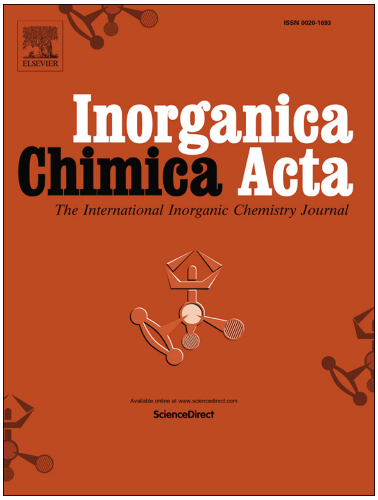

Research paper

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PII: S0020-1693(19)30060-X
DOI: https://doi.org/10.1016/j.ica.2019.04.036
Reference: ICA 18881

To appear in: *Inorganica Chimica Acta*

Received Date: 12 January 2019
Revised Date: 18 April 2019
Accepted Date: 18 April 2019

Please cite this article as: M. Bagherzadeh, H. Mahmoudi, S. Ataie, M. Hafezi-Kahnamouei, S. Shahrokhian, G. Bellachioma, L. Vaccaro, Synthesis, Characterization, and Comparison of Two New Copper(II) Complexes Containing Schiff-base and Diazo Ligands as New Catalysts in CuAAC Reaction, *Inorganica Chimica Acta* (2019), doi: https://doi.org/10.1016/j.ica.2019.04.036

Synthesis, Characterization, and Comparison of Two New Copper(II) Complexes Containing Schiff-base and Diazo Ligands as New Catalysts in CuAAC Reaction

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Abstract: Two copper(II) complexes were synthesized through the reaction of $Cu(OAc)_2.H_2O$ with a Schiff-base ligand (1-(((3,4-dichlorophenyl)imino)methyl)naphthalen-2-ol) and a diazo ligand (1-((3,4-dichlorophenyl)diazenyl)naphthalen-2-ol) in methanol. The complexes and ligands were characterized employing elemental analysis and electronic spectra. In addition, the ligands were fully characterized by using several 1D and 2D NMR techniques. Single crystal X-ray crystallography was also used for the characterization of some of these materials. Due to finding out the effect of Schiff-base and diazo ligands nature on the catalytic activity, the complexes were catalytically compared in one-pot azide-alkyne cycloaddition reaction in water. Furthermore, computational studies were performed on ligands and complexes for further understanding of the relationship between structure, bonding, and reactivity of these new materials.

Keywords: Copper Schiff-base complex, Copper diazo complex, AAC reaction, triazole compounds, click chemistry

1. Introduction

In the past two decades, click chemistry was introduced by Sharpless as a conceptual framework for the highly efficient assembly of molecules [1]. This term was first introduced in 1999 [2], and in 2001 Sharpless and his coworkers already applied click chemistry-type reactions, as a selective, powerful and reliable method for the synthesis of new useful materials [3]. More generally, click chemistry is not limited to a specific chemical reaction, but it describes those synthetic methods featuring modularity and a wide substrate scope, using simple reaction conditions that starting from easily available materials and benign solvents, allow the access of pure products in high yields. [4].

Among the click reactions, the Copper catalyzed Azide-Alkyne Cycloaddition (CuAAC) reaction has attracted the most attention [5], as it allows the totally selective preparation of high-value 1,2,3-triazoles that find applications in several different fields such as pharmaceutical, polymer, biochemistry, and agrochemicals [6]. CuAAC has also the additional merit of furnishing an effective and selective alternative to thermal azide-alkyne 1,3-dipolar cycloaddition developed a long time ago by Huisgen [7].

The main issue of the thermal Huisgen protocol is in fact related to the need for high temperature, and also to the lack of control of regioselectivity leading to a mixture of 1,4- and 1,5-disubstituted 1,2,3-triazole regioisomers [8]. On the contrary CuAAC reaction only produces 1,4- regioisomer, without any solvent sensitivity and being 10^7 times faster [9]. Moreover, according to the viewpoint of green chemistry, one of the remarkable points about CuAAC reaction is using water as a green solvent [10].

Since its discovery, theories describing CuAAC reaction, have been controversial. At first, there was a belief that the CuAAC reaction can be catalyzed only by Cu(I) complexes and in this regard, it has been described to use Cu(I) salts, or ion alternative Cu(II) salts combined with reducing agents to reduce Cu(II) to the active type Cu(I). But lately, variant works have been published in click chemistry reaction area using Cu(II) complexes as catalysts with no reducing agents, in one step without any side products [11]. Due to the nature of circulating electrons in the structure of the applied ligands, π-conjugation, used ligands definitely "impress" the catalytic system [12]. In CuAAC reaction using Cu(II) as a catalyst, ligands can help the system to maintain the copper metal center in its active state, Cu(I), which is able to promote more efficiently the reaction [13].

Schiff base and diazo groups (C=N and N=N) can establish π-conjugation chain with aromatic rings, and these systems provide two different environments around central metal and straightly affect catalytic potential [14].

In this regard, in this contribution we report our results in the synthesis of two copper(II) complexes containing Schiff-base (1-(((3,4-dichlorophenyl)imino)methyl)naphthalen-2-ol) and diazo (1-((3,4-dichlorophenyl)diazenyl)naphthalen-2-ol) ligands with the same geometries. The complexes have been employed as catalysts in CuAAC reaction in water without using additional reducing agents. Different parameters such as temperature, time, various media and the amount of catalyst were studied for the definition of the optimum conditions for each catalyst. Finally, the optimum conditions of both catalysts were compared together.

