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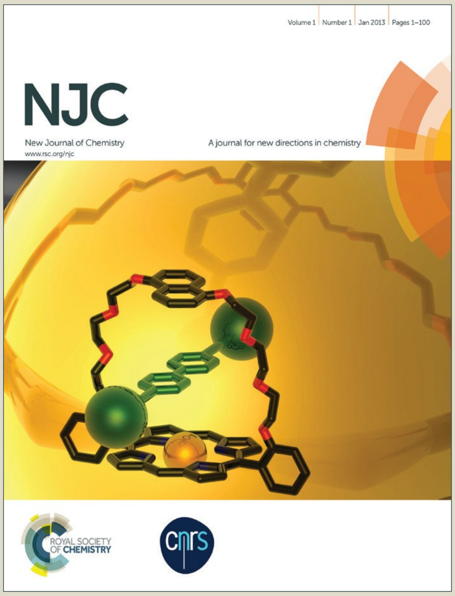

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New organometallic Schiff-base copper complexes as efficient “click” reaction precatalysts

Xiang Liu,[a] Néstor Novoa,[b] Carolina Manzur*,[b]
David Carrillo*[b] and Jean-René Hamon*[a]

[a] *UMR 6226 «Institut des Sciences Chimiques de Rennes», CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France. E-mail: jean-rene.hamon@univ-rennes1.fr*

[b] *Laboratorio de Química Inorgánica, Instituto de Química, Pontificia Universidad Católica de Valparaíso, Avenida Universidad 330, Valparaíso, Chile. E-mails: cmanzur@ucv.cl; david.carrillo@ucv.cl*

Abstract

A new ferrocenyl-containing unsymmetrical Cu^{II}-Schiff-base complex, **2** and its covalently poly(methyl) (methacrylate) (PMMA)-grafted counterpart **3** were synthesized and characterized by elemental analysis, electrospray ionisation (ESI) mass spectrometry for **2**, and FT-IR spectroscopy. The new complex **3** was employed as precatalyst in the copper-catalyzed [3+2] cycloaddition of organic azides to alkynes (CuAAC, “click reaction). The active Cu^{I} species generated from only 0.2 mol% of Cu^{II} precatalyst **2** and sodium ascorbate displayed high activity at room temperature in ethanol for 24 hours allowing the synthesis of a wide variety of 1,4-disubstituted 1,2,3-triazoles in high isolated yields. The PMMA-supported catalyst **3** is also efficient and has been reused at least three times in these “click” reactions without any lost of activity or copper leaching.

Introduction

1,2,3-Triazoles, one of the most vital type of *N*-containing heterocyclic compounds, are of continuing interest, not only as biological active drugs[1] but also as functional materials.[2] In addition, interest for these compounds is mainly due to their use in numerous fields of organic semiconductors,[3] dyes,[4] dehydroannulenes,[5] and electroluminescent material.[6] During the last decades, many methodologies for the preparation of 1,2,3-triazoles have been developed. Among them, the concept of a “click” reaction was designed by Sharpless and co-workers in 2001.[7] One year later, the research groups of Sharpless[8] and of Meldal[9] independently reported the efficient copper-catalyzed azide-alkyne cycloaddition (CuAAC) that has been proven to be the archetypal click reaction.[10] The popularity of the CuAAC reaction is mainly due to its 100% atom economy, mild reaction conditions, wide substrate scope and exclusive regioselectivity in the formation of the 1,4-disubstituted 1,2,3-triazoles. CuAAC has found widespread applications in organic[10]and material syntheses,[11] as for instance, preparation of ferrocene-containing polymers[12] and redox-active metallocene-containing dendrimers.[13]

