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Copper(I) Complexes of Normal and Abnormal Carbenes and Their Use as Catalysts for the Huisgen [3+2] Cycloaddition between Azides and Alkynes

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Complexes of general formula [(NHC)Cu(μ-I)$_2$Cu(NHC)] (NHC = 1-benzyl-3-butylbenzimidazolin-2-ylidene for **7**; NHC = 1-benzyl-3-isopropylbenzimidazolin-2-ylidene for **8** NHC = 1-butyl-3-isopropylbenzimidazolin-2-ylidene for **9**) and [(*a*NHC)CuI] {*a*NHC = 1-benzyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium-5-ylidene for **10**; 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1*H*-1,2,3-triazol-3-ium-5-ylidene for **11**} were synthesized from CuI and the corresponding azolium salts. All complexes were fully characterized by spectroscopic methods, and single-crystal X-ray structural analyses were performed for **7** and **11**. Complex **7** exhibits an iodido-bridged dicopper(I) form in the solid state. The copper centers in **7** adopt a trigonal coordination. The intramolecular Cu–Cu distance is 2.896(2) Å. In contrast to **7**, **11** is mononuclear, and the copper center has a linear coordination. All the complexes were tested for their efficiency as catalysts in the [3+2] cycloaddition reaction between azides and alkynes. The benzimidazolin-2-ylidene-containing complexes **7**–**9** as well as the triazol-3-ium-5-ylidene-containing complexes **10**–**11** turned out to be highly efficient catalysts for the 1,3-cycloaddition reaction, both under neat conditions and in water. Short reaction times as well as low catalyst loadings could be achieved, and all the manipulations were carried out under proper "click" conditions with simple product isolation and no purification steps. The efficiency of the catalysts seems to correlate well with the σ-donor ability of the NHCs. Cycloaddition reaction with an internal alkyne was also achieved with these catalysts. Finally a bulky azide was used as a substrate to prepare compound 1-(2,6-dimesityl)phenyl-4-(2-pyridyl)-1,2,3-triazole (**14**) with the above mentioned copper catalysts. Such bulky azides are usually unreactive towards cycloaddition reactions with alkynes in the presence of the Cu^{II}/ascorbate/tbta catalytic system.

Introduction

The Huisgen [3+2] cycloaddition between azides and alkynes,[1,2] which was re-tooled as the copper catalyzed "click reaction",[3,4] has turned out to be one of the most efficient and widely used catalytic reactions for the chemical community. This reaction has found use in medicinal chemistry,[5] biology,[6] material science,[7] anion binding,[8–10] and sensing studies[11] as well as in building ligands for coordination and organometallic chemistry.[12–24] After the initial discovery of the use of tris[(1-benzyl-1*H*-1,2,3-triazole-4-yl)methyl]amine (tbta) as an additional component of the catalytic mixture, which leads to acceleration of reactions and improvement of yields,[25] efforts have been made to use other such ligands for improving this method.[26–29] In this regard, the use of copper(I) complexes of N-heterocyclic carbene (NHC) ligands as catalysts for the click reaction as pioneered by Nolan and Diéz-Gonzaléz[30–33] has turned out to be highly efficient, subsequent work by other groups stressing the use of additional donor ligands for catalytic improvement.[34] NHCs and complexes thereof have become valuable reagents for a wide variety of chemical transformations[35–43] with the relatively recent discovery of their redox-active character[44–47] as well as of abnormal carbenes[48–51] and/or mesoionic compounds (*a*NHC),[52,53] which add to the continuous development of this field. We have been interested in the use of the click method for developing 1,2,3-triazole-based ligands and their metal complexes and investigating their structural and electronic properties.[54] In view of this, we looked for efficient ways of performing the click reaction and possibly finding catalyst systems that might perform catalytic transformations that are not possible with the now popular Cu^{II}/ascorbate/tbta system. In view of the importance of strong σ-donor ligands on Cu^{I} for the improved efficiency of the click reaction,[28,32,34] we chose benzimidazole-based NHCs with alkyl substituents on the nitrogen atoms as well as 1,2,3-triazole-based *a*NHCs. Both of these should be better σ-donors as compared to aromatic substituted imidazole-based NHCs. In addition, we used CuI salts as precursors, because of the more labile nature of the Cu–I bond as compared to the Cu–Br or the Cu–Cl bonds. Activation of this bond is one of the crucial steps in the click catalytic cycle. While we were carrying out these studies, a report on the

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use of Cu^{I} complexes of 1,2,3-triazole-based *a*NHCs as catalysts for the "click" reaction appeared in the literature.[55] In the following, we have used the salts 1-benzyl-3-butylbenzimidazolium iodide (**1**),[56,57] 1-benzyl-3-isopropylbenzimidazolium bromide (**2**),[57,58] 1-butyl-3-isopropylbenzimidazolium bromide (**3**),[56,57] 1-benzyl-3-methyl-4-phenyl-1,2,3-triazolium iodide (**4**),[48] and 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazolium iodide (**6**) as carbene precursors. The Cu^{I} complexes bis(μ-iodido)bis(1-benzyl-3-butylbenzimidazolin-2-ylidene)dicopper(I) (**7**), bis(μ-iodido)bis(1-benzyl-3-isopropyl-benzimidazolin-2-ylidene)dicopper(I) (**8**), bis(μ-iodido)bis(1-butyl-3-isopropylbenzimidazolin-2-ylidene)dicopper(I) (**9**), (iodido)(1-benzyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium-5-ylidene)copper(I) (**10**), and (iodido){3-methyl-1-[2-(methylthio)phenyl-4-phenyl-1*H*-1,2,3-triazol-3-ium-5-ylidene}copper(I) (**11**) were synthesized from CuI and the corresponding carbene precursor. All compounds were characterized by NMR spectroscopy and elemental analyses. X-ray crystal structures of **1**, **3**, **6**, **7**, and **11** are also presented. All the Cu^{I} complexes were tested for their catalytic efficiency in the [3+2] dipolar cycloaddition reactions between azides and alkynes with special emphasis on short reaction times and low catalyst loading under strict click conditions. In order to test the effectiveness of the catalysts, internal alkynes as well as extremely bulky azides were used as substrates.