2. Results and discussion

2.1. Synthesis and characterization

Complexes 3 and 4 were prepared in good yield by addition of $Cu(OAc)_2$.H2O to a methanolic solution of 1 or 2 (For details, refer to supporting information) (Scheme1). Complex $[Cu(L_1)_2)]_3$ was formed as light brown solid and showed insolubility in water and only very little solubility in methanol, acetonitrile, acetone, 1,2-dichloroethane, ethanol, or chloroform. On the other hand, the complex was quite soluble in DMF, DMA, or DMSO. The complex **4** had a dark brown appearance and was insoluble in water, methanol, ethanol, acetonitrile, acetone, 1,2-dichloroethane but also poorly soluble in chloroform, DMSO, DMA, or DMF.

Structure of Schiff base ligand **1** was confirmed by ^{1}H NMR (Fig. S2 in supporting information). In fact, its spectrum features a resonance at δ=15.30 ppm (d, 1H, $^3J_{HH}$=2.9 Hz) which corresponds to the keto–amine form (H7 in Fig. S1a), this signal is correlated with the other one at δ=9.70 ppm (d, 1H, J=2.4 Hz) according to ^{1}H-^{1}H COSY NMR spectrum (Fig. S4 and S5) and therefore this peak can be assigned to aldimine hydrogen (H11, Fig. S1a). This correlation also indicates that in solution the keto-enol tautomerization equilibrium the keto-amine form is more stable than the enol-imine form, and this observation is in accordance with previously published results [15] (see section 2.3 for the results of DFT calculations on the stability of keto-amine form). In the aromatic area, three sets of resonance appeared in δ=7.61, 7.71 and 8.06 ppm and they correlate altogether and are assigned to H8, H9 and H10 (Fig. S1a), respectively. In the ^{1}H-^{1}H COSY NMR spectrum the resonance of hydrogens H1-6, that correlate to each other, appeared in δ=7.82, 7.38, 7.58, 8.55, 7.97 and 7.07 ppm, respectively. Similarly, for the ligand **2**, the ^{1}H NMR (Fig. S8) shows a singlet resonance at δ=15.35 ppm which was assigned to H7 (Fig. S1b). Similar tautomerization between azo and hydrazone form was also observed in this compound and in solution, it appears that the hydrazone form is more stable than the azo form [16]. In addition, three other sets of peaks had a resonance at δ=7.87, 7.77 and 8.16 ppm which are assigned to H8, H9 and H10 (Fig. S1b), respectively. These three peaks were correlated together according to the ^{1}H-^{1}H COSY NMR spectrum (Fig. S10 and S11). Finally, the resonance of hydrogens 1-6 were appeared in δ=7.77, 7.48, 7.62, 8.54, 7.97

and 6.89 ppm, respectively. Furthermore, ^{13}C NMR, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC analyses were performed to confirm these assignments (Fig. S3, S6, S7, S9, S12, and S13).

Both complexes were characterized by elemental analysis. CHN analysis shows that 58.80% Carbon, 2.91% Hydrogen and 3.95% Nitrogen was found in complex **3** As well as, the copper content of this complex was determined by using ICP-AES instrument and the result showed 9.17% w/w Cu in the structure of this complex. The elemental analysis demonstrated that the molar ratios of N/Cu, C/Cu and H/Cu were ~1.97, ~34.19 and 20.31 respectively, which complies with the molecular formula of this complex ($C_{34}H_{20}Cl_4CuN_2O_2$). And also, about complex **4**, we found 55.12% C; 2.55% H; 8.18% N and 9.10 Cu. As well as, Elemental analysis showed that the molar ratios of N/Cu, C/Cu and H/Cu were ~4.08, ~32.05 and ~17.80 respectively, that complies with the molecular formula of this complex ($C_{32}H_{18}Cl_4CuN_4O_2$). These results confirmed that two ligands are coordinated to central Copper (II) in each case. As well as, all structures were characterized by UV-Vis spectroscopy. The modest changes in the complexes' spectra, compared to the ligands' spectra, can be considered as a sign of complexation (Fig. S35 and S36).

2.2. Single crystal X-ray structure analysis

Crystals of ligand **1** and complex **3**, suitable for X-ray diffraction, were obtained as described in the Synthesis and Characterization part of supporting information (Scheme 1). The ORTEP diagrams of the structures **1** and **3** are shown in Fig. 1.

Selected bond lengths, angles, structural parameters and refinements for the ligand **1** and complex **3** are given in the supporting information.

2.3. DFT studies

Full geometry optimization was performed for both ligands and both complexes. After optimization, the vibrational frequency illustrates that all structures were in the minimum energy level. Optimized structures of **1-4** are illustrated in Fig. S24. (Details of optimized bonds lengths and angles are alleged in table S24-S31 in supporting information).

For both ligands, a tautomeric equivalency between enol and keto forms exists (Fig. 2). The energy comparison for the ligands show the keto form is stable form and the energy gap between enol and keto form is 3.80 and 8.06 kJ.mol^{-1} for ligand **1** and **2** respectively. This calculation shows activation energy for this tautomerization is 12.94 and 17.26 kJ.mol^{-1} for **1** and **2**, respectively.

The contour plot of frontier molecular orbitals of **1** and **2** are shown in Fig S25 and S26. Analysis of frontier molecular orbitals, confirms that both ligands have a closed-shell structure, and also the large energy gap between HOMO and LUMO (3.30 eV for **1** and 2.99 eV for **2**) illustrates the kinetic stability and low chemical activity of these structures [17]. Also, the molecular orbital analysis showed that an acceptable percentage of HOMO was found on Nitrogen and Oxygen fragment, which is a good reason for the ability of these structures to form a complex with any metals (Table S20 and S21 and Fig. S31 and S32 in supporting information).

The conditions for the complexes **3** and **4** are different and the type of electronic system is open-shell. There are two series of alpha and beta orbital existed in the system, these orbitals are demonstrated in Fig. S27-30. The HOMO orbitals were made by the large contribution of ligand orbitals. In contrast, a large contribution of β-LUMO orbitals in both complexes was located on the copper ion, which emphasizes the basic role of copper in the reactivity of these complexes. The energy and contribution of frontier molecular orbitals **3** and **4** are shown in table S22 and S23, respectively.