Schiff base ligands have attracted considerable attention due to their facile synthesis, diversity in structural topology and their ability to produce stable complexes with a large number of transition metal ions.[14] Such types of ligands can also stabilize metal ions in various oxidation states and, therefore, play a crucial role in controlling the conversions of organic reactions catalyzed by their transition metal complexes. Schiff base metal complexes present effective applications in various fields of scientific research such as magnetism,[15] catalysis[16] and functional molecular-based materials.[17,18] Among them, unsymmetrical tetradentate N_2O_2 salen-type Schiff base complexes[19] are easily obtained by the 1:1:1 stepwise condensation of β-diketone, salicylaldehyde and a primary alkyl- or aryldiamine in the presence of a metal salt.[20] Using this methodology, our groups have synthesized and fully characterized a lot of robust neutral heterobimetallic unsymmetrical salen-type complexes of nickel(II) and copper(II), and thoroughly investigated their electrochemical, linear and second order nonlinear optical properties.[21,22] Side-chain metallopolymers containing an unsymmetrical ferrocenyl substituted Schiff base complex of Ni(II) linked to a polymethylmethacrylate (PMMA) matrix were also prepared.[23]

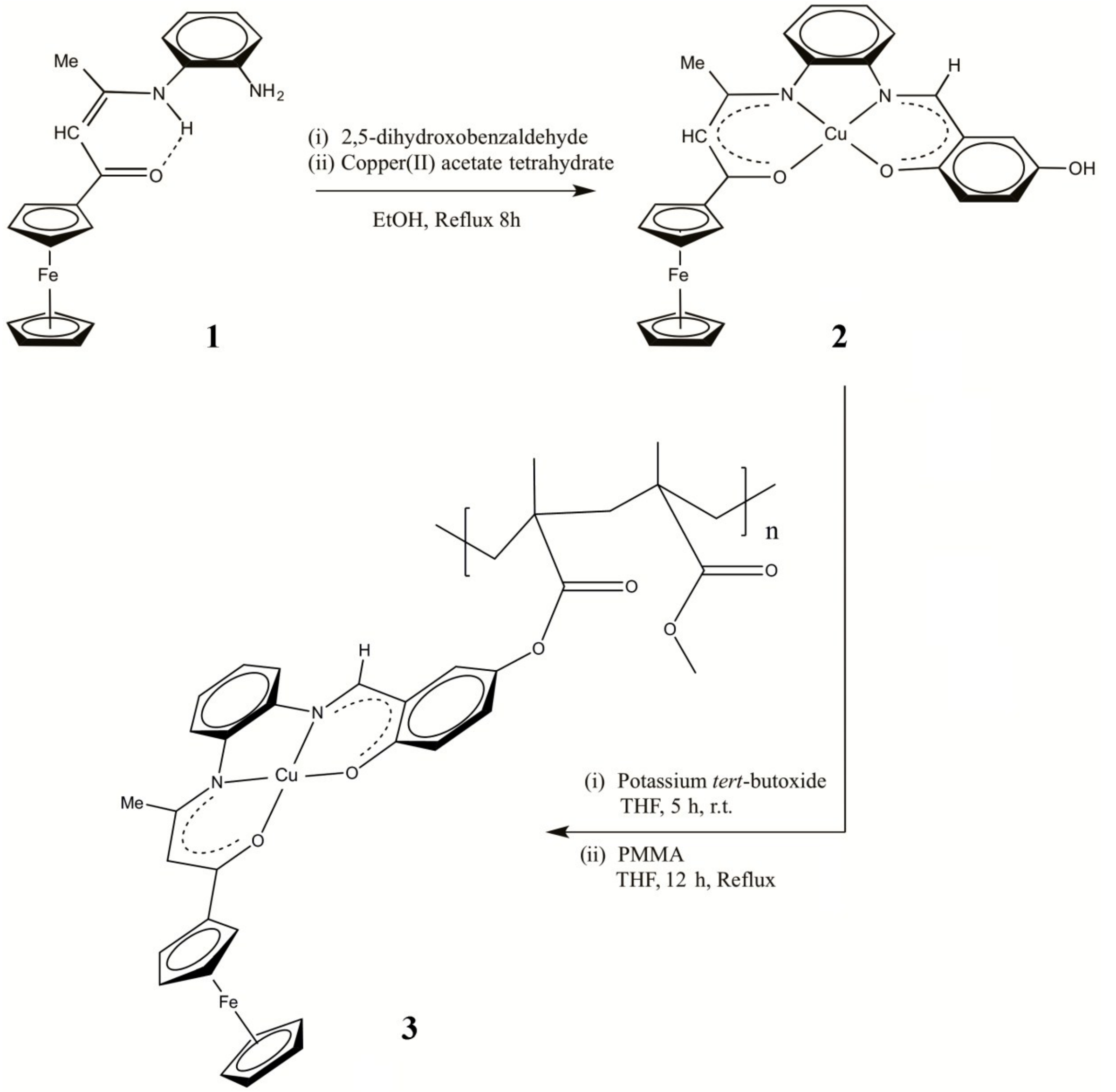
To the best of our knowledge, there are no examples of the use of such Cu^{II} tetradentate Schiff base complexes as catalysts or catalyst precursors for the CuAAC reaction.

