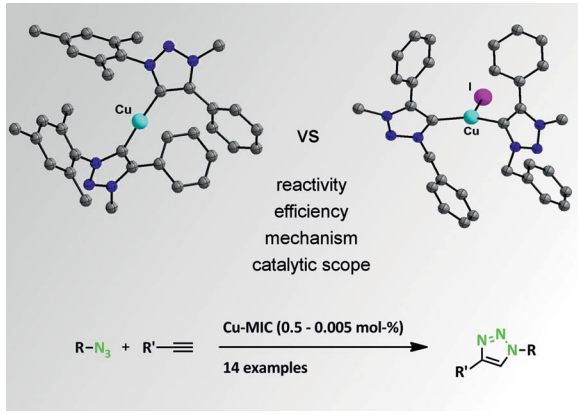
EurJIC European Journal of Inorganic Chemistry
ChemPubSoc Europe

Abnormal-Carbene Ligands

Keywords: Copper / Abnormal carbenes / Triazolylidenes / Cycloaddition / Homogeneous catalysis / 1,2,3-Triazoles



Cationic copper(I) complexes containing two triazolylidene carbenes of the abnormal type are shown to be excellent catalysts for the [3+2] cycloaddition reaction between azides and alkynes. A range of azides and a couple of alkynes are activated by these copper(I) complexes towards the catalytic formation of the corresponding substituted 1,2,3-triazoles.

EurJIC European Journal of Inorganic Chemistry

www.eurjic.org FULL PAPER

DOI:10.1002/ejic.201300150

Activating Azides and Alkynes for the Click Reaction with [Cu(*a*NHC)$_2$I] or [Cu(*a*NHC)$_2$]$^+$ (*a*NHC = Triazole-Derived Abnormal Carbenes): Structural Characterization and Catalytic Properties

Stephan Hohloch,[a] Damaris Scheiffele,[b] and Biprajit Sarkar*[a]

Keywords: Copper / Abnormal carbenes / Triazolylidenes / Cycloaddition / Homogeneous catalysis / 1,2,3-Triazoles

Neutral, iodido-containing copper(I) complexes [Cu(*a*NHC)$_2$I] {*a*NHC = 1-benzyl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene (for **6**) and 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazol-5-ylidene (for **7**)} and cationic, halide-free copper(I) complexes [Cu(*a*NHC)$_2$](BF$_4$) {*a*NHC = 1-benzyl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene (for **8**), 3-methyl-1,4-diphenyl-1,2,3-triazol-5-ylidene (for **9**), 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazol-5-ylidene (for **10**), and 1-mesityl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene (for **11**)}, both containing two monodentate abnormal-carbene ligands (*a*NHC), were synthesized from [Cu(CH$_3$CN)$_4$](BF$_4$) and the corresponding triazolium salts. It was possible to selectively synthesize both kinds of complexes by simply variing the counter-anion of the triazolium salts and keeping the metal precursor the same. All complexes were characterized by elemental analysis and spectroscopic methods. **6** and **11** were studied with single-crystal X-ray diffraction analyses. In **6**, the copper(I) center is tricoordinated, and its geometry is in between trigonal planar and T-shaped. In halide-free **11**, the copper(I) center is linearly coordinated by two abnormal-carbene ligands. All complexes were tested as catalysts in the Huisgen [3+2] cycloaddition reaction between azides and alkynes, and they showed excellent efficiencies under neat conditions. A comparison between the efficiencies of the halide-containing complexes **6** and **7** and the halide-free cases **8**–**11**, shows that the halide-free Cu–*a*NHC complexes are significantly more efficient than their halide-containing counterparts. The best catalyst was used for a substrate screening by utilizing a variety of azides and a couple of alkynes. The efficiency of the catalyst was maintained with loadings as low as 0.005 mol-%. Mechanistic studies were carried out as well.