Results and Discussion

Syntheses of Azolium Salts and X-ray Crystal Structures of 1, 3, and 6

Benzimidazolium salts **1**, **2** and **3** (known)[56–58] were prepared in a one-pot reaction of benzimidazole with the stepwise addition of two different alkyl halides in the presence of a base by reported procedures.[58,59] The products obtained by this route can be purified by simple extraction and recrystallization procedures.

The 1,2,3-triazoles were prepared by starting from the synthesis of the corresponding azides by standard procedures. The azides were then converted into the 1,2,3-triazoles by using the $CuSO_4$/ascorbate/TBTA mixture under click conditions (Scheme 1). These triazoles were then converted into triazolium salts **4** (known)[48] and **6** by using methyl iodide as an alkylating agent (Scheme 1). Product identity and purity was established with ^{1}H and ^{13}C NMR spectroscopy, elemental analyses, and mass spectrometry.

Salt **1** was crystallized from a hot 2-propanol solution by slow cooling, **3** could be crystallized from a mixture of dichloromethane/ethyl acetate/petroleum ether (1:10:1) at –20 °C, and **6** was crystallized by layering a dichloromethane solution of it with diethyl ether at 8 °C. Salt **1** (Figure 1) crystallizes in the orthorhombic, $Pna2_1$ space group, **3** (Figure 2) in the trigonal *R*3 space group, and **6** (Figure 3) in the monoclinic $P2_1/c$ space group. Crystallographic details are given in Table 6, and important bond lengths are depicted in Tables 1 and 2. The structural parameters are in the expected range,[58] similar to known examples of related compounds, and hence they do not warrant further comment. The *n*-butyl group in **3** is disordered.

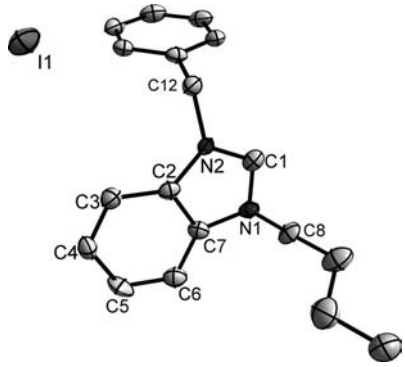


Figure 1. ORTEP plot of **1**. Ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity.

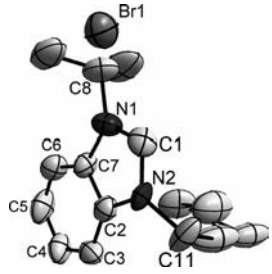


Figure 2. ORTEP plot of **3**. Ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity.

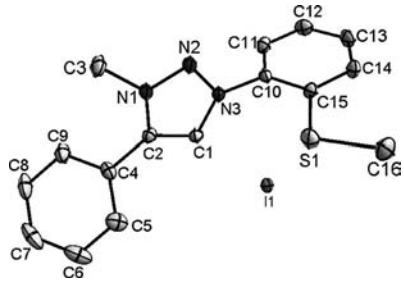
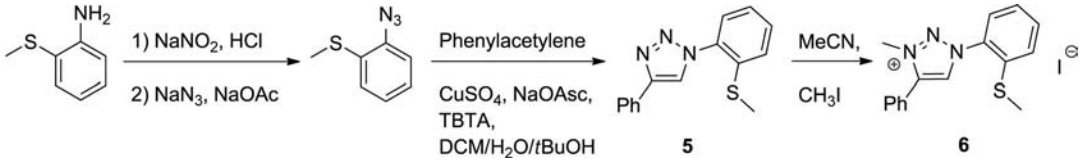


Figure 3. ORTEP plot of **6**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.



Scheme 1. Synthesis of **6**.

Table 1. Selected bond lengths in Å.

	1	3	7
C1–N1	1.344(7)	1.35(2)	1.362(7)
C1–N2	1.324(7)	1.32(1)	1.343(8)
C7–N1	1.388(6)	1.39(1)	1.378(8)
C2–N2	1.373(6)	1.37(1)	1.404(8)
C2–C3	1.395(7)	1.39(2)	1.377(10)
C3–C4	1.369(8)	1.33(2)	1.397(12)
C4–C5	1.411(9)	1.43(2)	1.396(14)
C5–C6	1.389(8)	1.31(2)	1.379(12)
C6–C7	1.396(7)	1.38(2)	1.398(8)
Cu–I	–	–	2.565(1)
Cu–C1	–	–	1.927(6)

Table 2. Selected bond lengths in Å.

	6	11
N1–N2	1.319(3)	1.32(2)
N2–N3	1.323(2)	1.34(1)
N3–C1	1.354(3)	1.35(1)
C1–C2	1.367(3)	1.39(2)
C2–N1	1.362(2)	1.33(2)
N1–C3	1.463(3)	–
N1–C15	–	1.48(2)
Cu–C1	–	1.89(1)
Cu–I	–	2.236(2)

Synthesis of Copper Complexes and Crystal Structures of 7 and 11

Copper complexes **7**–**11** were all prepared by a general route starting from CuI and the azolium salts with a base used for deprotonation (Scheme 2). This route provided the desired copper complexes in high yield and purity after a simple recrystallization step (see Experimental Section). In the complexes **7**–**9** the carbenes are based on benzimidazolin-2-ylidene, and these are normal NHCs. Complexes **10** and **11** have 1,2,3-triazol-5-ylidene-based carbenes, and these have been designated as "abnormal" carbenes (*a*NHCs)[48] or more recently as mesoionic carbenes,[53] because of the known problem of sketching a localized non-charge separated form of these ligands. The carbene character of most of the ligands in these complexes was established by ^{13}C NMR spectroscopy (Experimental Section and Supporting Information).