Polydentate nitrogen donor ligands are commonly used to enhance the rate of the CuAAC reactions[24] and catalysts based on the tren architecture were shown to behave as highly efficient and reusable catalysts.[25] As part of our current studies on the application of tetradentate N_2O_2 Schiff base metal complexes, herein, we report: (i) the synthesis and characterization of a new ferrocenyl-containing substituted copper(II) unsymmetrical Schiff base complex **2** and of its polymeric counterpart **3** obtained by a covalent grafting of the heterobimetallic complex **2** onto a PMMA matrix upon *trans*-esterification; (ii) their use, efficiency, scope and recyclability as catalysts for the synthesis of 1,4-disubstituted 1,2,3-triazoles via “click” reactions of organic azides and alkynes.

Results and discussion

*Synthesis and characterization of the catalysts **2** and **3***

The paramagnetic heterobimetallic Fe^{II}-Cu^{II} unsymmetrical Schiff base complex **2** was prepared by a one-pot template procedure reacting the metalloligand **1**, and equimolar amounts of 2,5-dihydroxobenzaldehyde and copper(II) acetate monohydrate in refluxing ethanol for 8 hours (Scheme 1). The ferrocenyl group was introduced because (i) its functionalization and branching to the Schiff-base is easy and convenient, (ii) its color provides easy trace of the catalyst, and (iii) it involves specific bulk that differ from simple organic fragments and allows to study this bulk effect on catalytic results. Compound **2** was isolated in a reasonable yield of 60% as an air and moisture insensitive, thermally stable dark red powder, exhibiting a rather good solubility in common polar organic solvents, but it is insoluble in diethylether and hydrocarbons. The metallopolymer **3** was synthetized under basic conditions by a *trans*-esterification reaction between the *in situ* deprotonated form of the heterobimetallic Schiff base complex **2** with a polymethylmetacrylate matrix in refluxing THF overnight (Scheme 1). The PMMA-supported catalyst **3** was obtained as a dark brown amorphous solid upon slow evaporation of a THF solution at room temperature (rt). Compound **3** shows good solubility in dichloromethane and THF, but is insoluble in ethanol and other common solvents. Both compounds **2** and **3** were characterized by FT-IR spectroscopy and the bulk composition of **2** was firmly established by elemental analysis and confirmed by the molecular peak in the ESI mass spectrum (see the experimental section).



Scheme 1 Synthesis of the heterobimetallic complex **2** and of its PMMA-supported derivative **3**[a]

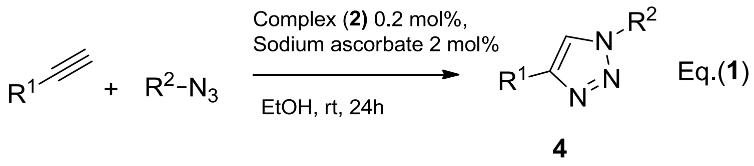
[a] The PMMA-supported derivative **3** is a mixture resulting from random ordering of the monomer units and bulk effect of the inorganometallic group in the polymer. The monomer ordering that is represented in the drawing of **3** is a simplification.

