CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201202472

Copper-Catalyzed Huisgen and Oxidative Huisgen Coupling Reactions Controlled by Polysiloxane-Supported Amines (AFPs) for the Divergent Synthesis of Triazoles and Bistriazoles

Zhan-Jiang Zheng,[a] Fei Ye,[a] Long-Sheng Zheng,[a] Ke-Fang Yang,[a] Guo-Qiao Lai,[a] and Li-Wen Xu*[a, b]

Abstract: An interesting example of a divergent catalysis with a copper(I) and amine-functional macromolecular polysiloxanes system was successfully presented in click chemistry. In this manuscript, we demonstrate the remarkable ability of the secondary amine-functional polysiloxane to induce oxidative coupling in the copper-mediated Huisgen reactions of azides and alkynes, thereby achieving good yields and selectivities. The click reactions mediated by a polysiloxane-supported secondary amine allow the preparation of novel heterocyclic compounds, that is, bistriazoles. Comparably, it is also surprising that the use of a diamine-functional polysiloxane as ligand led to a classic Huisgen [3+2] cycloaddition in excellent yields. From the results of the present amine-functional polysiloxanes-controlled Huisgen reaction or oxidative Huisgen coupling reaction to divergent products and the proposed mechanism, we suggested that the mononuclear bistriazole–copper complex stabilized and dispersed by the secondary amine-functional polysiloxane was beneficial to prevalent the way to oxidative coupling.

Keywords: bistriazoles · click chemistry · copper · oxidative coupling · polysiloxanes

Introduction

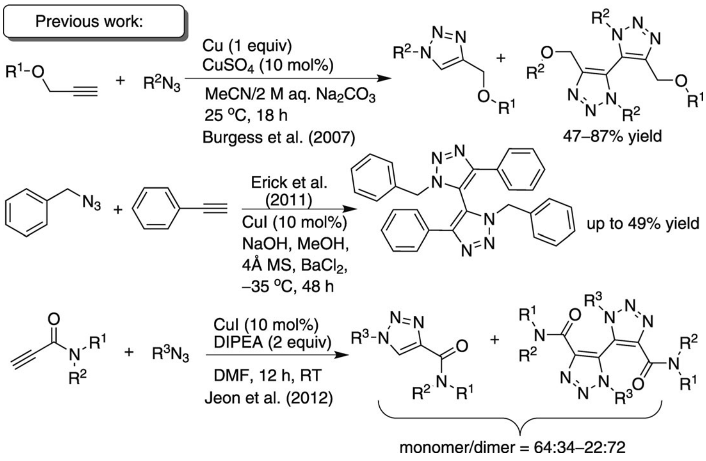
Since Sharpless et al. disclosed the concept of click chemistry in 2001,[1] the Huisgen [3+2] cycloaddition[2] has emerged as a powerful chemical reaction to 1,4-disubstituted triazoles and promoted the progress of click chemistry.[3,4] In the past decade, the catalytic Huisgen click reaction of azides with alkynes, with its many creative and effective variations, have found a wide application in numerous areas due to its privileged status. The reaction is easy to perform with high yields, little or no byproducts are formed, the reaction can be carried out under mild conditions, it works well under many chemical and biological conditions, functional groups are tolerated, and the reaction is high atom economical.[4] In particular, the corresponding triazoles motif has become increasingly important building blocks and linkers in polymeric materials, drug and medicinal chemistry, bioconjugate chemistry, surface science, and combinational chemistry.[5] Undoubtedly, the discovery of the catalytic effect of Cu^I in the Huisgen reaction of alkynes and azides was a milestone in the development of click chemistry.[6] The success of the Cu^I-catalyzed Huisgen reaction has been highlighted by numerous reports with clean addition and little byproducts.[4–6] Because of the established importance of click chemistry with the triazole motif, most works reported in the past ten years ignored the isolation and characterization of the minor amount of side products in this reaction. Interestingly, only three examples have reported that the minor byproduct of the Huisgen reaction, bistriazoles, was not a negligible molecule (Scheme 1).[7] For example in 2007, Burgess et al.[7a] reported that the bistriazoles could be the major product in the presence of a catalytic amount of $CuSO_4$ (10 mol %) and one equivalent of Cu power under meticulously modified conditions: 1:1 mixture of MeCN/2 M aqueous Na_2CO_3 solution at 25 °C for 18 h. Jeon et al.[7c] also reported the formation of bistriazoles in low to moderate yields and selectivities in the presence of CuI or CuBr and two equivalents of diisopropylethylamine (DIPEA). However, it was observed that only the alkynes containing propargylic ethers and acetylenic amides could specifically result in moderate to good yields in previous reported examples. The oxidative coupling–click dimerization did not work well when the alkynes or azides were linked directly with hindered group or aromatic moiety.