The main reason for conducting theoretical studies was the recognition of the structure and bonding in the synthesized compounds. Understanding the structure and bonding relationship can help us to find the relationship between structure and reactivity. Natural Bond Orbitals (NBOs) calculations were carried out to understand the Lewis-like molecular bonding pattern of electron pairs in an optimally compact form. In other words, NBOs are a set of occupancy orbitals which give the accurate Lewis description of the total electron. NBO analysis of complexes **3** and **4** have been performed in DFT B3LYP level with 6-31g* basis set for all ligands' atoms and SDD basis set for Copper centers. Summary of Natural Population Analysis (NPA) for a selected atom of complexes **3** and **4** are listed in table S32 and S33. According to the table S32 and S33, the natural electron configuration of Cu in complexes **3** and **4** is: [core]$4s^{0.03}3d^{9.99}4p^{0.38}4d^{0.02}5d^{0.01}$ and [core]$4s^{0.03}3d^{9.99}4p^{0.40}4d^{0.02}5d^{0.01}$, respectively. These calculations showed that the natural charge of the copper center is almost the same in both complexes (1.75216 in complex **3** and 1.75260 in complex **4**). In comparison, the natural charge on chelating nitrogens in complex 4 is more positive than complex 3 (natural charge of N28 and N60 in complex 3 is -0.66930 and -0.70284 respectively and natural charge of N26 and N56 in complex 4 is -0.51334 and -0.42495 respectively) and regarding to the same value of natural charge in the copper center of both complexes, it can be said that the Cu-N bond in the complex **4** is weaker than the similar bond in complex **3**. These observations are consistent with the results of the calculated bond length, as the calculated nitrogen-copper bond length in complex **4** is slightly longer than the length of the same bond in complex 3 (Table S28 and S30).

2.5. Electrochemical studies

In order to the electrochemical study on the two prepared complexes, CV's of complex **3**/GCE and complex **4**/GCE were conducted in phosphate buffer solution (pH=7.0) at a scan rate 50 mV.s^{-1} as presented in Fig. 3. As can been seen, the corresponding CV's demonstrated a cathodic (c) and two anodic (a_1, a_2) peaks for both complexes at different peak potentials. For complex **3**, cathodic peak (c) was observed at -0.92 V and in the reverse sweep, two anodic peaks (a_1) and (a_2) appeared at 0.53 V and 0.75 V, respectively (Fig. 3A). While for complex 4, cathodic peak (c) was at -0.57 V and two anodic peaks (a_1) and (a_2) were appeared at -0.21 V and 0.05 V, respectively (Fig. 3B). The cathodic peak (c) can be considered as a two-electron reduction process of the Cu(II) to Cu(I), and also, anodic peaks were related to oxidation of Cu(0) to Cu(I) (a_1) and Cu(I) to Cu(II) (a_2). In comparison with complex **4**, the oxidation peak for complex **3** is appeared in more positive potentials and consequently, its reduction in more negative potential. The results revealed more thermodynamic stability for complex **3**, relative to complex **4**. The difference between reduction and oxidation potentials in two complexes were originated from different ligands, which affect the stability of the central metal, and therefore the catalytic behavior of complexes. the origin of the difference in thermodynamic stability is related to the difference in the stabilization of ligands.

2.6. Catalytic activity

To evaluate the catalytic potential of complexes **3** and **4**, they were utilized in AAC reaction. First, a blank reaction with no catalyst was considered between phenylacetylene (put always the number of the structures in bold, in parenthesis if it is the actual IUPAC name otherwise not) and benzyl chloride in the presence of sodium azide in water (Table 1, entry 1). As expected no conversion to the product was observed. In order to compare the catalytic activity of complexes **3** and **4** in AAC reaction, each of the complexes was studied separately to reach the optimum reaction condition and then compared together. To optimize the reaction condition for complex **3**, phenylacetylene (0.5 mmol) and benzyl chloride (0.55 mmol) with sodium azide (0.55 mmol) were chosen as starting stoichiometric ratios. According to the previously published work [18], the temperature 70 ^{o}C and water (2 mL) were chosen as starting non-optimized parameters. When catalyst **3** was used as 0.28 mol%, the yield obtained was 58%

(entry 2). By increasing the amount of catalyst **3** step by step from 0.28 to 1.15 mol%, the yield increased to 97% (entry 5). As it is shown in Table 1, entries 6 and 7, by using catalyst amounts larger than 1.15 mol%, no progress was obtained in the yield. In a quite similar procedure, the optimal amount of catalyst **4** resulted to be 0.86 mol% with a 76% yield (entry 10) and also, in this case, using more amount of catalyst no significant increase was obtained in terms of yield (entries 11-13). Furthermore, different temperatures were applied while using the optimal amounts of catalysts **3** and **4**. For catalyst **3**, at room temperature, only 18% yield was obtained (entry 14). By increasing the temperature to 50 ˚C, the product was obtained in 96% yield, and from 60 to 100 ˚C, no remarkable improvement was observed in the isolated yield (entries 17-19). Also, in the same manner for the catalyst **4**, the best temperature was found to be 70 ˚C where a yield of 76% could be obtained (entry 10) and no relevant improvement could be observed at higher temperatures (entries 24 and 25).

In order to find out the active species of copper in the catalytic cycle, two reactions were designed with the ratio 2:1 of Sodium ascorbate:catalyst (Sodium ascorbate used as a mild reducing agent) in the catalytic system and the results were included in Table 1, entries 27 and 28. These results show no remarkable progress was detected by adding a reducing agent.