The solid-state FT-IR spectrum of **2** (Fig. S1)† presents a set of medium- to strong-intensity bands in the range 1603-1512 cm^{-1} due to the C-C/C-N/C-O stretching vibrations of the organic Schiff base skeleton. The shift by about 30 cm^{-1} of these absorptions and the disappearance of the enamine N-H vibration observed at 3203 cm^{-1} in the spectrum of the starting metalloligand[26] clearly indicate that coordination of the Cu^{II} metal ion takes place through the imine nitrogen and carbonyl oxygen atoms. On the other hand, the solid-state FT-IR spectrum of the metallopolymer **3** (Fig. S1)† is superimposable to that of its PMMA-supported Ni(II) counterpart,[23] exhibiting the characteristic band of the ester carbonyl group

(1732 cm^{-1}) and the vibrational pattern of the organic Schiff base skeleton in the range 1636-1566 cm^{-1}. In addition, the disappearance of the δ(O-H) vibration at 1447 cm^{-1} in the spectrum of **3** bears testimony of the successful *trans*-esterification reactions.

Catalysis

Both catalysts **2** and **3** were used in the [3+2] cycloaddition of organic azides to alkynes in CuAAC click reactions. All the reactions were performed on a 0.50 mmol scale relative to alkyne and azide reagents in 2 mL of solvent at rt during 24 h under N_2 in the presence of sodium ascorbate as reducing agent (eq. 1). This means that the Cu^{II}-Schiff base complex is reduced to Cu^{I} by sodium ascorbate as shown by ^{1}H NMR by the shift of the imine proton (see Fig. S2)†, and as anticipated from the previously well-known reduction of $CuSO_4$ to Cu^{I} by sodium ascorbate.[8]



First, the reaction conditions were optimized for the synthesis of **4** using ethynylbenzene and (azidomethyl)benzene as model substrates, with the heterobimetallic Fe(II)-Cu(II) Shiff base complex **2** as catalyst (Table 1). The first attempt performed in ethanol with 5 mol% loading of catalyst afforded the desired 1-benzyl-4-phenyl-1H-1,2,3-triazole product **4a** in almost quantitative yield (Table 1, entry 1). Such a result is not surprising with respect to the amount of catalyst used.[8-10] Thus, we investigated the reaction at different loading of complex **2**, and found that the isolated yield of the 1,2,3-triazole **4a** slightly decreased from 98.2 to 92.0% when the loading of catalyst is reduced from 5 to 0.2 mol% (Table 1, entry 1-5). Further decreasing of the catalyst loading to 0.1 mol% caused a dramatic drop of the yield to 45.2%, however (Table 1, entry 6). Based on these results, it appeared that the best yield to catalyst compromise is provided in entry 5 (Table 1) and we, therefore, chose to run the click reactions with 0.2 mol% loading of catalyst.

Next, with this 0.2 mol% loading of catalyst **2**, the reactions were carried out in different solvents including water, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (Table 1, entry 7-10). Under these reaction conditions, the 1,2,3-triazole **4a** is formed in lower yields, ranging from 12.2% in water to 83.3% in THF. Thus, among the solvents tested, ethanol was found to be the best one (Table 1, entry 5). The very low conversion observed in water is presumably due to the lack of solubility of the organic reagents and catalyst in this medium. On the other hand, the organic substrates are soluble in ethanol. The reaction is heterogeneous as the precatalyst and catalyst are not soluble in ethanol without copper leaching.

Table 1 Optimization of the click reaction conditions[a] using complex **2** as catalyst, and ethynylbenzene and benzylazide as reagents.