---

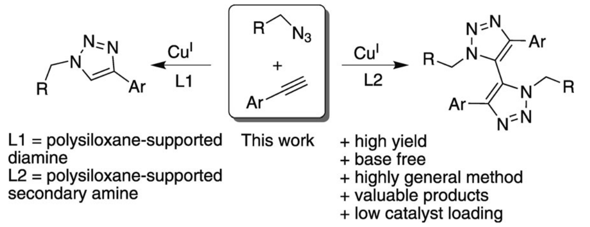
[a] Dr. Z.-J. Zheng, F. Ye, L.-S. Zheng, Dr. K.-F. Yang, Dr. G.-Q. Lai, Prof. Dr. L.-W. Xu
Key Laboratory of Organosilicon Chemistry and
Material Technology of Ministry of Education
Hangzhou Normal University
Hangzhou 310012 (P. R. China)
Fax: (+86) 571-28865135
E-mail: liwenxu@hznu.edu.cn

[b] Prof. Dr. L.-W. Xu
State Key Laboratory for Oxo Synthesis and Selective Oxidation
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences
Lanzhou, 730000 (P. R. China)
E-mail: licpxulw@yahoo.com

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201202472.



Scheme 1. Copper-catalyzed Huisgen-oxidative coupling reaction: previous work on the synthesis of bistriazoles.[7]

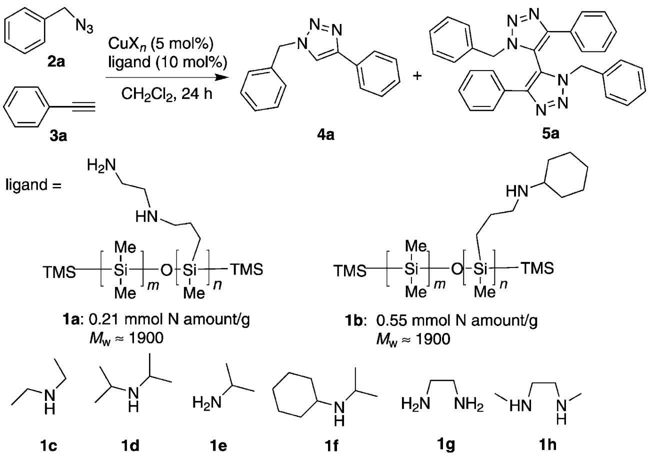


Scheme 2. Amine-functional polysiloxanes-controlled divergent synthesis of triazoles and bistriazoles in the click addition of azides and alkynes.

Inspired by previous studies on the oxidative Huisgen reaction and mechanistic investigation,[6,7] we were aware of the possibility of modifying the stability and the catalytic activity of active Cu^{I} species with amine-functional polysiloxanes (AFPs). Amine-functional polysiloxanes or polysiloxane-supported amines that possess a Si−O bond in the main backbone and an amino functional group in the Si−C linking side arm, are among the most important and environmentally benign organosilicon materials in use today, in which most of the applications of the polysiloxanes in the textile industry were derived from the extraordinary flexibility and superhydrophobility of the siloxane backbone.[8] To the best of our knowledge, very few examples are known where the polysiloxane-supported amines were used as a macromolecular ligand or functional polymer in catalysis, even as an environmentally benign supporter in organocatalysts.[9] In a recent study by our group, we disclosed the effect of amine-functional polysiloxanes on the copper-catalyzed Buchwald–Hartwig C−N cross-coupling reaction of aryl iodides with amides for the generation of N-arylated products, which evidenced their utility as a potent macromolecular or polymer ligand with promising activities (see the Supporting Information).[10] Also in the past, despite the potential role played by Cu^{I} in the Huisgen reaction, the use of nitrogen-based ligands was shown to enhance the reaction rate and restrict the inherent thermodynamic stability of active Cu^{I} catalytic species from unavoidable oxidation under aerobic conditions.[11] Furthermore, the polysiloxanes have been described as a protecting medium that allows the manipulation and storage of air- and moisture-sensitive N-heterocyclic carbenes,[12] we thus wondered if such amine-functional polysiloxanes would work as a soluble macromolecular or polymer ligand to generate stable Cu^{I} species and give rise to oxidative dimerization. Herein, we report the finding that the synthesis of triazoles and bistriazoles controlled by polysiloxane-supported amines (Scheme 2), in which the secondary amine-functional polysiloxane is indeed an effective ligand in the Cu^{I}-catalyzed oxidative dimerization of triazoles and secondary–primary diamine-containing polysiloxane led to a facile Huisgen [3+2] cycloaddition of azides and alkynes.