In this regard, professor Lei Zhu and his coworkers have done a wide study on this issue, and they monitored the reduction of Cu(II) to Cu(I) during the catalytic reaction employing EPR and UV analysis [19],and also they have found that the active state of copper during catalytic reaction is Cu(I), which means when a source of Cu(II) is used as a catalyst of azide-alkyne cycloaddition, it must be reduced to Cu(I) and then the catalytic reaction cycle starts. In the absence of reducing agent, the mechanistic studies indicated that the real catalytic Cu(I) species were generated in a short induction period via reducing Cu(II) salts by alcohol oxidation, homocoupling of terminal alkyne [5c, 20] or sodium azide [21], and in the present case, due to lack of alcoholic solvents, Cu(II) is reduced through homocoupling of terminal alkyne or by sodium azide.

At the end of the optimization process, three catalytic reactions were performed to illustrate the capabilities of synthesized catalysts **3** and **4**. In two of the reactions, the ligands **1** or **2** were used as a catalyst and after 14h no conversion to the product was observed (Table 1, entries 29 and 30). And also, another reaction was performed by using copper acetate monohydrate as a catalyst and after 14 h, 67% of the product was obtained (Table 1, entry 31). This observation, emphasizes that complexes **3** and **4** are good catalysts and show perfect catalytic ability in comparison with ligand-free copper (II) ion.

In the next step, various solvents were tested as reaction media for both catalysts under the optimized reaction condition. Among different solvents such as DMSO, acetone, ethanol, 1,2-dichloroethane, chloroform, acetonitrile and water (Table 2, entries 1-6 and 8), the highest yield was obtained in water for both catalysts (entry 8). Anyway, due to the low solubility of sodium azide in organic solvents, negligible yields were achieved for both catalysts. Accordingly, a mixture solvent including water and DMSO (1:1) was evaluated for both catalysts in their optimized reaction conditions (entry 7). Nevertheless, the best yields were obtained in aqueous media for both catalysts.

Additionally, for both catalysts, several reactions were conducted by increasing the reaction time from 1 to 18 hours using optimal reaction conditions and evaluating the yields obtained for the corresponding isolated product. The results are illustrated in Fig. 4. For catalyst **3**, the reactions proceeded in 6 h and the highest yields reported were obtained. For catalyst **4** the reaction proceeded more slowly and the highest yield could be achieved only after 14 h and after which time stayed constant.

In order to further study both catalysts, they were utilized in AAC reaction with different halides and alkynes (Table 3). The presence of a group (electron withdrawing or electron donating) on the ortho position of benzyl chloride (entries 2 and 4) leads the reaction to lower yield in comparison with the presence of a group on para position. This can be due to the higher steric hindrance for ortho position. By changing phenylacetylene to propargyl alcohol or 2-methyl-3-butyn-2-ol small decrease is resulted in outputs and this decrease is more considerable for 2-methyl-3-butyn-2-ol according to higher steric hindrance. The products ^{1}H NMR spectra are depicted in Fig. S14-S21 respectively (In supplementary material). Even though in the optimized reaction condition for catalyst 4, the temperature and time are higher, but catalyst 3 treated obviously much more efficient than catalyst 4 in their optimized reaction conditions. Also, for the same amount of both catalysts, higher turnover number and yield have been obtained for the catalyst 3 (Table 1, entries 4 and 10). As shown in Table 2, in all used solvents, catalyst 3 exhibited higher activity than catalyst 4. And finally, for all different used substrates, catalyst 3 presented higher activity than catalyst 4.

Overall, this comparison between two complexes containing Schiff-base and diazo ligands can confirm that the Schiff-base ligand helps the copper to be more active in AAC reaction. As mentioned in some published literature [20b, 20d] when the Cu(I) is generated and the catalytic process is begun, the ligand nature can stabilize the +1 state of copper, and help the reaction to be progressed efficiently. In this study, it is clear that Schiff-base ligand is more potentiated to stabilize the Cu(I) in comparison with the diazo ligand. Also, according to the literature [19, 20b], the product of the reaction can act as a ligand in the system, and product inhibition does not occur and it can be the reason for the difference in the performance of progress in two catalytic systems.

Due to the insolubility of both complexes in water, and also with regard to the better results of **3** compared to **4** in Azide-Alkyne cycloaddition, complex **3** was selected to perform catalyst recycling tests. The amounts of the reactants and the catalysts increased by five times, and the test was carried out under the previous reaction conditions (For details, refer to supporting information). When the reaction was complete, ethanol was added to the system to dissolve the product. Then the catalyst was filtrate and wash with ethanol and dry in air and subjected to a new cycle of the reaction. The results indicated that the used material was also active as a catalyst for four runs without a dramatic loss of catalytic activity (Fig. 5).

Finally, we performed a comparison between present catalysts, introduced in this work, and some other previously published catalytic systems, and the results were demonstrated in Table 4. This comparison clearly shows the efficiency of the present catalysts.

3. Conclusions

In summary, we have successfully synthesized and characterized two new Cu(II) complexes containing Schiff-base and diazo ligands. Both complexes were utilized in AAC reaction as new catalysts. By comparing the catalytic activity of them in the same procedure, it was understood that the complex with Schiff-base ligand is able to progress the AAC reaction much more efficient than the complex with a diazo ligand. In addition to higher yields, the reaction condition was milder for Schiff-base complex in comparison with the diazo complex. All the observations confirmed that the nature of Schiff-base ligand is more powerful in maintaining the copper catalyst in its active form progressing the reaction.

4. Acknowledgments

M.B. acknowledges the research council of the Sharif University of Technology for the research funding of this work. The Università degli Studi di Perugia and MIUR are also acknowledged for financial support to the project AMIS, through the program "Dipartimenti di Eccellenza - 2018-2022".

Supporting Information

Experimental details, full characterization data, and Additional data for the computational study are available in the electronic supporting information. **CCDC 1859484** and **CCDC**

1859485 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailed data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033..