Introduction

N-heterocyclic carbenes (NHCs) have come to occupy a prominent place in the toolbox of chemists working in the organometallic and catalysis field. Since the seminal discovery of the first stable, crystalline NHC by Arduengo,[1] these classes of ligands have been used in various fields of chemistry, and catalysis is the most prominent example of their application.[2] In recent years, redox-active NHCs have been reported.[3] Another new development in this field has been the introduction of new kinds of carbene ligands, which have been variously named, for example, abnormal N-heterocyclic carbenes (*a*NHCs) or mesoionic carbenes (MIC).[4] An emerging class of *a*NHC ligands are those based on triazolylidenes.[4a,4f–4h] One reason for the current popularity of this class of *a*NHC ligands is their easy accessibility through the Cu(I)-catalyzed click [3+2] cycloaddition reaction between azides and alkynes (CuAAC).[5] Ligands synthesized through the click reaction have found extensive use in coordination chemistry in recent years.[6] Their corresponding metal complexes were studied for their electron transfer[7] and magnetic properties[8] and used as metallosupramolecular assemblies[9] and as homogeneous catalysts.[10] Triazolylidene-based *a*NHC ligands have been postulated to surpass even their normal NHC counterparts in their σ-donor capability,[4a,4f–4h] a property that makes their metal complexes attractive for homogeneous catalysis.[11]

Cu(I) complexes of NHC ligands are potent catalysts for the click cycloaddition reaction between azides and alkynes.[12] Furthermore, the addition of additional nitrogen donor ligands to the Cu(I)–NHC complexes increases their catalytic activity.[13] In recent years, we[14a] and others[14b] have shown that copper(I) complexes with triazolylidene-based *a*NHC ligands of the type (*a*NHC)Cu–X (X = halide) are excellent catalysts for the CuAAC. These catalysts are also able to catalyze cycloaddition reactions with bulky azides or internal alkynes as substrates, which cannot be catalyzed with the original click recipe of CuSO$_4$ and ascorbate. We have also extended our work in this field to study the

[a] Institut für Chemie und Biochemie, Anorganische Chemie, Freie Universität Berlin,
Fabeckstraße 34–36, 14195, Berlin, Germany
E-mail: biprajit.sarkar@fu-berlin.de,
Homepage: http://www.bcp.fu-berlin.de/en/chemie/ac/agsarkar/index.html
[b] Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300150.

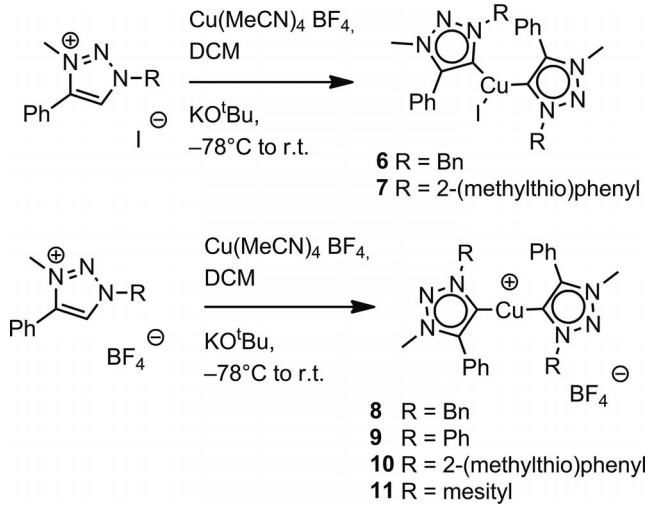
effect of additional donor ligands on the catalytic efficiency of (*a*NHC)CuI complexes.[14c] As part of our continuing interest in developing the coordination chemistry of various click-derived ligands[6d] and in finding applications of the corresponding metal complexes,[7d,7e,8c,10] we here present new types of copper(I) complexes with triazolylidene ligands. Neutral complexes of the form [Cu(*a*NHC)$_2$I] {*a*NHC = 1-benzyl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene (for **6**) and 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazol-5-ylidene (for **7**)} and cationic complexes of the form [Cu(*a*NHC)$_2$](BF$_4$) {*a*NHC = 1-benzyl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene (for **8**), 3-methyl-1,4-diphenyl-1,2,3-triazol-5-ylidene (for **9**), 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazol-5-ylidene (for **10**), and 1-mesityl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene (for **11**)} are presented below. Structural characterizations are presented to illustrate the effect of an additional halido ligand on the coordination geometry of the copper(I) complexes. All complexes were tested for their efficiency in the CuAAC. We particularly focused on the comparison between the halide-containing complexes **6** and **7** and their halide-free counterparts **8**–**11**, with respect to their catalytic potency. The best catalyst was used for screening a range of substrates. Evidence from ^{1}H NMR spectroscopy is used to shed light on the mechanism of the azide and alkyne activation and on the CuAAC with this class of catalysts in general.