Results and Discussion

Initially, we investigated the reaction of benzyl azide with phenylacetylene in the presence of various copper salts (Scheme 3, 5 mol %) and commercially available amine-functional polysiloxane (10 mol % referred to the amine moiety). In these screenings, a mixture of benzyl azide and phenylacetylene (1:1) in CH_2Cl_2 was stirred at room temperature overnight. The resulting reaction mixture was then analyzed by GC-MS. As revealed in Table 1, secondary–primary diamine-functional polysiloxane (**1a**; AFP-NH_2) did not promote the oxidative Huisgen coupling but led to the formation of 1,2,3-triazoles in excellent yields (>99 %; Table 1, entries 4 and 5), and interestingly, when CuCl was used as catalytic source, the secondary amine-functional polysiloxane (**1b**; AFP-NH) afforded the bistriazole as major product in promising yield (58 %) and moderate selectivity (1.5:1) under similar conditions (Table 1, entry 11). Furthermore, experiments performed on various secondary amines and primary amines did not yield any expected bistriazoles (Table 1, entries 8–10 and 16–19), highlighting the key role



Scheme 3. Effect of the amine ligands on the copper-catalyzed Huisgen [3+2] cycloaddition.

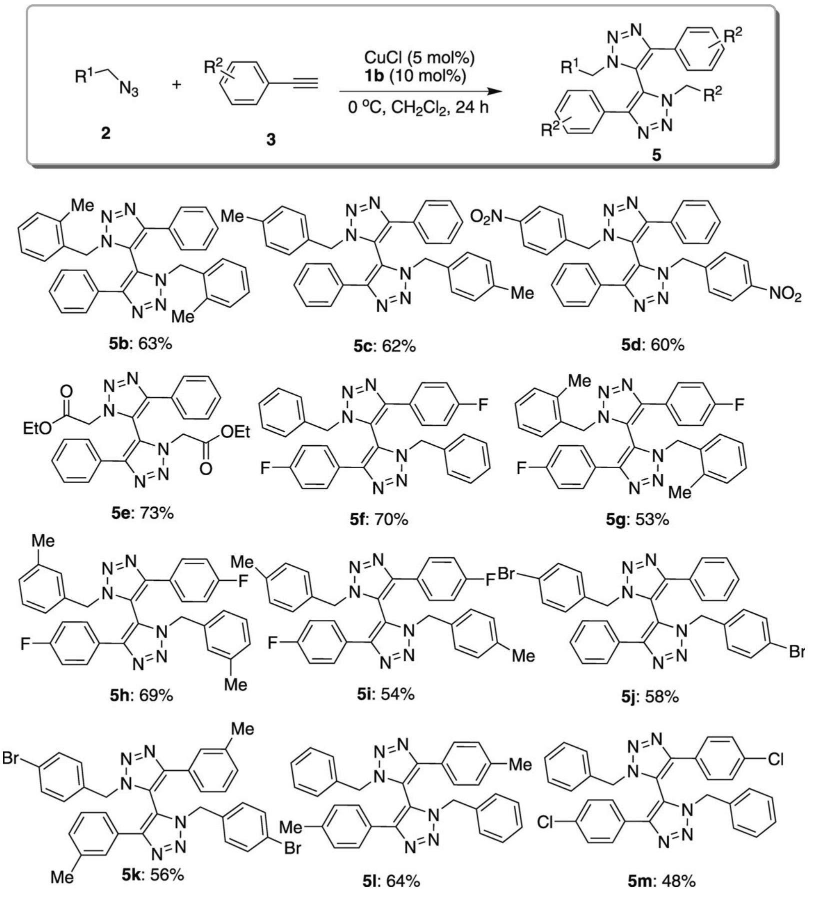
Table 1. Screening of catalysts for the copper-catalyzed Huisgen cycloaddition of phenylacetylene and benzyl azide.

Entry	Cu catalyst	Ligand	T [°C]	Products[a]	
				4a	**5a**
1	$CuSO_4{\cdot}5H_2O$	**1a**	20	–	–
2	$Cu(OAc)_2{\cdot}2H_2O$	**1a**	20	–	–
3	$Cu(OTf)_2$	**1a**	20	–	–
4	CuI	**1a**	20	>99	–
5	CuBr	**1a**	20	>99	–
6	CuCl	**1a**	20	>99 (93)[b]	–
7	CuI	**1b**	20	93	7
8	CuI	**1c**	20	80	–
9	CuI	**1d**	20	90	–
10	CuI	**1e**	20	70	–
11	CuCl	**1b**	20	39	58
12	CuCl	**1b**	0	13	85 (80)[b]
13	CuCl	–	0	36	–
14	CuCl	**1b**	−10	22	78 (75)[b]
15	CuBr	**1b**	0	44	51
16	CuCl	**1f**	0	>99	–
17	CuCl	**1g**	0	>99	–
18	CuCl	**1h**	0	18	–
19	CuCl	**1d**	0	21	–

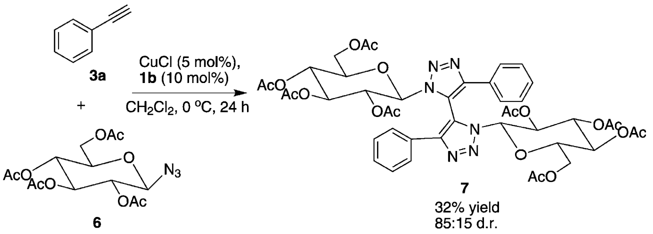
[a] Reagents and reaction conditions: phenylacetylene (1 mmol), benzyl azide (1 mmol), copper salt (0.05 mmol, 5 mol %), nitrogen ligand (10 mol % refer to one nitrogen atom), solvent (4 mL). Yields determined by gas chromatography and GC-MS. [b] The yield of the isolated product is given within the parentheses.