Complex **7** could be crystallized by diffusion of diethyl ether into a dichloromethane solution of the compound at 8 °C, and **11** was crystallized by layering a dichloromethane solution of it with *n*-hexane at 8 °C. Complex **7** crystallizes in the monoclinic, *C*2/*c* space group and **11** in the monoclinic $P2_1/c$ space group. Complex **7** turned out to be an iodido-bridged dimer in the solid state (Figure 4). Such an iodido-bridged dimer has been recently observed for related Cu^I complexes with other NHC ligands.[32] The copper centers in **7** are trigonally coordinated through one carbon atom (on each Cu) from the carbene ligands and the two bridging iodide ligands. The bond lengths inside the benzimidazolin-2-ylidene group are in the expected range (Table 2).[58] The Cu–C1 distance of 1.927(6) Å and the Cu–I distance of 2.565(1) Å are as expected. The N2–C1–Cu and N1–C1–Cu angles of 125.5(5) and 128.3(5)° around the C1 center show the sp^2 hybridized nature of this carbon atom. The Cu–I–Cu angle is 68.69(4)°, and the Cu–Cu distance is 2.896(2) Å. In

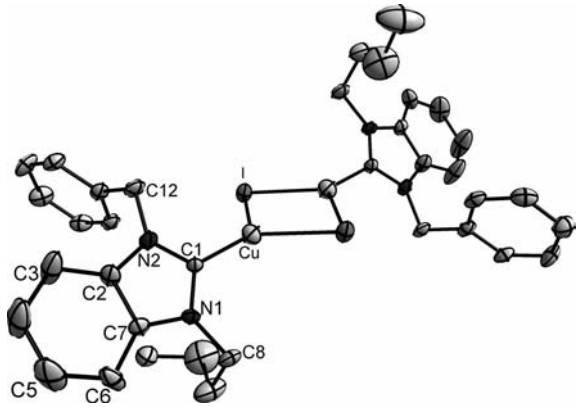
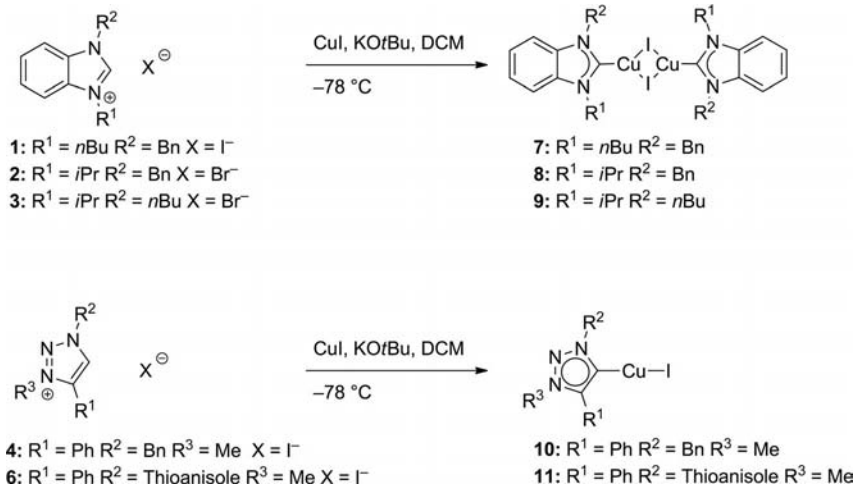


Figure 4. ORTEP plot of **7**. Ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity.



Scheme 2. Synthesis of copper complexes.

contrast to **7**, **11** turned out to be a mononuclear complex in the solid state (Figure 5). The Cu^{I} center is linearly coordinated with a Cu–C1 distance of 1.89(1) Å and a Cu–I distance of 2.236(2) Å. The presence of heavy I atoms in the crystal of **11** causes severe absorption although cylindrical corrections were applied, resulting in large electron residuals around the Cu and I atoms and high *R* values in the final refinement. The dihedral angle between the phenyl ring and the triazol-3-ium-5-ylidene ring is 51(2)°, and that between the thioether-substituted phenyl ring and triazol-3-ium-5-ylidene ring is 69(1)°.

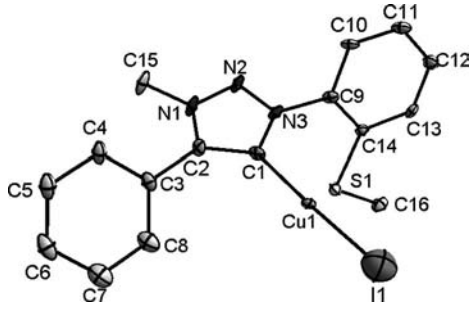
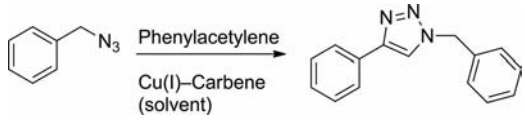


Figure 5. ORTEP plot of **11**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Use of 7–11 as Catalysts for the [3+2] Cycloaddition between Azides and Alkynes

After the recognition of the Cu^{II}/ascorbate mixture as a catalytic system for the [3+2] cycloaddition between azides and alkynes and the definition of this process as a click reaction,[3,4] efforts have been made to find ligands that accelerate this catalytic reaction or make reactions possible, which otherwise do not function without an additional ligand.[26–29] The ligand tbta turned out to be a good candidate during the initial studies, and follow-up work showed the importance of the donating nature of ligands for the efficiency of the catalytic system.[16,25,27] Pioneering work by Nolan and Diéz-Gonzaléz showed the efficiency of NHC ligands, which are excellent σ-donors, for this reaction.[30–33,41] We argued that NHCs containing alkyl substituents on the nitrogen atoms should be good ligands for this reaction, because of the better donor capabilities of the alkyl groups compared to their aryl counterparts. Substituted 1,2,3-triazol-5-ylidenes (*a*NHCs) should also be good ligands for this reaction, because of their excellent donor capabilities.[48]

As a test reaction we chose the 1,3-dipolar cycloaddition reaction between benzyl azide and phenylacetylene (Scheme 3). According to the click laws, no precaution was taken to exclude moisture or oxygen.[3] All the reactions were followed by ^{1}H NMR spectroscopy, by the characteristic singlet of benzyl azide at δ = 4.31 ppm. The resulting triazole has a signal at 5.55 ppm, and the ratio of these two signals can be used to calculate the percentage conversion. After completion of the reactions, the isolated yields were calculated after a simple aqueous workup. Figure 6 shows a representative ^{1}H NMR spectroscopic experiment, the conversion vs. time graphs are shown in Figure 7, and Table 3 summarizes the reactions tested and conditions used.