Results and Discussion

Synthesis and Characterization

The substituted 1,2,3-triazoles that were used in this work to generate the triazolylidene ligands were all prepared by literature methods.[7d,7e,14a,14b] The corresponding triazolium salts with iodide as a counter-anion are also known.[14] The triazolium salts with BF_4^- as the counter-anion were prepared by reacting the corresponding 1,2,3-triazoles with the Meerwein salt (see Exp. Sect.).

The copper(I) complexes with two triazolylidene ligands bound to the copper center were synthesized by reacting two equivalents of the triazolium salts with one equivalent of [Cu(CH$_3$CN)$_4$](BF$_4$) in the presence of excess KO*t*Bu (Scheme 1 and Exp. Sect.). Both the halide-containing and the halide-free bistriazolylidene complexes could be selectively synthesized by choosing the nature of the triazolium salt. Thus, the use of iodide-containing triazolium salts led to the selective formation of the iodide-containing complexes **6** and **7**. On the contrary, the use of the tetrafluoroborate-containing triazolium salts selectively led to the isolation of the halide-free complexes **8**–**11**. We note here that the copper(I) precursor [Cu(CH$_3$CN)$_4$](BF$_4$) is the same for both sets of reactions (Scheme 1). Thus, the synthetic method reported here allows us to selectively synthesize the halide-containing and the halide-free bistriazolylidene complexes in very good yields by simply choosing the appropriate counter-anion of the triazolium salts.



Scheme 1. Synthetic route for the reported copper(I) complexes.

The complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. In the ^{1}H NMR spectra of the triazolium salts, the signal of the triazolium-ring C–H proton is shifted to low field. Upon the formation of the Cu(I) complexes, this signal disappears, which is a first indication of the binding of the triazolylidene ligands through the carbene C atom. In the ESI mass spectrum of each of the complexes **6**–**11**, the molecular peak corresponding to the respective monocation was observed. In the ^{13}C NMR spectra of the complexes, the signal of the carbene C atom appears in the range 162–167 ppm. Signals in this range were also observed for the carbene C atom for the monocarbene complexes of the type [(*a*NHC)CuI], which we reported recently.[14a]

Crystal Structures

Single crystals of suitable quality could be obtained for the newly synthesized triazolium salts 3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazolium tetrafluoroborate (**4**) and 1-mesityl-3-methyl-4-phenyl-1,2,3-triazolium tetrafluoroborate (**5**). **4** crystallizes in the monoclinic $P2_1/n$ space group and **5** crystallizes in the monoclinic $P2_1/c$ space group (Table 6). The bond lengths within both triazolium salts are in a range similar to those of related triazolium salts reported recently (Figures S1 and S2 and Table 1).[14a]

Table 1. Selected bond lengths [Å].

Atoms	4	5	6	11
C1–C2	1.374(4)	1.371(3)	1.405(4)	1.386(5)
C2–N3	1.364(4)	1.362(2)	1.372(4)	1.374(4)
N3–N2	1.321(4)	1.319(2)	1.324(3)	1.320(4)
N2–N1	1.326(3)	1.327(2)	1.328(4)	1.337(4)
N1–C1	1.348(4)	1.350(2)	1.367(4)	1.370(4)
N3–C18	1.463(4)	1.463(2)	1.466(4)	1.467(4)
C1–Cu1	–	–	1.935(3)	1.899(3)
C1A–Cu1	–	–	1.937(3)	1.895(3)
Cu1–I1	–	–	2.810(1)	–