Entry	Catalyst (%)	Sodium ascorbate (%)	Solvent	Yield (%)[b]
1	5	50	EtOH	98.2
2	2	20	EtOH	97.8
3	1	10	EtOH	95.2
4	0.5	5	EtOH	94.9
5	0.2	2	EtOH	92.0
6	0.1	1	EtOH	45.2
7	0.2	2	THF[c]	83.3
8	0.2	2	H_2O	12.2
9	0.2	2	DMSO[d]	67.3
10	0.2	2	DMF[e]	70.1

[a]Reaction conditions: 0.50 mmol of alkyne and azide reagents in 2 mL of solvent, 25 °C, 24 h, N_2. [b]Isolated yield of 1-benzyl-4-phenyl-1H-1,2,3-triazole (**4a**). [c]Tetrahydrofuran. [d]Dimethylsulfoxide. [e]Dimethylformamide.

The scope extension of the protocol to other azides and alkynes was also investigated under the previously optimized reaction conditions. As shown in Table 2, various organic azides and alkynes were well suited for the “click” reaction with the Cu^{II} Schiff base complex **2** as catalyst. For example, in the presence of ethynylbenzene, either the electron withdrawing substituted azides or electron donating substituted azides including $PhCH_2N_3$,3-$MeC_6H_4N_3$, PhN_3, 4-$BrC_6H_4CH_2N_3$, and 4-$CNC_6H_4CH_2N_3$ undergo facile conversion into corresponding 1,4,disubstituted 1,2,3-triazole derivatives **4a-e** in good to excellent yields (Table 2, entries 1-5). Similar high isolated yields (87.5 to 93.6%) of 1,4-disubstituted 1,2,3-triazoles **4f-h** are obtained when (azidomethyl)benzene is reacted with variously electronically substituted R^1-C≡CH alkynes (R^1 = 4-anisyl, 4-bromophenyl or 2-pyridyl ; Table 2, entry 6-8). In addition, $C_6H_5N_3$, 4-$BrC_6H_4CH_2N_3$, 4-$CNC_6H_4CH_2N_3$, 4-$BrC_6H_4N_3$, and 4-$MeOC_6H_4N_3$, are also suitable for the cycloaddition reactions with 2-ethynylpyridine affording the corresponding 1,2,3-triazole products **4i-m** in very good yields (Table 2, entries 9-13). Even though no strong trend can be traced from Table 2, one can, however, note that the lowest yields are obtained when the azide reagent bears the strong 4-CN electron withdrawing substituent (entries 5 and 11).

Table 2 Substrate scope of alkynes and azides in the click [3 + 2] cycloaddition reactions catalyzed by complex **2**.[a]

Entry	R^1-C≡CH	R^2-N_3	Product	Yield (%)[b]
1	C_6H_5	$C_6H_5CH_2$	**4a**	92.0
2	C_6H_5	3-$MeC_6H_4CH_2$	**4b**	88.7
3	C_6H_5	C_6H_5	**4c**	88.5
4	C_6H_5	4-$BrC_6H_4CH_2$	**4d**	93.4
5	C_6H_5	4-$CNC_6H_4CH_2$	**4e**	82.5
6	4-$MeOC_6H_4$	$C_6H_5CH_2$	**4f**	87.5
7	4-BrC_6H_4	$C_6H_5CH_2$	**4g**	93.6
8	2-NC_5H_4	$C_6H_5CH_2$	**4h**	91.3
9	2-NC_5H_4	C_6H_5	**4i**	90.4
10	2-NC_5H_4	4-$BrC_6H_4CH_2$	**4j**	92.5
11	2-NC_5H_4	4-$CNC_6H_4CH_2$	**4k**	83.5
12	2-NC_5H_4	4-BrC_6H_4	**4l**	90.4
13	2-NC_5H_4	4-$MeOC_6H_4$	**4m**	88.4

[a]Reaction conditions: alkyne (0.50 mmol), azide (0.50 mmol), complex **2** (0.2 mol%), sodium ascorbate (2 mol%), EtOH (2 mL), rt, 24 h, N_2. [b]Isolated yield.