Scheme 3. General catalytic reaction.

At first a blank test was done with just CuI as a catalyst under neat conditions. A look at Figure 6 shows that the cycloaddition reaction is rather slow with only 50% conversion after 7 hours (entry 1, Table 3). It is also clear from this curve that the CuI-catalyzed reaction has a certain induction

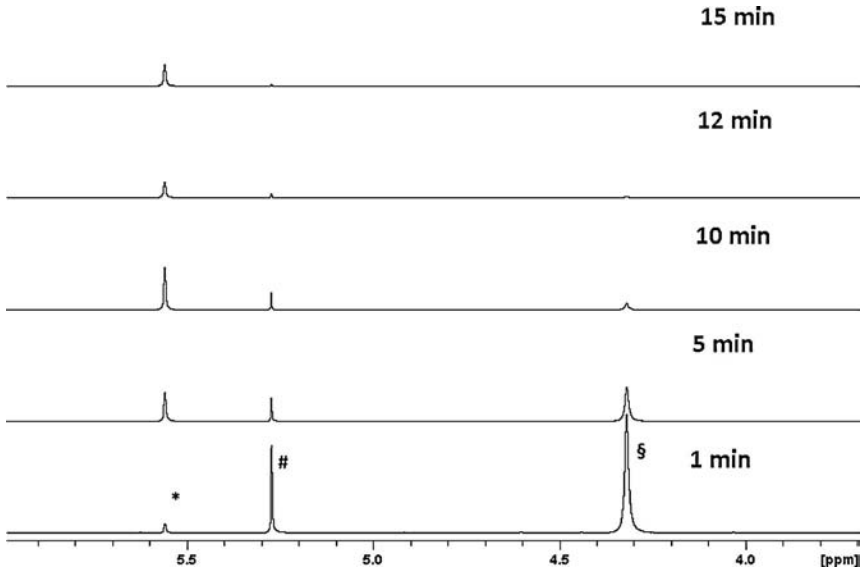


Figure 6. Conversion of benzyl azide and phenylacetylene as followed by ^{1}H NMR spectroscopy with 0.25 mol-% **7** as catalyst; *: signal from benzyl of formed triazole, §: signal from benzyl azide, #: signal from dichloromethane.

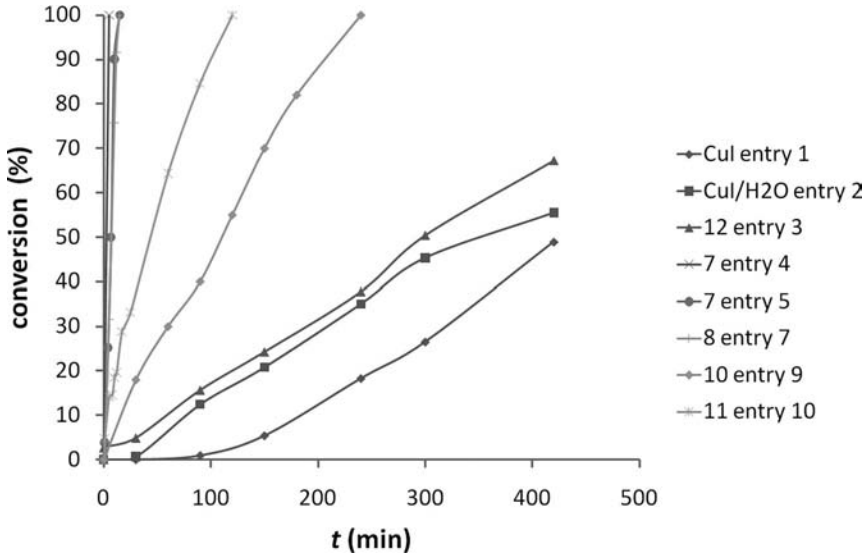


Figure 7. Time vs. conversion curves for the tested catalyst in the reaction between benzyl azide and phenylacetylene.

Table 3. Results of catalytic tests between phenylacetylene and benzyl azide.

Entry	Catalyst	Solvent	Time	Yields[a]
1	CuI[b]	–	7 h	48.5%*; 42%#
2	CuI[b]	H_2O	7 h	55.5%*; 51%#
3	**12**[b]	–	7 h	67%*; 61%#
4	**7**[b]	–	5 min	100%*; 99%#
5	**7**[c]	–	13 min	100*; 99%#
6	**7**[d]	–	3 h	100%*; 99%#
7	**8**[c]	–	13 min	100%*; 99%#
8	**9**[c]	–	10 min	100%*; 98%#
9	**10**[d]	–	4 h	100%*; 98%#
10	**11**[d]	–	2 h	100%*; 98%#
11	**8**[c]	DCM/H_2O/*t*BuOH	25 h	88%*; 86%#
12	CuI/KO*t*Bu/**1**[b]	–	3 min	100%*; 99%#
13	CuI/KO*t*Bu/**1**[b]	DCM/H_2O/*t*BuOH	17 h	94%*; 90%#

[a] *Conversions by NMR spectroscopy; #Isolated yields, determined over at least two runs. [b] Catalyst: 2.5 mol-%. [c] Catalyst: 0.25 mol-%. [d] Catalyst: 0.05 mol-%.

period. This observation led us to speculate that the product formed (in minute amounts) in this reaction might form a complex (**12**, Figure 8) with CuI, which actually catalyzes the reaction. To prove this 2.5 mol-% CuI and 1-(benzyl)-4-(phenyl)-1,2,3-triazole were used as a catalyst mixture, and this reaction showed a conversion of 70% after 7 hours (entry 3, Table 3). This also led to a much reduced induction period, as expected. Addition of water to the CuI catalyst also led to increased reaction rates, as would be expected for a cycloaddition reaction (entry 2, Table 3).

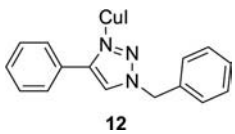


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Figure 8. Probable complex formed during catalysis with CuI.