We could crystallize the halide-containing complex **6**·CH_2Cl_2 and the halide-free complex **11**·CH_2Cl_2 (see Exp. Sect.), and we analyzed them by single-crystal X-ray diffraction. **6**·CH_2Cl_2 crystallizes in the monoclinic $P2_1/n$ space group, and **11**·CH_2Cl_2 crystallizes in the triclinic $P\bar{1}$ space group (Table 6). In **6**·CH_2Cl_2, the copper center is tricoordinated by the two carbene C atoms of the two triazolylidene rings and an iodido ligand (Figure 1). The copper center does not contain a local center of symmetry. The Cu–C(carbene) distance of 1.93 Å (Table 1) matches well with the corresponding distance in a similar complex that we reported recently.[14a] The C–C and C–N distances (Table 1) within the triazolylidene ring point to a delocalized situation inside that ring. This is in contrast to bonding situations observed for neutral 1,2,3-triazole ligands, where a localization of the double bonds and a corresponding tendency to favor an azo-like N=N bond inside the ring have been observed.[7d] The C2–C1–N1 angle of 100.4(3)° around the carbene C atom (Table 2) shows the large deviation from the 120° angle that would be expected for an ideally sp^2-hybridized carbon atom. The C1–Cu1–C1A angle of 148.4(1)°, the C1–Cu1–I1 angle of 113.5°, and the C1A–Cu1–I1 angle of 98.0° all point towards a coordination geometry around the copper center that is in between a trigonal planar and a T-shaped structure. Accordingly, the iodido ligand is more tilted towards one of the triazolylidene rings as compared to the other. The phenyl as well as the benzyl substituents on the triazolylidene ring point in a syn fashion with respect to each other. The dihedral angle between the phenyl and the triazolylidene ring is 49.9° for one ligand and 50.9° for the other. One of the benzyl groups is more tilted away from its triazolylidene ring than the other.

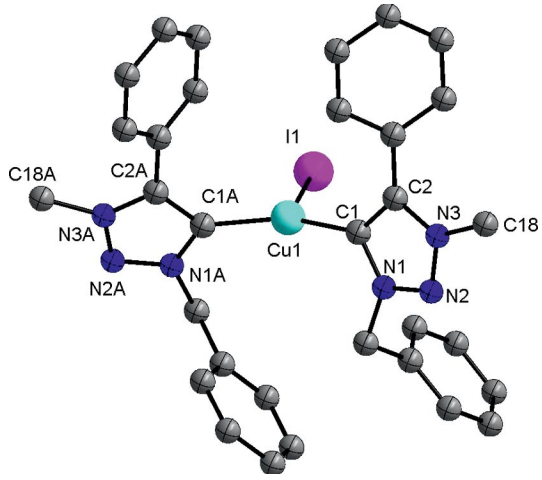


Figure 1. ORTEP plot of **6**·CH_2Cl_2. Ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity.

In contrast to the iodide-containing complex **6**·CH_2Cl_2, the halide-free complex **11**·CH_2Cl_2 displays a twofold coordinated copper center, and the two triazolylidene rings are oriented trans to each other (Figure 2). As in the case of

Table 2. Selected bond angles [°].

Atoms	4	5	6	11
C2–C1–N1	105.9(3)	106.44(16)	100.4(3)	101.9(3)
C1–Cu1–C1A	–	–	148.4(1)	173.7(1)
C1–Cu1–I1	–	–	113.5(1)	–
C1A–Cu1–I1	–	–	98.0(1)	–

6·CH_2Cl_2, the copper center in **11**·CH_2Cl_2 does not contain any crystallographic center of inversion. The Cu–C(carbene) distance of 1.89 Å is in the expected range and fits well with reported distances between Cu(I) and triazolylidene C atoms.[14a] Just as in the case of **6**·CH_2Cl_2, the C–C and C–N distances within the triazolylidene rings point to a delocalized situation within the rings. The C2–C1–N1 angle around the carbene C center is 101.9(3)° and shows the deviation of this value from that of an ideally sp^2-hybridized carbon atom. The C1–Cu1–C1A angle is 173.7(1)° and points to a near linear coordination geometry around the copper(I) center. Both the mesityl groups of the two triazolylidene rings and the phenyl groups are oriented in a syn fashion with respect to each other. The dihedral angle between the phenyl ring and the central triazolylidene ring is 51.6° for one ligand and 35.5° for the other, and that between the mesityl ring and the central triazolylidene ring is 69.9° and 85.6°, respectively. The phenyl and mesityl substituents of one of the triazolylidene rings are more bent towards the Cu(I) center compared to the substituents of the other triazolylidene ring (Figure 2).