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Table 1. Evaluation of temperature and amount of the catalysts on the cycloaddition of benzyl chloride with phenylacetylene in the presence of sodium azide.[a]

Entry	Cat. (mol %)	Temp. (°C)	Yield (%)[b]	TON
1	-	70	0	-
2	**3**(0.28)	70	58	201
3	**3**(0.57)	70	63	109
4	**3**(0.86)	70	83	96
5	**3**(1.15)	70	97	84
6	**3**(1.44)	70	96	66
7	**3**(1.73)	70	97	56
8	**4**(0.28)	70	51	178
9	**4**(0.57)	70	64	111
10	**4(0.86)**	**70**	**76**	**88**
11	**4**(1.14)	70	78	67
12	**4**(1.44)	70	75	52
13	**4**(1.73)	70	78	45
14	**3**(1.15)	r.t.	18	15
15	**3**(1.15)	40	80	69
16	**3(1.15)**	**50**	**96**	**83**
17	**3**(1.15)	60	96	83
18	**3**(1.15)	90	98	85
19	**3**(1.15)	100	98	85
20	**4**(0.86)	r.t.	6	6
21	**4**(0.86)	40	39	45
22	**4**(0.86)	50	64	74
23	**4**(0.86)	60	71	82
24	**4**(0.86)	90	77	89
25	**4**(0.86)	100	76	88
26	**4**(1.14)	100	78	68
27[b]	**3**(1.15)	50	95	83
28[b]	**4**(0.86)	70	77	89
29	**1**(1.15)	70	0	0
30	**2**(1.15)	70	0	0
31	**Cu(OAc)$_2$.H2O**(1.15)	70	67	58

[a] Reaction conditions: 0.5 mmol of phenylacetylene, 0.55 mmol of benzyl chloride, 0.55 mmol of sodium azide, 2 mL of H_2O, Time = 6 h for the catalyst 3 and 14 h for the catalyst 4. [b]Isolated yields.

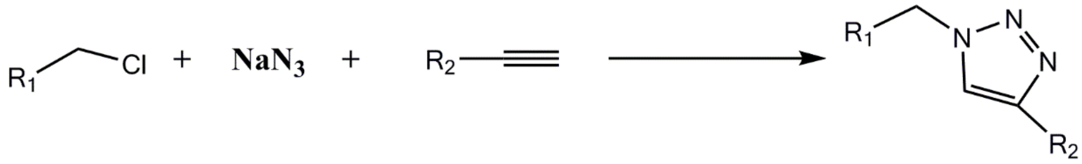
[b] The reactions were performed by adding sodium ascorbate as a reductant with a molar ratio of 2:1 of sodium ascorbate to the catalyst.

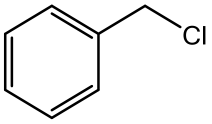
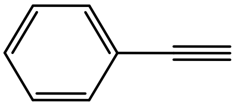
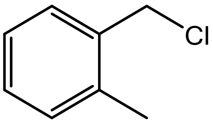
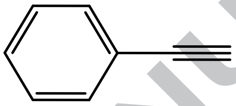
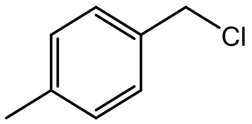
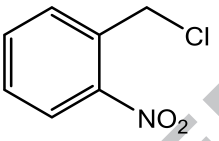
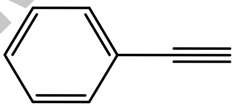
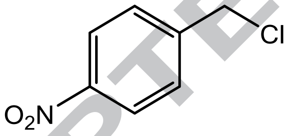
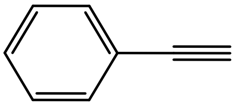
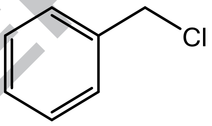
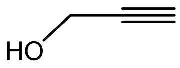
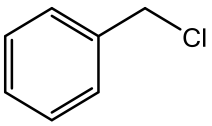
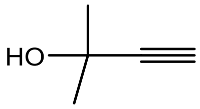
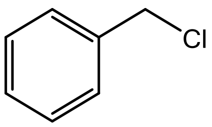
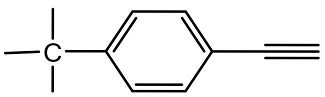
Table 2. The effect of solvent on the cycloaddition of benzyl chloride with phenylacetylene in the presence of sodium azide.[a]

Entry	Solvent	Yield (%)[b]	
		(**3**)	(**4**)
1	DMSO	54	38
2	Acetone	~0	~0
3	Ethanol	37	24
4	1,2-Dichloroethane	12	5
5	Chloroform	~0	~0
6	Acetonitrile	9	5
7	DMSO/Water (1:1)	83	61
8	Water	96	76

[a] Reaction conditions: 0.5 mmol of phenylacetylene, 0.55 mmol of benzyl chloride, 0.55 mmol of sodium azide, solvent 2 mL, (50˚C, 6 h and 1.15 mol% for catalyst 3) and (70˚C, 14 h and 0.86 mol% for catalyst 4). [b] Isolated yields.

Table 3. CuAAC in the presence of catalysts 3 or 4 and NaN_3 under the optimized reaction conditions.[a]