We then turned to carbene complexes **7**–**11**. Using 2.5 mol-% **7** as a catalyst under neat conditions at room temperature in air led to nearly 100% conversion within 5 min with heat evolution (entry 4, Table 3). Encouraged by these results, we decided to lower the catalyst loading to 0.25 mol-%. In this case, full conversion was achieved within 13 min (entry 5, Table 3). Catalysts **8** and **9** showed results comparable to **7** under identical reaction conditions, and the reaction was fastest with **9** (entries 7 and 8, Table 3). This can be rationalized by the better σ-donor ability of the NHC in **9** as compared to those in **7** or **8**. Remarkably, no decomposition of the catalysts or precipitation of metallic copper was observed during these reactions, showing the robust nature of these systems and the ability of NHCs to stabilize Cu^I centers. We then tried to further lower the catalyst loading to 0.05 mol-% for catalyst **7** and we were able to achieve full conversion in about 3 hours. (Figure S4). The *a*NHC-based complexes **10** and **11** were then tested as catalysts for the same reaction. These "abnormal carbenes"[48] or "mesoionic"[53] compounds are also excellent σ-donors, and hence one would intuitively except their Cu^I complexes to be highly efficient as catalysts for the cycloaddition reactions. With 0.05 mol-% catalyst loading, **10** and **11** also achieved full conversion of the click reaction (entry 9 and 10, Table 3). The reaction time with **7** as a catalyst is between those for **10** and **11**, and this shows the comparable activity of these complexes and hence their high efficiency. Thus, the Cu^I complexes with alkyl-substituted NHCs and *a*NHCs show comparable catalytic activity owing to the excellent σ-donor properties of these ligands (Figure S5).

Since the click reaction is highly exothermic, carrying out such reactions under neat conditions have some obvious disadvantages,[34] despite the high yields and short reaction times. In order to address this problem, we also tested the catalytic activity of **8** (0.25 mol-%) in a dichloromethane/*tert*-BuOH/water (1:2:1) mixture at room temperature: 85% con-

version was achieved under those conditions in 25 hours, demonstrating the efficiency of the catalyst even in those solvent mixtures (entry 11, Table 3). Isolation of the catalyst is sometimes a problem and in any case is an additional reaction step. Hence, in some cases in situ formation of the catalyst is preferred from simple metal salts and ligand precursors. In order to test this, a mixture of **1**/CuI/KO*t*Bu was used under neat conditions at room temperature, and this lead to a full conversion within 3 min (entry 12, Table 3). The same mixture was also used in the dichloromethane/*t*BuOH/water (1:2:1) mixture, and in that case 94% conversion was achieved in 17 hours (entry 13, Table 3), thus showing that the system is efficient even when the catalyst is generated in situ in a solvent mixture.

We were also interested in testing whether the catalysts are capable of undergoing multiple catalytic cycles. In order to check this we first reacted **7** (0.25 mol-%) with 1 mmol each of the substrates to realize the first full conversion within 13 min. Subsequently, the same amounts of the substrates were added to this mixture every 25 min, and this was repeated five times. The changes were followed by ^{1}H NMR spectroscopy. An overview of the results is depicted in Table 4.

Table 4. Conversion after several catalytic cycles with **7**.

Cycle [min]	Yields[a]
1 [15]	100%
2 [15]	83%
3 [15]	68%
4 [15]	60%
5 [15]	50%
5 [60]	90%

[a] Determined by NMR spectroscopy.

As can be seen in Table 4, the activity of the catalyst seems to decrease starting from the second cycle itself. However, this probably does not have to do with real catalyst deactivation, but more with precipitation of the solid products that are insoluble in the reaction mixture. Small amounts of the catalyst probably get embedded on the solid surface, which leads to an apparent catalyst deactivation. On stirring the mixture for a longer time (last entry, Table 4) the activity of the catalyst increases again, and this would support our theory of apparent catalyst deactivation mentioned above.

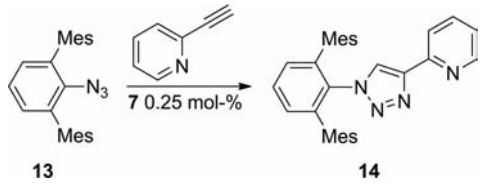
Internal alkynes are considered to be difficult substrates for the click reaction, because the formation of the Cu–acetylide complex, critical for the catalytic cycle, is clearly favored for terminal alkynes. However, it has been recently shown that Cu^{I}-carbene complexes are capable of catalyzing the click reaction even with internal alkynes, and this has been attributed to the superb donating power of the NHC ligands and the flexibility of the (NHC)Cu–X (X = halide) framework that facilitates their binding to internal alkynes.[30] We wanted to test whether our copper catalysts are capable of performing such transformations as well. Complex **7** was used as catalyst for the cycloaddition reaction between diphenylacetylene and benzyl azide. The reaction, carried out at 80 °C, resulted in a conversion of 80% with 5 mol-% of the catalyst within 24 hours. We also tried to decrease the catalyst loading to 0.25 mol-%. This worked as well, and a similar conversion as mentioned above was realized after a reaction time of 96 hours at 80 °C (Table 5).

Table 5. Tested conditions for the conversion of internal alkynes with **7**.

Entry	Catalyst loading	Time	Conversion[a]
1	0.5 mol-%	96 h	86.1%
2	5 mol-%	24 h	80%

[a] Conversion determined by NMR spectroscopy.

Finally, we wanted to test whether our catalysts are capable of catalyzing the click reaction with a "super" bulky azide such as 2,6-(dimesityl)-phenyl azide. When we used the popular Cu^{II}/ascorbate/tbta mixture as the catalytic system, we did not observe any conversion of the aforementioned azide in the cycloaddition reaction. Gratifyingly, the use of 0.25 mol-% of **7** at 100 °C as catalyst was enough to successfully convert a mixture of 2,6-(dimesityl)phenyl azide and pyridylacetylene to the corresponding 1,2,3-triazole within 2 hours. (Scheme 4). Ligands with such steric bulk might facilitate the use of appropriate metal complexes of these ligands for other catalytic processes such as selective polymerization of olefins.



Scheme 4. The "click" reaction with bulky azides.