The next step was the recycling study of the catalytic material anchored onto the PMMA matrix. Recycling investigations were carried out using catalyst at 2 mol% in the click [3 + 2] cycloaddition reaction between the (azidomethyl)benzene and three different alkynes (Table 3). The supported precatalyst **3** was recovered by filtration and reused three times in the same reaction. Na ascorbate was added again for each recycling, because the Cu^I catalyst is air sensitive and oxidized by air to Cu^{II}. No leached copper was detected in solution by TEM (nanoparticles, Fig. S3)† and ^{1}H NMR spectroscopy (Cu^{II}) after catalysis (Figs. S4-S6)†. We know that the presence of Cu^I in solution containing triazole significantly shifts the triazole proton from 7.6 downfield to 8 ppm,[27] and this was shown again by adding $CuSO_4$ and sodium ascorbate to a solution of **4**. The absence of Cu^{II} in the solution resulting from the click reaction catalyzed by **3** was shown by the absence of shift of the triazole proton in the ^{1}H NMR spectrum of this solution to which sodium ascorbate was added. This shows the stability of the catalyst **3** under the reaction condition and the heterogeneous mechanism of the reaction, the precatalyst **3** being insoluble in EtOH. Under the above conditions, catalyst **3** afforded the expected 1-benzyl-4-phenyl-1H-1,2,3-triazole **4a** in 95.2-95.0% yield in three cycles in the reaction involving the model substrate (Table 3, entry 1). The reusability test was extended to two other alkynes, namely, 4-ethynylanisole and 4-bromophenylacetylene, providing the desired 1,4-disubstituted 1,2,3-triazoles **4f** and **4g** in 88.3% and 94.2-93.4% yields, respectively, in three cycles (Table 3, entries 2 and 3). These results clearly indicate that the highly active PMMA-supported heterobimetallic unsymmetrical Schiff base complex

3 can be reused at least three times without significant loss of its catalytic activity and without copper ion leaching.

Table 3 Reusability tests of the PMMA-supported catalyst **3** in the click [3 + 2] cycloaddition reactions[a]

Entry	R^1-C≡CH	R^2-N_3	Product	Run 1 yield (%)[b]	Run 2 yield (%)[b]	Run 3 yield (%)[b]
1	C_6H_5	$C_6H_5CH_2$	**4a**	95.2	95.0	95.0
2	4-MeOC_6H_4	$C_6H_5CH_2$	**4f**	88.4	88.3	88.3
3	4-BrC_6H_4	$C_6H_5CH_2$	**4g**	94.2	93.8	93.4

[a] Reaction conditions: alkyne (0.50 mmol), azide (0.50 mmol), catalyst **3** (2 mol%), sodium ascorbate (20 mol%) , EtOH (2 mL), rt, 24 h, N_2. [b] Isolated yield.

Conclusion

In summary, a new heterobimetallic Cu(II) complex of ferrocene-based unsymmetrical tetradentate Schiff base ligand has been synthesized, characterized, and its efficient catalytic performances have been investigated in the [3 + 2] cycloaddition of organic azides to alkynes. The procedure is general, convenient, simple to carry out, eco-friendly, with a broad scope and atom economy, leading to the regioselective formation of a wide variety of 1,4-disubstituted 1,2,3-triazoles in high isolated yields. The PMMA-supported catalyst was obtained by *trans*-esterification of the novel copper(II) complex of unsymmetrical dianionic quadridentate organometallic salen-type Schiff base ligand **2** with the polymer matrix. The heterobimetallic Schiff base complex **2** and its PMMA-anchored derivative **3** were characterized by elemental analysis and solid-state infrared spectroscopy. The heterobimetallic Schiff base complex **2** exhibits a good catalytic activity with a 0.2 mol% of loading with various organic alkynes and azides under ambient conditions in ethanol. The ferrocenyl group appears fully compatible to the catalytic activity of both precatalysts. The catalytic results favorably compare with literature data[27] using here a practical catalyst in very low loading. The Cu^{II} precatalysts **2** and **3** are not active unless sodium ascorbate is added, which fully parallels the finding by the Sharpless group with $CuSO_4$.[8] Recycling the catalyst supported on PMMA matrix **3** was also investigated. The experiments involving (azidomethyl)benzene and three different alkynes gave the corresponding 1,2,3-triazoles in excellent yields after three cycles without copper leaching from the precatalyst **3** to solution.