of the secondary amine-functionalized polysiloxane **1b** in this oxidative Huisgen reaction. It is interesting that ligands **1c** and **1d**, being also secondary amines, only resulted in the triazole in good yields (Table 1, entries 8 and 9) but no bistriazole was detected. Thus, these data show that the catalytic activity of Cu^I is significantly modified and enhanced by the amine-functional polysiloxanes with a sensitive function and effect of the ligand in this oxidative Huisgen reaction. The effect of temperature on the oxidative coupling reaction was also studied, and good to high yields (78–85 % yield) as well as good selectivities (up to ≈7:1) were obtained at lower temperature (0 or −10 °C, Table 1, entries 12, 14) and even CuBr could led to moderate yield at 0 °C (51 % yield). After selection of the most efficient hydrophobic macromolecular ligand and copper catalyst, we screened different solvents to adjust the reaction conditions (Table S1, see the Supporting Information). Among the solvents examined, dichloromethane was still proven to be the best solvent. From these experiments, it can be clearly concluded that the amine-functional polysiloxanes are very efficient macromolecular ligands in the classic or oxidative Huisgen reaction, in which the secondary–primary diamine-functional polysiloxane **1a** lead to the formation of the triazole and the secondary amine-functional polysiloxane **1b** resulted in the bistriazole.

By using the secondary amine-functional polysiloxane **1b** as ligand and the conditions noted in Table 1 (entry 12), the oxidative Huisgen coupling reaction of various azides and alkynes were carried out at 0 °C in good yields and selectivities (Scheme 4). Simple functionalized aromatic alkynes reacted with benzyl azides and ethyl 2-azidoacetate very efficiently, giving the expected bistriazoles as major products in good yields. To the best of our knowledge, this protocol exhibited the best selectivity and conversion in comparison to previous reports.[7] For example, the best yield of compound **5a** reached 49 % when lower temperature (−35 °C) and high NaOH concentrations were used,[7b] whereas the Cu^I–polysiloxane-supported secondary amine catalyst system gave better conversion and selectivity (80 %). With substituted benzyl azides, no significant difference was observed with ar-



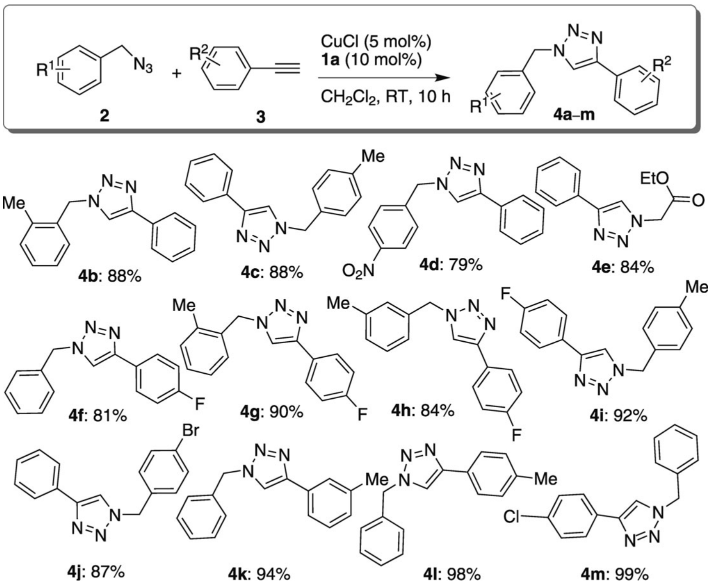
Scheme 4. AFP **1b** promoted copper-catalyzed oxidative Huisgen coupling reaction of various azides and alkynes to bistriazoles.



Scheme 5. Synthesis of the sugar-based bistriazole **7**.

omatic alkynes functionalized with methyl or halide groups. With ethyl 2-azidoacetate, the oxidative Huisgen coupling reaction gave the expected bistriazole **5e** in good yield (73 %). The reaction shown in Scheme 5 is interesting, because it highlights the fact that the core of the sugar-based bistriazole **7** is chiral and the diastereoselectivity is high (85:15).

