. Chem. Trans. Year. 4 (2016) 47–61, https://doi.org/10.13179/canchemtrans.2016.04.01.0270.

[55] K. Kacprzak, Efficient one-pot synthesis of 1,2,3-triazoles from benzyl and alkyl halides, Synlett. 2005 (2005) 0943–0946, https://doi.org/10.1055/s-2005-864809.

[56] J. Liu, M. Liu, Y. Yue, M. Yao, K. Zhuo, Environmental Friendly Azide-Alkyne Cycloaddition Reaction of Azides, Alkynes, and Organic Halides or Epoxides in Water: Efficient “Click”; Synthesis of 1,2,3-Triazole Derivatives by Cu Catalyst, Chinese J. Chem. 30 (2012) 644–650, https://doi.org/10.1002/cjoc.201280012.