Conclusions

We have reported on azolium salts as precursors for synthesizing iodido-bridged dicopper(I) complexes, which then contain either substituted benzimidazolin-2-ylidenes or substituted 1,2,3-triazol-5-ylidenes as carbene ligands. Structural characterization of **7** shows trigonally coordinated di-Cu^{I} centers, which are bridged by iodido ligands. In contrast, **11** shows a linearly coordinated mononuclear Cu^{I} center. The Cu^{I}–carbene complexes have been shown to be highly efficient catalysts for the Huisgen [3+2] cycloaddition reaction between azides and alkynes. Complexes of both the alkyl-substituted benzimidazolin-2-ylidenes as well as the substituted 1,2,3-triazol-5-ylidenes are efficient catalysts for the "click" reaction owing to the strong σ-donating power of these carbene ligands. Very low catalyst loading as well as short reaction times were sufficient for these reactions. The catalysts were also shown to be effective for the cycloaddition reaction of diphenylacetylene, which is an internal alkyne. Furthermore, an extremely bulky azide could also be used as a substrate for the cycloaddition reaction with our catalysts. Future efforts will be dedicated to further lowering catalyst loadings in order to increase the efficiency of this process. In

addition, we would also explore the use of the reported "super" bulky 1,2,3-triazole as a ligand in other catalytic processes.

Experimental Section

General Considerations: All commercially available reagents were used as received. Solvents were dried and distilled according to standard procedures. Syntheses of the organic compounds were carried out in air, and the copper complexes were synthesized under an argon atmosphere. Salts **1**, **2**, **3**, and **4** were synthesized according to literature procedures.[48,56–58] Azide **13** was synthesized by following a literature report.[60,61]

Instrumentation: The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker AC 250 spectrometer. Elemental analyses were performed with a Perkin–Elmer Analyzer 240. Mass spectrometry experiments were carried out with a Bruker Daltronics Mictrotof-Q mass spectrometer.

Syntheses

1-[2-(Methylthio)phenyl]-4-phenyl-1,2,3-triazole (5): (2-Azidophenyl)(methyl)sulfane {prepared from 2-(mercaptomethyl)aniline according to a literature procedure} (1 equiv., 1.86 g, 0.0113 mol) and phenylacetylene (1 equiv., 1.15 g, 0.0113 mol, 1.23 mL) were dissolved in a mixture of dichloromethane/water/*tert*-butyl alcohol (14 mL:28 mL:14 mL). Then copper sulfate (0.05 equiv., 0.14 g, 0.00056 mol), sodium ascorbate (0.2 equiv., 0.437 g, 0.00226 mol), and tbta (0.01 equiv., 0.06 g, 0.00011 mol) were added to the reaction mixture, and the reaction mixture was heated to reflux overnight at 55 °C. After heating, water (50 mL) was added, and the product was extracted with dichloromethane (4 × 20 mL). The combined organic phases were dried with sodium sulfate, filtered, and the solvent was evaporated. The crude product was then purified by flash column chromatography over silica gel by using a gradient from 0 to 10% methanol in dichloromethane. The product was obtained as a brown oil in a yield of 95% (2.85 g, 0.0106 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 8.12 (s, 1 H, Triazol-5*H*), 7.92–7.88 (m, 2 H, Aryl-H), 7.50–7.29 (m, 7 H, Aryl-H), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR (60 MHz, $CDCl_3$, 25 °C, TMS): δ = 147.6, 135.6, 135.1, 130.2, 128.8, 126.8, 126.0, 125.9, 121.6, 120.0 (all Aryl-C), 16.0 (CH_3) ppm.

3-Methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazolium Iodide (6): 1-[2-(Methylthio)phenyl]-4-phenyl-1,2,3-triazole (**5**) (1 equiv., 0.723 g, 0.0027 mol) was dissolved in acetonitrile (5 mL, c = 0.5 mol L^{-1}), and methyl iodide (10 equiv., 3.83 g, 0.027 mol, 1.7 mL) was added. Then the mixture was heated to reflux for 24 h. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane (5 mL) and precipitated by the addition of ethyl ether (50 mL). The yellow precipitate was collected by filtration and recrystallized from dichloromethane/diethyl ether (2:1). The product was obtained in a yield of 55% (0.607 g,0.00149 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 8.61 (s, 1 H, Triazol-5*H*), 8.39 (m, 1 H, Aryl-H), 7.96–7.92 (m, 2 H, Aryl-H), 7.66–7.58 (m, 4 H, Aryl-H), 7.49–7.41 (m, 2 H, Aryl-H), 4.44 (s, 3 H, NCH_3), 2.54 (s, 3 H, SCH_3) ppm. ^{13}C NMR (60 MHz, $CDCl_3$, 25 °C, TMS): δ = 143.6, 134.4, 133.1, 132.7, 132.1, 130.3, 129.6, 129.0, 127.8, 127.1, 121.5 (all Aryl-C), 39.7 (NCH_3), 16.4 (SCH_3) ppm. MS (ESI): m/z = 282.1052 $[C_{16}H_{16}N_3S]^+$. $C_{16}H_{16}IN_3S$ (409.29): calcd. C 46.95, H 3.94, N 10.27; found. C 46.77, H 3.94, N 10.32.

General Procedure for the Copper Complexes: A suspension of the azolium salt (1 equiv., 0.0002 mol) and copper(I) iodide (1 equiv., 0.0002 mol, 0.038 g) in dichloromethane was cooled to –78 °C. Afterwards, potassium *tert*-butoxide (1.5 equiv., 0.0003 mol, 0.033 g) dissolved in dichloromethane (5 mL) was slowly added to the solution, and the solution was stirred at –78 °C overnight. The next day, the solution was filtered through a pad of Celite, and the solvent was evaporated. The white solid was recrystallized from dichloromethane/hexane (1:10) to afford colorless crystals.