We have realized our best results by using the secondary–primary diamine-functional polysiloxane **1a** with CuX (X = Cl, Br, I) in the click Huisgen reaction of benzyl azide with phenylacetylene (Table 1). For compassion, to explore the scope of the CuCl/**1a** catalytic system in this reaction, similar alkynes bearing aromatic rings were submitted to various azides under the optimized reaction conditions. As shown in Scheme 6, a broad range of substrates were led to high levels of selective synthesis of triazoles in excellent yields (79–99 %). The production of general triazoles in the presence of the Cu^I–polysiloxane-supported diamine system is expected to be of most interest for the comparable study of the divergent mechanistic procedure induced by the polysiolxane-supported secondary amine. Therefore the kinetic significance of alkyne deprotonation was further investigated by using kinetic isotope exchange (KIE) experiments (Figure 1) with deuterium. The kinetic significant of alkyne (for example, phenylacetylene (**3a**)) deprotonation revealed that a primary deuterium KIE (K_H/K_D) of 2.8 was observed in the oxidative Huisgen coupling reaction shown in Figure 1. This result suggested that deprotonation of the alkyne component is the rate-determining step.



Scheme 6. AFP **1a** promoted copper-catalyzed Huisgen reaction of various azides and alkynes to triazoles.

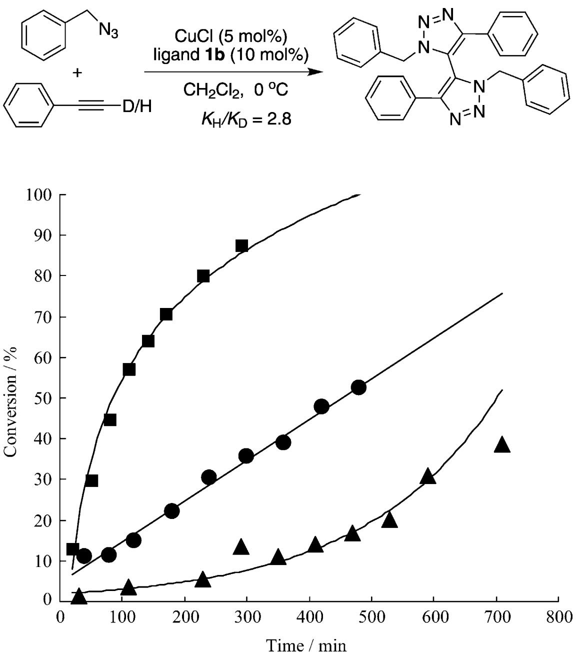
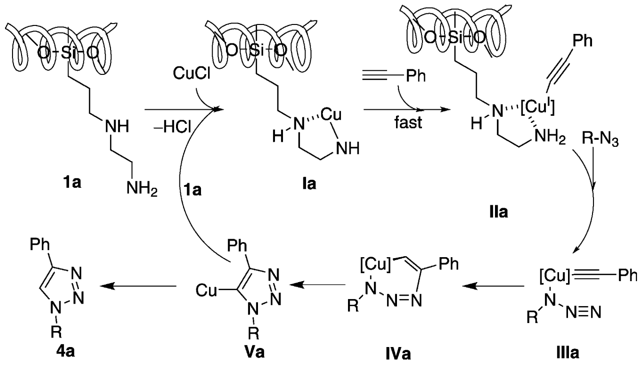


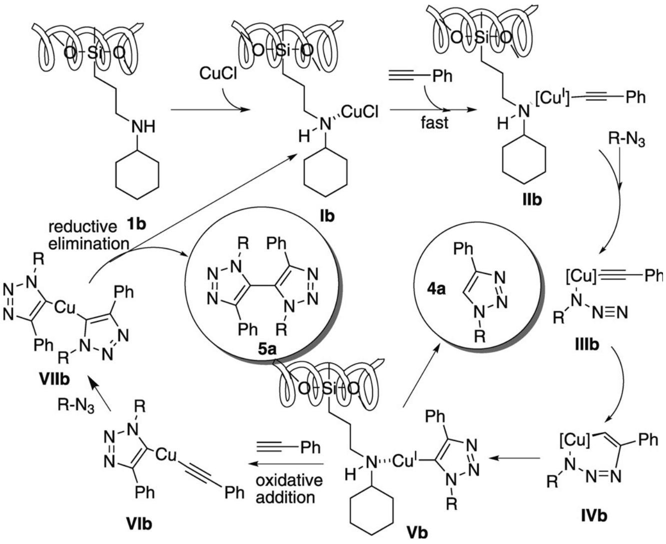
Figure 1. Time courses of triazole or bistriazole product formation as determined by GC-MS. ■ = Classic copper-catalyzed Huisgen cycloaddition of azide **2a** and alkyne **3a** to triazole **4a** promoted by the primary amine **1a**. ● = Copper-catalyzed oxidative Huisgen cycloaddition of azide **2a** and alkyne **3a** to bistriazole **5a** promoted by the secondary amine **1b**. ▲ = Copper-catalyzed oxidative Huisgen cycloaddition of azide **2a** and [D]phenylacetylened to bistriazole **5a** promoted by the secondary amine **1b**.