This does, therefore, demonstrate that this material shows good recyclability without any loss in activity, opening new potential applications for copper(II) Schiff base compounds in catalysis.

Experimental

General methods

All manipulations were performed under a dinitrogen or argon atmosphere using standard Schlenk techniques. All the solvents and reagents needed were purchased from commercial sources and used without further purification. The organometallic tridentate metalloligand **1** was synthesized according to the procedures described in the literature.[26] PMMA beads (average MW 35000) were purchased from ACROS Organics. Column chromatography was carried out on silica gel. Solid-state FT-IR spectra were recorded on a Perkin-Elmer, Model Spectrum One or a Bruker IFS28 FT-IR spectrophotometer, with KBr disks in the 4000 to 400 cm^{-1} range. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 298 K with either a Bruker AC 300 or a Bruker AVIII 400 spectrometer. All NMR spectra are reported in parts per million (ppm, δ) relative to tetramethylsilane (Me_4Si), with the residual solvent proton resonance and carbon resonances used as internal standards. Coupling constants (*J*) are reported in Hertz (Hz), and integrations are reported as number of protons. Microanalyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1 (France).

Synthesis of the heterobimetallic Schiff base complex 2

To a Schlenk tube containing a stirred solution of the metalloligand **1** (400 mg, 1.11 mmol) in ethanol (30 mL) was added a solution of 2,5-dihydroxobenzaldehyde (153.3 mg, 1.11 mmol) in ethanol (10 mL). The resulting solution was stirred for 15 min at rt. A solution of copper(II) acetate monohydrate (334 mg, 1.67 mmol) in ethanol (10 mL) was then added, and the resulting solution was refluxed for 8 h. The mixture was allowed to cool to r. t. evaporation of the solution to half of its volume under vacuum gave a dark red precipitate. The solid material was filtered off, washed with cold methanol (5 x 10 mL) and diethyl ether (5 x 10 mL), and dried *in vacuo* for 1 h to afford 364 mg (0.67 mmol, 60 % yield) of a dark red powder. Found: C, 59.43; H, 3.75; N, 5.35. $C_{27}H_{22}N_2O_3FeCu$ requires C, 59.85; H, 4.09; N, 5.17%. ESI MS (m/z), calcd for $C_{27}H_{22}N_2O_3Na^{56}Fe^{63}Cu$: 564.0168, found: 564.0167 (0 ppm) $[M^{+}Na]^{+}$. FT-IR (KBr pellet, cm^{-1}): 3436(w) ν(O-H), 3096(w) ν(C-H aryl), 2965–2925(w) ν(C-H alkyl), 1603(m)-1512(s) $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$, 1447(m) δ(O-H).