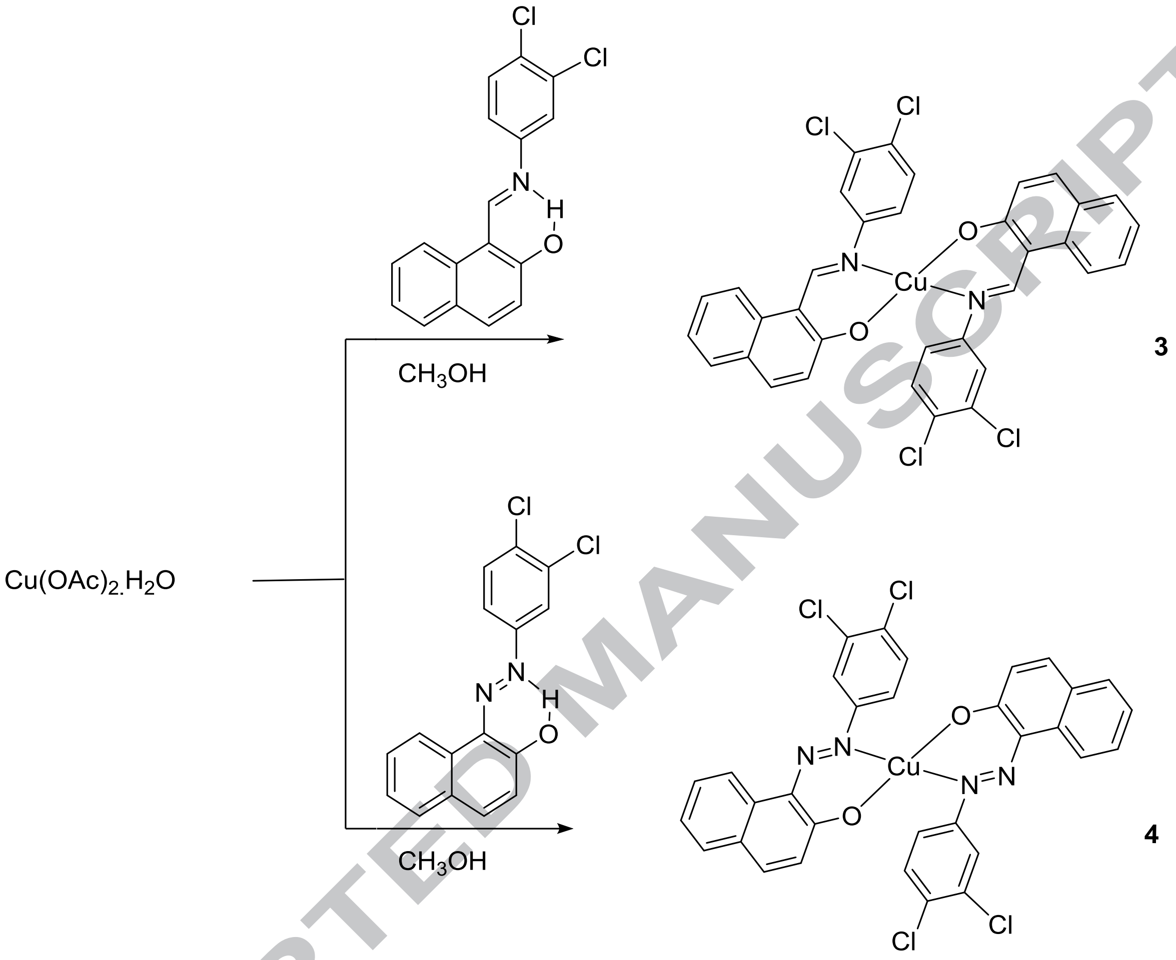


Entry	Aliphatic halide	Alkyne	Yield (%)[b]	
			(3)	(4)
1			96	76
2			91	69
3			97	73
4			89	64
5			94	73
6			90	65
7			82	46
8			85	49

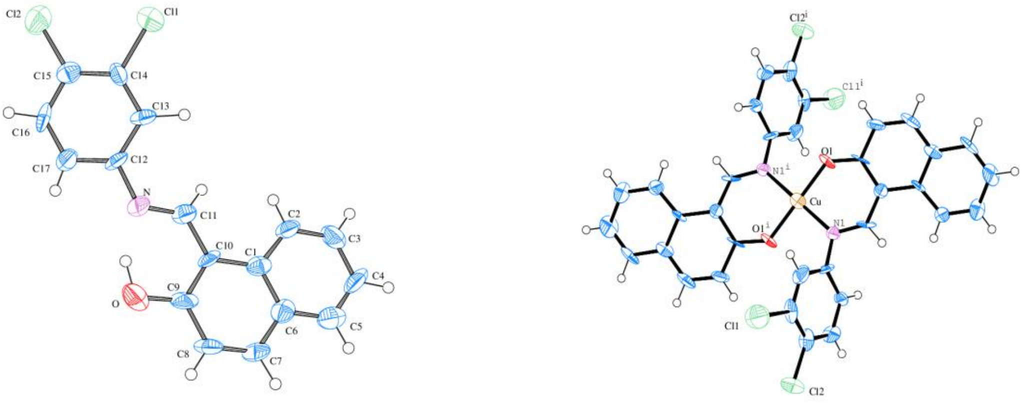
[a] Reaction conditions: 0.5 mmol of a terminal alkyne, 0.55 mmol of alkyl halide, 0.55 mmol of sodium azide, 2 mL of H_2O, (50˚C, 6 h and 1.15 mol% for the catalyst 3) and (70˚C, 14 h and 0.86 mol% for the catalyst 4). [b] Isolated yields.

Table 4. A comparative study of present catalysts with the previously published catalysts in the azide-alkyne cycloaddition reaction

Entry	Catalyst	Condition	Yield (%)	Ref.
1	[Cu(tzol)$_2$]	Catalyst (2.4 mol%)/H_2O/12 h/70°C	96	[11c]
2	[Cu(dppo)$_2$]	Catalyst (2.0 mol%)/H_2O/8 h/RT	86	[6a]
3	$C_3H_7COOCu(PPh_3)_2$	Catalyst (1.0 mol%)/CH_2Cl_2/5 h/r.t.	98	[22]
4	Cu NPs/silica coated maghemite	Catalyst (4.3 mol%)/H_2O/2 h/70°C	83	[23]
5	**3**	**Catalyst (1.15 mol%)/H_2O/6 h/50°C**	**96**	**This work**
6	**4**	**Catalyst (0.86 mol%)/H_2O/14 h/70°C**	**76**	**This work**



Scheme 1. Synthesis of complexes **3** and **4**.