Perhaps the most intriguing outcome was that the copper-catalyzed Huisgen reaction of azides and alkynes to divergent products did depend on the amine-functional polysiloxanes. The main chain of the two polymeric ligands **1a** and **1b** was the same but the side chain was functionalized differently by a secondary amine or a secondary–primary diimine, respectively, which led to a divergent Huisgen [3+2] cycloaddition and oxidative Huisgen coupling reaction. In the CuCl-catalyzed click reactions of azides and alkynes in all cases the oxidative Huisgen coupling occurred with good yields and selectivities when **1b** was used as a ligand but almost complete conversion of the Huisgen reaction to triazoles was observed when **1a** was used. In the past years, the mechanistic investigations have revealed that the active Cu^I catalytic species are formed from Cu^I or Cu^{II} salts in the presence of ligands,[13] and the click addition presumably involved the formation of binuclear Cu^I complexes in the rate-determining step.[14] Two copper centers that are involved in the Huisgen cycloaddition resulted in accelerated cycloaddition, especially in the pre-equilibrium step prior to the formation of the in-cycle copper(I)–

acetylide. Direct evidence for the existence of the mononuclear or binuclear Cu^I–triazole complex or intermediate was also provided by Straub et al. in 2007.[15] Consistent with prior experimental and mechanistic results by other groups,[13–15] the origin of this difference in the chemoselectivity between the two ligands can be rationalizes as follows (Schemes 7 and 8).



Scheme 7. Proposed mechanistic steps in the polysiloxane-supported copper-catalyzed Huisgen reaction of azides and alkynes promoted by diamine **1a**.



Scheme 8. Proposed mechanistic steps in the polysiloxane-supported copper-catalyzed oxidative Huisgen coupling reaction of azides and alkynes promoted by the secondary amine **1b**.

For the copper-mediated click addition assisted by the diamine-functional polysiloxane **1a**, we believed that the existence of diamine–Cu^I complexes with multi-coordination led to well-accepted mechanistic significance of copper(I)–acetylide, and the diamine accelerated the transmetalation of intermediate **Va** (Scheme 7). In the case of the secondary amine-functional polysiloxane **1b**, we assumed that a stable mononuclear Cu^I complex with linear two-coordination was formed directly from CuCl involving the single nitrogen ligand **1b** and then induced the copper(I)–acetylide formation by slow deprotonation of the alkyne prior to the interaction between the azide and the copper(I)–acetylide. Consequently, the following [3+2] cycloaddition was observed as another kinetically significant steps to the desired triazole,[16] and a copper triazolide complex would be stabilized and dispersed by the secondary amine-functional polysiloxane **1b** by two-coordination to yield a mononuclear polysiloxane@-copper complex **Vb** that could led to the formation of a bistriazole–copper complex **VIIb** through transmetalation and oxidative addition. Then the intermediate **VIIb** subsequently gives the bistriazole through reductive elimination and regenerates the active copper catalyst (Scheme 8). As also shown in Figure 1, in comparison to the Huisgen [3+2] cycloaddition, the domino oxidative Huisgen coupling process occurred slowly and the reaction involving [D]phenylacetylene sustained a longer induction period, indicating that the rate-determining step of the oxidative coupling to generate the triazole–Cu^I–acetylide intermediate **VIb** and the bistriazole–Cu^I intermediate **VIIb** through deprotonation of the terminal alkyne and oxidative addition, respectively.

Conclusion

In summary, we have demonstrated an interesting example of a divergent catalysis[17] with a copper(I) catalyst controlled by amine-functional macromolecular polysiloxanes. We successfully demonstrated the remarkable ability of the secondary amine-functional polysiloxane **1b** to induce oxidative coupling in the copper-mediated Huisgen reactions of general azides and alkynes by achieving good yields and selectivities. The reactions described here allow the preparation of novel heterocyclic compounds, that is, bistriazoles. Comparably, it is also surprising that the use of the diamine-functional polysiloxane **1a** as ligand led to a classic Huisgen [3+2] cycloaddition in excellent yields. From the results of the present amine-functional polysiloxanes-controlled Huisgen reaction or oxidative Huisgen coupling reaction to divergent products and the proposed mechanism, we suggested that the mononuclear bistriazole–copper complex, stabilized and dispersed by the secondary amine-functional polysiloxane, was beneficial to prevalent the way to oxidative coupling. This contrasts with the diamine-functional polysiloxane for which proposed binuclear Cu^I complexes exist predominantly. Although the mechanism is unclear at present, we believed that it should be possible to open up a simple and flexible entry to the synthesis of pharmaceutical useful triazole or bistriazole products with environmentally benign polysiloxane-based amine ligands and provide a foundation for the enantioselective oxidative coupling of triazoles with chiral amine-functional polysiloxanes. Further investigations are ongoing to clarify the true mechanism of the oxidative Huisgen coupling and the effect of the polysiloxane and the amine moiety on the oxidative coupling reaction.

Acknowledgements

This Project was supported by the National Natural Science Founder of China (No. 20973051 and 21173064), the Zhejiang Provincial Natural Science Foundation of China (Q12B020037), the Qianjiang talent project of Zhejiang Province of China (No. 2010R0017), and the Program for Excellent Young Teachers in Hangzhou Normal University (HNUEYT, JTAS 2011-01-014) is appreciated. X.L.W thanks Dr. Li Li (Hangzhou Normal University) for her helpful suggestions.