Synthesis of the PMMA-supported Schiff base complex 3

A Schlenk tube was charged with a magnetic stir bar, complex **2** (101 mg, 0.186 mmol), potassium *tert*-butoxide (31mg, 0.279 mmol) and 1.5 mL of THF. After 15 min of stirring a dark purple precipitate was formed, the reaction mixture was vigorously stirred for 5 h. Then, 93 mg of PMMA (complex **2** / monomeric unit PMMA = 1/5) was slowly added. After 10 min of stirring, 2 mL of THF were added, and vigorous stirring was continued for 30 min while the resulting solution was refluxed overnight. The mixture was cooled to r. t. and evaporation of the solution to half of its volume under reduced pressure gave a precipitate that was filtered off, washed with cold THF (3 x 3 mL), diethyl ether (2 x 3 mL), and dried *in vacuo* for 2 h. The solid material was dissolved in THF at 35°C, filtered off and the filtrate allowed to slowly evaporate to afford 180 mg of a dark brown amorphous solid. Elemental analysis: C, 38.53; H, 2.97; N, 2.88%. The compared elemental analyses of **2** and **3** gives 6.53% Cu in complex **3**, i.e. a ratio complex **2**: PMMA = 1: 4.3 in complex **3**. FT-IR (KBr pellet, cm^{-1}): 3443(w) ν(O-H), 3012 (w) ν(C-H aryl), 2966-2929 (w) ν(C-H alkyl), 1732(s) $\nu(CO_2)$, 1636-1566 (m) $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$.

General procedure for the synthesis of the 1,2,3-triazoles 4a-m catalyzed by 2

The alkyne (0.50 mmol), the azide (0.50 mmol), the heterobimetallic Schiff base catalyst **2** (0.2 mol%), sodium ascorbate (2 mol%) and ethanol (2 mL) were placed in a round bottom flask equipped with a magnetic stirrer. The resulting mixture was stirred for 24 h at rt under dinitrogen atmosphere. Then, water (2 mL) was added to the reaction mixture that was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with brine (2 × 5 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to flash column chromatography with hexanes/ethyl acetate (5/1) as eluent, to provide, upon evaporation of the solvents and vacuum drying, the desired 1,4-disubstituted 1,2,3-triazoles **4a-m** as white solids. Reagents and yields are given in Table 2, whereas NMR data and spectrum of the 13 triazole derivatives are provided in the ESI.†

Recyclability of the PMMA-supported catalyst 3

The PMMA-anchored precatalyst **3** (10.5 mg, 2 mol%) and sodium ascorbate (20 mol%) were added in a Schlenk flask. The system was purged three times with N_2 and alkyne (0.50 mmol), azide (0.50 mmol) and 2 mL of degassed ethanol were successively added by syringe. The resulting mixture was stirred for 24 h at RT under N_2. Then, the mixture was diluted with diethyl ether and filtered through a filter paper. Water (20 mL) was added to the filtrate, and then extracted three times with ethyl acetate (3×10 mL). The combined organic phases were washed with brine (2×5 mL), dried over anhydrous $MgSO_4$, filtered, and the organic solution was concentrated *in vacuo*. The residue was purified by silica gel flash chromatography with hexane/EtOAc (5/1) as eluent to obtain the desired product **4a** as a white solid (95.2% yield). The collected solid containing **3** was washed with water, ethanol and dichloromethane then transferred into a round bottom flask and dried by a N_2 flux. Sodium ascorbate (20 mol%) was introduced, and the system was purged three times with N_2 before adding the alkyne (0.50 mmol), azide (0.50 mmol) and 2 mL of degassed ethanol like previously. This process was repeated three times without correction of the amounts of reactants compared to the mass loss of catalyst at each cycle. The reagents, products, and yields of the various runs are provided in Table 3.

Acknowledgements

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Notes and References

[†] Electronic supplementary information (ESI) available: Solid-state FT-IR spectra of the catalysts (Fig. S1), Fig. S2-S6, spectral data and ^1H and ^{13}C NMR spectra of compounds **4a-m** (Figs. S7-S25).

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Table of contents entry

New organometallic Schiff-base copper complexes as efficient “click” reaction precatalysts

Xiang Liu, Néstor Novoa, Carolina Manzur, David Carrillo and Jean-René Hamon

In the presence of sodium ascorbate, the recyclable CuAAC precatalysts displayed high activity allowing the synthesis of a wide variety of 1,4-disubstituted 1,2,3-triazoles in high isolated yields.