1 **3**

Figure 1. ORTEP diagram of the structures **1** and **3**

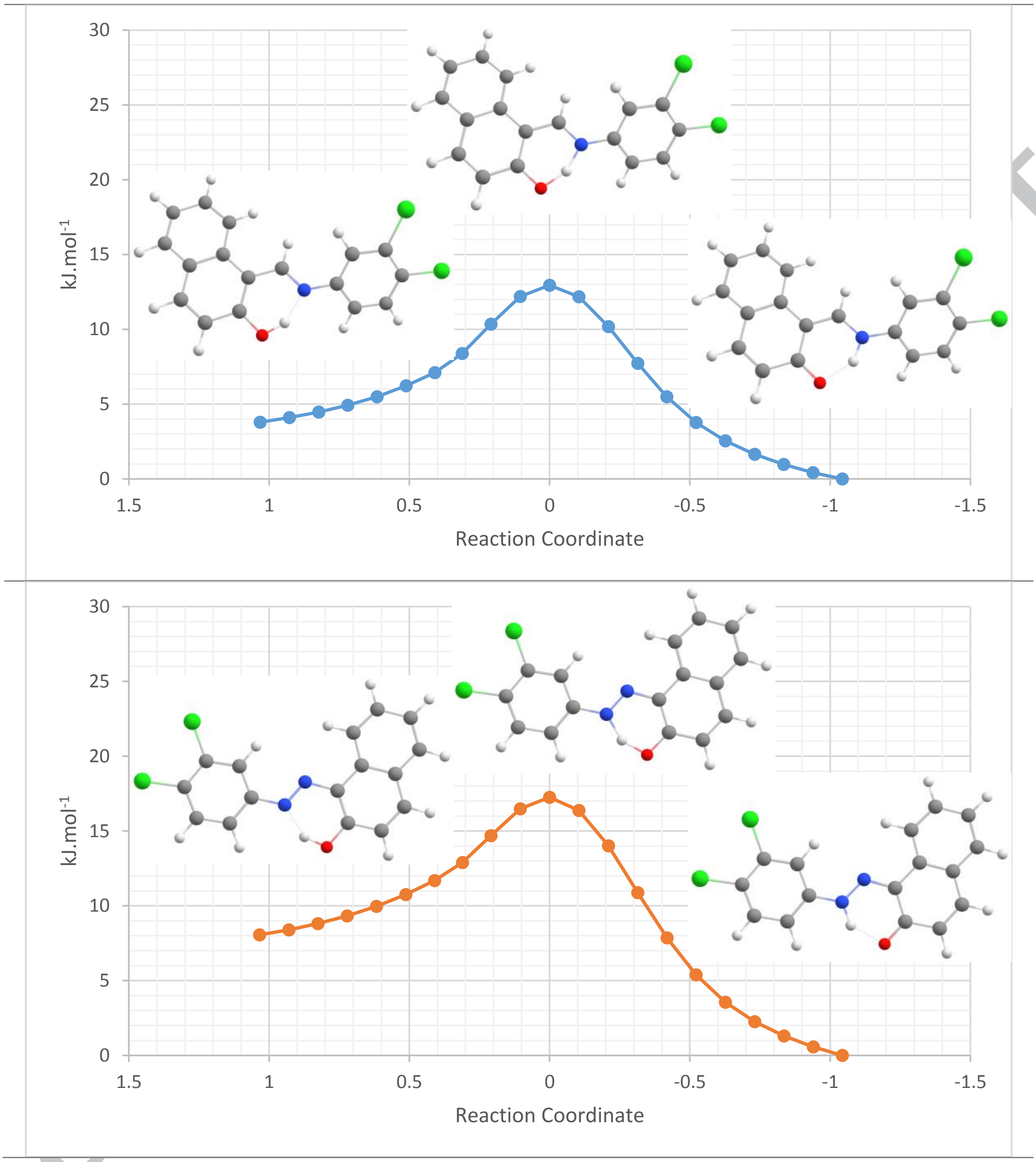


Figure 2. Energy profiles for enol-keto tautomerization of a) ligand **1** and b) ligand **2**

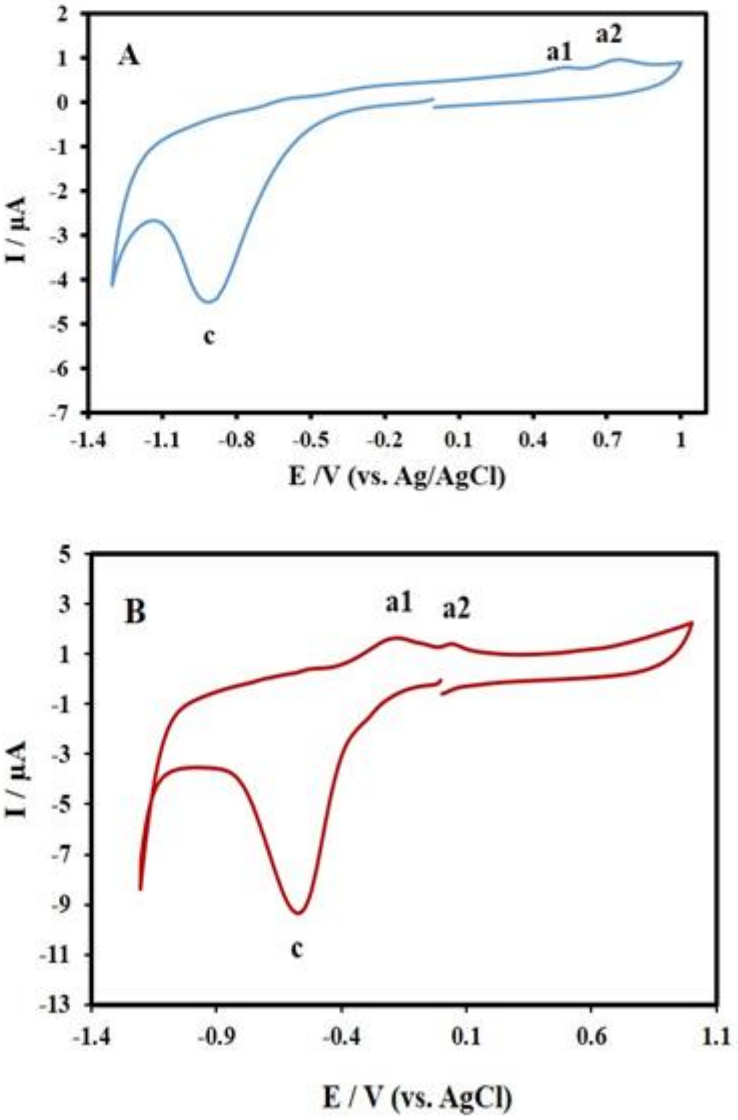


Figure. 3. (**A**) CV of complex **3** and (**B**) CV of complex **4** in phosphate buffer solution (pH= 7.0) and scan rate was 50 mV.s^{-1}.