---

[1] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.

[2] R. Huisgen, *Pure Appl. Chem.* **1989**, *61*, 613–628.

[3] Recent examples of other click reactions except the Huisgen [3+2] cycloaddition: a) G. de Almeida, E. M. Sletten, H. Nakamura, K. K. Palaniappan, C. R. Bertozzi, *Angew. Chem.* **2012**, *124*, 2493–2497; *Angew. Chem. Int. Ed.* **2012**, *51*, 2443–2447; b) J. N. Brantley, K. M. Wiggins, C. W. Bielawski, *Science* **2011**, *333*, 1606–1609; c) C. E. Hoyle, C. N. Bowman, *Angew. Chem.* **2010**, *122*, 1584–1617; *Angew. Chem. Int. Ed.* **2010**, *49*, 1540–1573; d) R. Hoogenboom, *Angew. Chem.* **2010**, *122*, 3489–3491; *Angew. Chem. Int. Ed.* **2010**, *49*, 3415–3417; e) R. M. Hensarling, V. A. Doughty, J. W. Chan, D. L. Patton, *J. Am. Chem. Soc.* **2009**, *131*, 14673–14674; f) C. R. Becer, R. Hoogenboom, U. S. Schubert, *Angew. Chem.* **2009**, *121*, 4998–5006; *Angew. Chem. Int. Ed.* **2009**, *48*, 4900–4908.

[4] Recent examples: a) J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007**, *36*, 1249–1262; b) M. G. Finn, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1231–1232; c) V. Ganesh, V. S. Sudhir, T. Kundu, S. Chandrasekaran, *Chem. Asian J.* **2011**, *6*, 2670–2694; d) B. Dervaux, F. E. Du Prez, *Chem. Sci.* **2012**, *3*, 959–966; e) S. S. van Berkel, S. Brauch, L. Gabriel, M. Henze, S. Stark, D. Vasilev, L. A. Wessjohann, M. Abbas, B. Westermann, *Angew. Chem.* **2012**, *124*, 5437–5441; *Angew. Chem. Int. Ed.* **2012**, *51*, 5343–5346.

[5] Selected examples: a) H. C. Kolb, K. B. Sharpless, *Drug Discovery Today* **2003**, *8*, 1128–1137; b) J. F. Lutz, *Angew. Chem.* **2007**, *119*, 1036–1043; *Angew. Chem. Int. Ed.* **2007**, *46*, 1018–1025; c) S. I. van Kasteren, H. B. Kramer, D. P. Gamblin, B. G. Davis, *Nat. Protoc.* **2007**, *2*, 3185–3194; d) D. S. Pedersen, A. Abell, *Eur. J. Org. Chem.* **2011**, 2399–2411; e) Y. Li, C. Z. Cai, *Chem. Asian J.* **2011**, *6*, 2592–2605; f) X. P. Deng, C. Friedmann, J. Lahann, *Angew. Chem.* **2011**, *123*, 6652–6656; *Angew. Chem. Int. Ed.* **2011**, *50*, 6522–6526; g) A. R. Davis, J. A. Maegerlein, K. R. Carter, *J. Am. Chem. Soc.* **2011**, *133*, 20546–20551; h) L. S. Campbell-Verduyn, L. Mirfeizi, A. K. Schioonen, R. A. Dierckx, P. H. Elsinga, B. L. Feringa, *Angew. Chem.* **2011**, *123*, 11313–11316; *Angew. Chem. Int. Ed.* **2011**, *50*, 11117–11120.

[6] a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708–2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599; b) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064; c) M. Meldal, C. W. Tornoe, *Chem. Rev.* **2008**, *108*, 2952–3015.

[7] a) Y. Angell, K. Burgess, *Angew. Chem.* **2007**, *119*, 3723–3725; *Angew. Chem. Int. Ed.* **2007**, *46*, 3649–3651; b) J. González, V. M. Pérez, D. O. Jiménez, G. Lopez-Valdez, D. Corona, E. Cuevas-Yañez, *Tetrahedron Lett.* **2011**, *52*, 3514–3517; c) M. Kwon, Y. Jang, S. Yoon, D. Yang, H. B. Jeon, *Tetrahedron Lett.* **2012**, *53*, 1606–1609.

[8] a) S. C. Ni, P. L. Kuo, *J. Polym. Sci. Part B* **2002**, *40*, 1795–1803; b) Y. Kaneko, N. Iyi, T. Matsumoto, K. Fujii, K. Kurashima, T. Fujita, *J. Mater. Chem.* **2003**, *13*, 2058–2060; c) M. M. Colilla, M. Darder, P. Aranda, E. Ruiz-Hitzky, *J. Mater. Chem.* **2005**, *15*, 3844–3851; d) M. Colilla, A. J. Salinas, M. Vallet-Regi, *Chem. Mater.* **2006**, *18*, 5676–5683.