Bis(μ-iodido)bis(1-benzyl-3-butylbenzimidazolin-2-ylidene)dicopper(I) (7): The product was gained from copper(I) iodide (1 equiv., 0.0002 mol, 0.038 g), azolium salt **1** (1 equiv., 0.0002 mol, 0.078 g), and KO*t*Bu (1.5 equiv., 0.0003 mol, 0.033 g) in dichloromethane (20 mL, c = 0.01 mol L^{-1}) under the general reaction conditions. The product was obtained as colorless crystals in a yield of 80% (0.036 g, 0.00008 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 7.77–7.60 (m, 2 H, Aryl-H), 7.52–7.46 (m, 2 H, Aryl-H), 7.39–7.26 (m, 14 H, Aryl-H), 5.69 (s, 4 H, NCH_2), 4.51 [t, ^3J(H,H) = 7.25 Hz, 4 H, NCH_2], 1.97 [p, ^3J(H,H) = 7.5 Hz, 4 H, CH_2], 1.43 [sex, ^3J(H,H) = 7.25 Hz, 4 H, CH_2], 0.99 [t, ^3J(H,H) = 7.5 Hz, 6 H, CH_3] ppm. MS (ESI): m/z = 591.2541 $[(C_{18}H_{20}N_2)_2Cu]^+$. $C_{36}H_{40}Cu_2I_2N_4$ (909.64): calcd. C 47.53, H 4.43, N 6.16; found C 47.14, H 4.27, N 6.51.

Bis(μ-iodido)(1-benzyl-3-isopropyl-benzimidazolin-2-ylidene)dicopper-(I) (8): Compound **8** was prepared by following the general procedure from copper(I) iodide (1 equiv., 0.0002 mol, 0.038 g), azolium salt **2** (1 equiv., 0.066 g, 0.0002 mol), and KO*t*Bu (1.5 equiv., 0.0003 mol, 0.033 g) in dichloromethane (20 mL, c = 0.01 mol L^{-1}). The product was obtained as a white solid in a yield of 80% (0.036 g, 0.00008 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 7.62–7.58 (m, 1 H, Aryl-H), 7.42–7.27 (m, 8 H, Aryl-H), 5.70 (s, 2 H, NCH_2), 5.10 [hept, ^3J(H,H) = 7 Hz, 1 H, NCH], 1.81 [d, ^3J(H,H) = 7 Hz, 6 H, CH_3] ppm. $C_{34}H_{36}Cu_2I_2N_4$ (881.59): calcd. C 46.32, H 4.12, N 6.36; found C 46.11, H 4.19, N 6.20.

Bis(μ-iodido)bis(1-butyl-3-isopropylbenzimidazolin-2-ylidene)dicopper(I) (9): Compound **9** was prepared by following the general procedure from copper(I) iodide (1 equiv., 0.0002 mol, 0.038 g), azolium salt **3** (1 equiv., 0.060 g, 0.0002 mol), and KO*t*Bu (1.5 equiv., 0.0003 mol, 0.033 g) in dichloromethane (20 mL, c = 0.01 mol L^{-1}). The product was obtained as a white solid in a yield of 80% (0.033 g, 0.00008 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 7.84–7.69 (m, 1 H, Aryl-H), 7.61–7.57 (m, 1 H, Aryl-H), 7.52–7.48 (m, 1 H, Aryl-H), 7.41–7.37 (m, 1 H, Aryl-H), 5.02 [hept., ^3J(H,H) = 6.75 Hz, 1 H, NCH], 4.48 [t, ^3J(H,H) = 7.25 Hz, 3 H, NCH_2], 1.96 [p, ^3J(H,H) = 7.25 Hz, 2 H, CH_2], 1.78 [d, ^3J(H,H) = 6.75 Hz, 6 H, CH_3], 1.46 [sex, ^3J(H,H) = 7.5 Hz, 2 H, CH_2], 0.99 [t, ^3J(H,H) = 7.5 Hz, 3 H, CH_3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$; 25 °C, TMS): δ = 186.1 (Carbene-C), 134.0, 132.8, 130.9, 126.8, 123.5, 123.2, 120.2, 113.2, 111.9, 111.2 (All Aryl-C), 53.9 (NCH_2), 52.8 (NCH_2), 32.3, 22.8 (all Butyl-C), 20.2 ($CHCH_3$), 13.6 (CH_3) ppm. $C_{38}H_{40}Cu_2I_2N_4$ (933.66): calcd. C 41.34, H 4.96, N 6.89; found C 41.33 H 5.12 N 7.05.

(1-Benzyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium-5-ylidene)(iodido)-copper(I) (10): Compound **10** was prepared by following the general procedure from copper(I) iodide (1 equiv., 0.0001 mol, 0.019 g), azolium salt **4** (1 equiv., 0.038 g, 0.0001 mol), and KO*t*Bu (1.5 equiv., 0.00015 mol, 0.016 g) in dichloromethane (10 mL, c = 0.01 mol L^{-1}). The product was obtained as a white solid in a yield of 60% (0.026 g, 0.00006 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 7.65–7.53 (m, 7 H, Aryl-H), 7.45–7.39 (m, 3 H, Aryl-H), 5.68 (s, 2 H, NCH_2), 4.09 (s, 3 H, NCH_3) ppm. ^{13}C NMR

(100 MHz, CD_2Cl_2; 25 °C, TMS): δ = 165.0 (Carbene-C), 148.7, 134.5, 131.9, 130.0, 129.9, 129.8, 129.7, 129.4, 129.0, 129.0, 128.9, 128.9, 127.4 (all Aryl-C), 59.1 (NCH_2), 37.9 (NCH_3) ppm. $C_{16}H_{15}CuIN_3$ (439.77): calcd. C 43.70, H 3.44, N 9.56; found C 43.33 H 3.35 N 9.68.

(Iodido){3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1*H*-1,2,3-triazol-3-ium-5-ylidene}copper(I) (11): Compound **11** was prepared by following the general procedure from copper(I) iodide (1 equiv., 0.0001 mol, 0.019 g), azolium salt **6** (1 equiv., 0.041 g, 0.0001 mol), and KO*t*Bu (1.5 equiv., 0.00015 mol, 0.016 g) in dichloromethane (10 mL, c = 0.01 mol L^{-1}). The product was obtained as a white solid in a yield of 75% (0.035 g, 0.000075 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 7.72–7.65 (m, 2 H, Aryl-H), 7.60–7.54 (m, 5 H, Aryl-H), 7.46–7.33 (m, 2 H, Aryl-H), 4.22 (s, 3 H, NCH_3), 2.47 (s, 3 H, SCH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2; 25 °C, TMS): δ = 167.1 (Carbene-C), 148.2, 137.5, 134.8, 130.8, 130.1, 130.0, 129.8, 129.5, 129.1, 127.3, 127.2, 126.8, 125.7 (all Aryl-C), 37.8 (NCH_3), 16.2 (SCH_3) ppm. $C_{16}H_{15}CuIN_3S$ (471.83): calcd. C 40.73, H 3.20, N 8.91; found C 40.90, H 3.46, N 8.79.