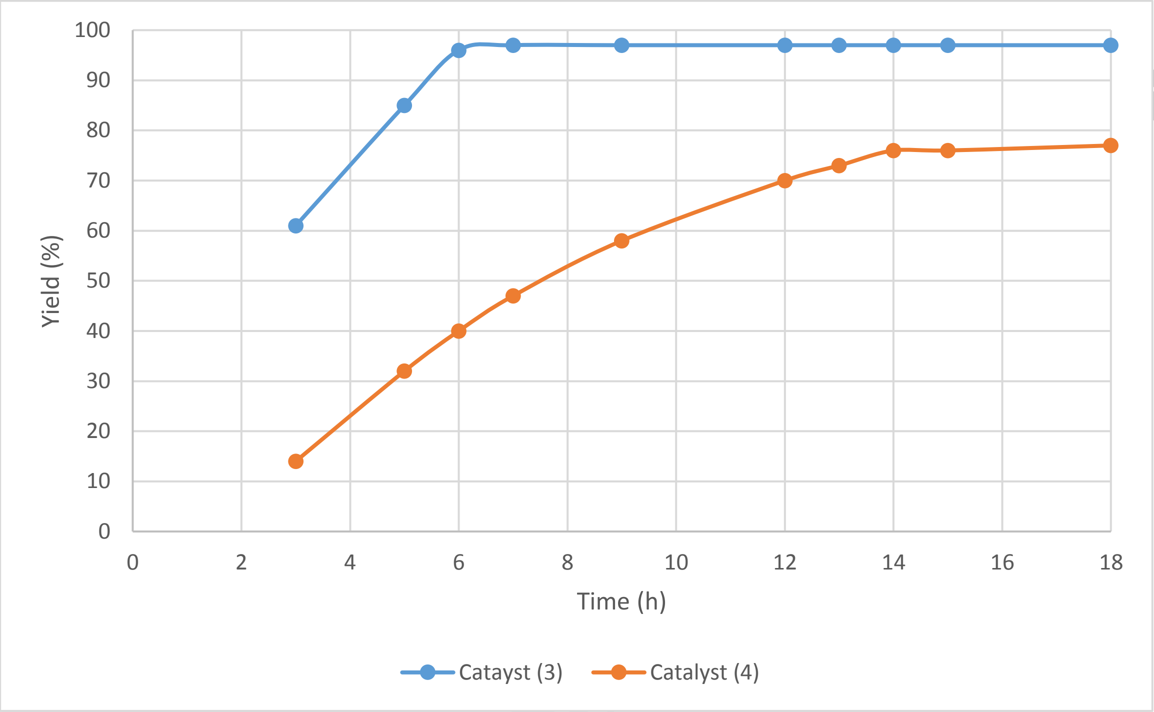


Figure 4. Reaction profile for the cycloaddition of benzyl chloride with phenylacetylene in the presence of azide under optimal conditions (Table 1, entry 16 for catalyst **3** and entry 10 for the catalyst **4**).

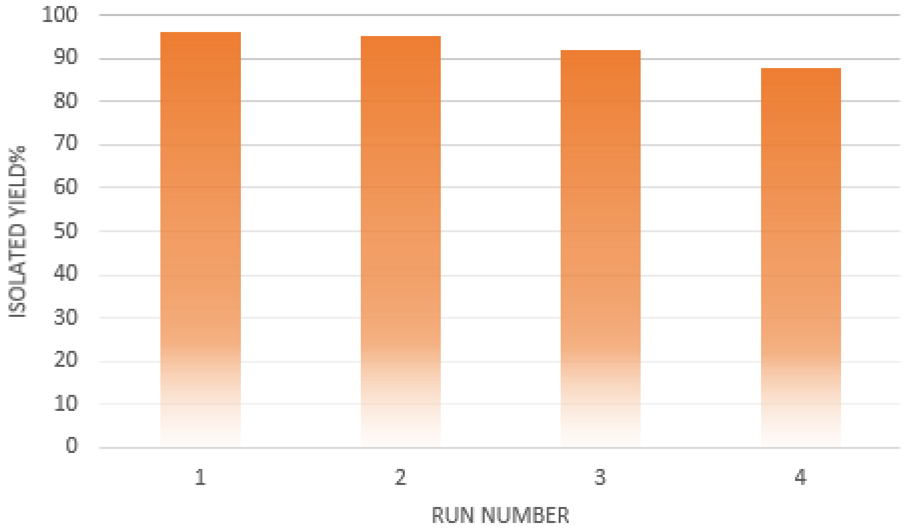


Figure 5. Reusability studies of the complex **3** as a catalyst in the azide-alkyne cycloaddition reaction.

Graphical Abstract- Synopsis

Synthesis, Characterization, and Comparison of Two New Copper(II) Complexes Containing Schiff-base and Diazo Ligands as New Catalysts in CuAAC Reaction.

Two Cu(II) complexes were synthesized including Schiff-Base and diazo ligands with the same geometry. The catalytic potential of the complexes was compared together in one-pot azide-alkyne cycloaddition reaction due to realize the effect of Schiff-Base and diazo ligands nature on the catalytic system. Finally, it was understood that the Schiff-base complex behaved much more efficient than the diazo complex.