[9] a) M. S. DeClue, J. S. Siegel, *Org. Biomol. Chem.* **2004**, *2*, 2287–2298; b) M. A. Grunlan, K. R. Regan, D. E. Bergbreiter, *Chem. Commun.* **2006**, 1715–1717; c) L. W. Xu, Y. D. Ju, L. Li, H. Y. Qiu, J. X. Jiang, G. Q. Lai, *Tetrahedron Lett.* **2008**, *49*, 7037–7041; d) Z. J. Zheng, L. X. Liu, G. Gao, H. Dong, J. X. Jiang, G. Q. Lai, L. W. Xu, *RSC Advances* **2012**, *2*, 2895–2901.

[10] Unpublished results (Scheme S1 in the Supporting Information), about the experiment process of the CuI-catalyzed Buchwald–Hartwig C–N cross-coupling reaction in the presence of amine-functional polysiloxanes; please see the Supporting Information. The amine-functional polysiloxanes were also effective polymeric organocatalysts in several organic transformations.

[11] a) T. R. Chan, R. Hilgraf, K. B. Sharpless, *Org. Lett.* **2004**, *6*, 2853–2855; b) V. O. Rodionov, S. I. Presolski, S. Gardinier, Y. H. Lim, M. G. Finn, *J. Am. Chem. Soc.* **2007**, *129*, 12696–12704; c) S. Ozcubukcu, E. Ozkal, C. Jimeno, M. A. Perocas, *Org. Lett.* **2009**, *11*, 4680–4683; d) P. Fabbrizzi, S. Cicchi, A. Brandi, E. Sperotto, G. Van Koten, *Eur. J. Org. Chem.* **2009**, 5423–5430; e) M. L. Teyssot, L. Nauton, J. L. Canet, F. Cisnetti, A. Chevry, A. Gautier, *Eur. J. Org. Chem.* **2010**, 3507–3515; f) S. I. Presolski, V. Hong, S. H. Cho, M. G. Finn, *J. Am. Chem. Soc.* **2010**, *132*, 14570–14576; g) H. A. Michaels, L. Zhu, *Chem. Asian J.* **2011**, *6*, 2825–2834.

[12] F. Bonnette, T. Kato, M. Destarac, G. Mignani, F. P. Coosío, A. Baceiredo, *Angew. Chem.* **2007**, *119*, 8786–8789; *Angew. Chem. Int. Ed.* **2007**, *46*, 8632–8635.

[13] V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51–68.

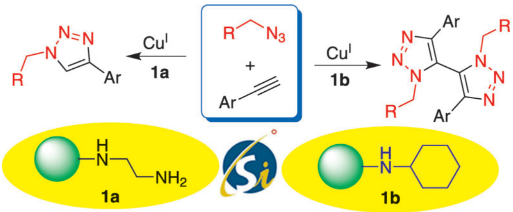
[14] a) F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless, V. V. Fokin, *J. Am. Chem. Soc.* **2005**, *127*, 210–216; b) V. O. Rodionov, V. V. V. Fokin, M. G. Finn, *Angew. Chem.* **2005**, *117*, 2250–2255; *Angew. Chem. Int. Ed.* **2005**, *44*, 2210–2215; c) B. R. Buckley, S. E. Sandra, H. Heaney, *Chem. Eur. J.* **2010**, *16*, 6278–6284.

[15] C. Nolte, P. Mayer, B. F. Straub, *Angew. Chem.* **2007**, *119*, 2147–2149; *Angew. Chem. Int. Ed.* **2007**, *46*, 2101–2103.

[16] a) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302–1315; b) G. C. Kuang, P. M. Guha, W. S. Brotherton, J. T. Simmons, L. A. Stankee, B. T. Nguyen, R. J. Clark, L. Zhu, *J. Am. Chem. Soc.* **2011**, *133*, 13984–14001.

[17] L. W. Xu, L. Li, G. Q. Lai, *Mini-Rev. Org. Chem.* **2007**, *4*, 217–230.

Received: July 11, 2012



Click, click, hurray: The remarkable ability of the secondary amine-functional polysiloxane **1b** to induce oxidative coupling in the copper-mediated Huisgen reaction of general azides and alkynes, thereby achieving good yields and selectivities, is successfully demonstrated, whereas the use of the diamine-functional polysiloxane **1a** led to the classic Huisgen [3+2] cycloaddition in excellent yields (see scheme).

Click Chemistry

*Z.-J. Zheng, F. Ye, L.-S. Zheng, K.-F. Yang, G.-Q. Lai, L.-W. Xu** .... ■■■■–■■■■

Copper-Catalyzed Huisgen and Oxidative Huisgen Coupling Reactions Controlled by Polysiloxane-Supported Amines (AFPs) for the Divergent Synthesis of Triazoles and Bistriazoles