1-(2,6-Dimesityl)phenyl-4-(2-pyridyl)-1,2,3-triazole (14): Terphenylazide **13** (1 equiv., 0.0005 mol, 0.178 g) was mixed with 2-ethinylpyridine at room temperature, and **7** (0.25 mol-%) was added to the reaction vessel. The mixture was then capped and heated under vigorous stirring to 100 °C for 2 h. After cooling to room temperature, the solids were dissolved in dichloromethane and purified by silica gel column chromatography by using an eluent of 0 to 10% acetone in dichloromethane. The product was gained as a yellow fluffy solid in a yield of 95% (0.220 g,0.00048 mol). ^1H NMR (250 MHz, $CDCl_3$; 25 °C, TMS): δ = 8.44–8.42 (m, 1 H, Aryl-H), 7.93–7.89 (m, 1 H, Aryl-H), 7.66–7.57 (m, 3 H, Aryl-H), 7.28 (m, 2 H, Aryl-H), 7.11–7.03 (m, 1 H, Aryl-H), 6.73 (s, 4 H, Aryl-H), 2.14 (s, 6 H, CH_3 *para*), 2.05 (s, 12 H, CH_3 *meta*, *ortho*) ppm. ^{13}C NMR (60 MHz, $CDCl_3$, 25 °C, TMS): δ = 148.8, 148.3, 139.2, 137.2, 135.7, 135.7, 133.9, 130.1, 127.9 (all Aryl-C), 20.9 (CH_3, *para*), 20.6 (CH_3 *ortho*, *meta*) ppm. $C_{31}H_{30}N_4$ (458.60): calcd. C 81.19, H 6.59, N 12.22; found C 79.44, H 6.64, N 11.34.

General Procedures for Catalysis: Phenylacetylene (1 equiv., 0.101 g, 0.001 mol, 0.11 mL) or diphenylacetylene (1 equiv., 0.178 g, 0.001 mol) and benzyl azide (1equiv., 0.133 g, 0.001 mol) were mixed, and the corresponding catalyst (2.5–0.05 mol-% in the case of phenylacetylene; 5–0.25 mol-% in the case of diphenylacetylene) was added. The reaction mixture was stirred at room temperature in the case of phenylacetylene or warmed to 80 °C in the case of diphenylacetylene. The reaction was monitored by ^1H NMR spectroscopy. After completion or a certain period of time, the reaction was quenched by dissolving the reaction mixture in dichloromethane (10 mL). After quenching, a simple aqueous workup was carried out, and the white solids were dried under high vacuum for several hours to gain the isolated yields.

X-ray Crystallography: Compound **1** was crystallized from a solution in hot 2-propanol by slow cooling, **3** could be crystallized from a mixture of dichloromethane/ethyl acetate/petroleum ether (1:10:1) at –20 °C, and **6** was crystallized by layering a dichloromethane solution of it with ethyl ether at 8 °C. Complex **7** could be crystallized by diffusion of diethyl ether into a dichloromethane solution of the compound at 8 °C, and **11** was crystallized by layering a dichloromethane solution of it with *n*-hexane at 8 °C. Data collection was performed by using an OXFORD XCALIBUR-S CCD, or a Kappa CCD, or a Stoe IPDS II, or a Bruker Kappa Apex 2 duo diffractometer. The measurements were carried out at 173, or 100, or 133 K by using a Mo-K_α radiation (graphite monochromator). The structures were solved and refined by full-matrix least-squares techniques on F^2 by using the SHELX-97 program.[62] The *n*-butyl group in **3** is disordered (Table 6). CCDC-790995, -790996, -790997, 804974, and 819819 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 6. Crystallographic details.

	1	**3**	**6**	**7**	**11**
Chemical formula	$C_{18}H_{20}IN_2$	$C_{14}H_{21}BrN_2$	$C_{16}H_{16}N_3SI$	$C_{36}H_{30}Cu_2I_2N_4$	$C_{16}H_{15}CuIN_3S$
M_r	392.17	297.24	409.28	899.52	471.81
Crystal system	orthorhombic	trigonal	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$R3$	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	12.7971(3)	20.83(1)	10.5679(4)	24.7422(10)	10.4241(6)
b (Å)	10.5105(5)	20.83(1)	15.6146(6)	8.9604(5)	16.3560(9)
c (Å)	8.0033(2)	8.72(1)	11.3519(4)	19.0640(6)	10.7096(6)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	117.583(3)	124.827(2)	115.3370(10)
γ (°)	90.00	120.00	90.00	90.00	90.00
V (Å)^3	1690.99(8)	3278(3)	1660.31(11)	3469.4(3)	1650.30(16)
Z	4	9	4	4	4
Density (g cm^{-3})	1.537	1.355	1.637	1.722	1.899
F(000)	780	1386	808	1752	920
Radiation type	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
μ (mm^{-1})	1.890	2.804	2.051	3.036	3.319
Crystal size (mm)	0.28 × 0.23 × 0.18	0.25 × 0.22 × 0.16	0.5 × 0.49 × 0.47	0.26 × 0.23 × 0.16	0.28 × 0.18 × 0.14
Measured refl.	7818	7048	23362	6896	12524
Independent refl.	2927	2446	3517	4045	3221
Obsd. [$I > 2\sigma(I)$] refl.	2590	1893	3479	3194	2853
R_{int}	0.022	0.081	0.0195	0.033	0.1485
R [$F^2 > 2\sigma(F^2)$]	0.029	0.078	0.0199	0.057	0.1577
$wR(F^2)$	0.070	0.200	0.0439	0.1461	0.3563
S	1.110	1.095	1.245	1.069	1.070
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	1.638; –0.841	0.622; –0.864	0.5009; 0.3805	1.135; –1.931	5.224; –5.060

Supporting Information (see footnote on the first page of this article): ^{13}C NMR spectra and conversion versus time curves.

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