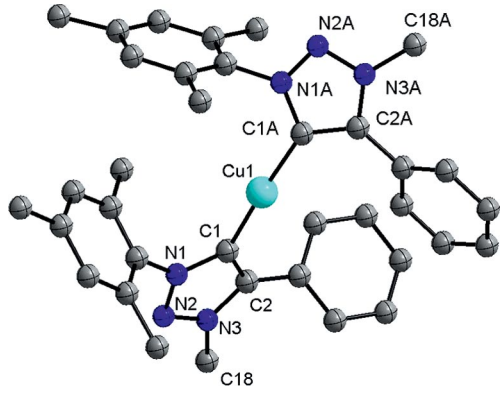
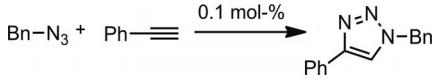


Figure 2. ORTEP plot of **11**·CH_2Cl_2. Ellipsoids are drawn at 50% probability. Hydrogen atoms, solvent molecules, and the counterion have been omitted for clarity.

Catalytic [3+2] Cycloaddition Reactions between Azides and Alkynes

Copper(I) complexes with NHC ligands are potent catalysts for the [3+2] cycloaddition reaction between azides and alkynes (CuAAC).[12,13] In recent years, our group has depicted the use of copper(I) complexes with *a*NHC ligands of the triazolylidene type as catalysts for the aforementioned reaction.[14a,14c] In the initial work, we reported on the catalytic activity of complexes of the form [Cu-

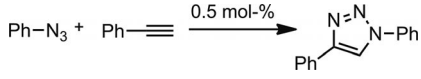
(*a*NHC)I]. We were then interested in testing copper(I) complexes with two abnormal-carbene ligands as catalysts for the CuAAC. In recent years, complexes containing two normal NHC ligands, that is, $[Cu(NHC)_2]X$ (X = BF_4^- or PF_6^-) have also been shown to be potent catalysts for the click reaction.[12c,12f] In the present work, we tested the performance of the *a*NHC counterparts of the bis(NHC) complexes mentioned above. In designing the catalysts, we chose to synthesize complexes of two different types: One class of complexes are the neutral bis(*a*NHC) complexes that contain an additional iodido ligand (**6** and **7**). The second class are those that are iodide-free and hence cationic in nature (**8**–**11**). Hence, the complexes reported here present us with an opportunity of testing the influence of charge as well as the presence or absence of an additional iodido ligand on the catalytic activity of the complexes. As a test reaction for screening of the catalysts, we chose the CuAAC between benzyl azide and phenylacetylene (Scheme 2).



Scheme 2. Test reaction used for comparing the efficiency of the iodido containing complexes **6**–**7** and iodide free complexes **8**–**11**.

In the test reaction shown in Scheme 2, a comparison was made between the catalytic efficiency of the iodide-containing complexes **6** and **7**, and the halide-free cationic complex **10**, which has the same substituents on the triazolylidene ring as **7**. With **10** as a catalyst and 0.1 mol-% of catalyst loading, a full conversion to the substituted 1,2,3-triazole was complete within 15 min. For the same reaction and with the same catalyst loading, the complexes **6** and **7** require 2 and 3 h, respectively, for full conversion. Under identical conditions, the precursor complex $[Cu(CH_3CN)_4](BF_4)$ requires 5 h for complete conversion (Table 3). All conversions were followed by ^{1}H NMR spectroscopy with a focus on the disappearance and appearance of the benzylic CH_2 proton of the products and reactants (see below). These results thus clearly point out the need for the *a*NHC ligands on the Cu(I) center to increase the catalytic efficiency of the catalysts. Another interesting observation made during the catalyst screening is the markedly higher potency of the cationic, halide-free complex **10** in comparison to its halide-containing counterparts **6** and **7**. The reasons for this are probably twofold. The substrate molecules are likely to bind more strongly to the cationic complex as compared to its neutral counterpart. More important is perhaps the fact that most likely more than one copper–ligand-bond breaking will be required for the tricoordinated halide-containing complexes **6** and **7**, in comparison to **10**, where only one copper–ligand bond needs to be broken to generate the active catalyst (see below for a discussion of the mechanism). The presence of additional donor atoms in the ligand backbone (SMe for **7**) does not seem to positively influence the catalyst activity, as indicated by the worse efficiency of **7** compared to **6**, which does not contain any additional donor atoms.

After having established that the halide-free, cationic complexes are far more efficient as catalysts in the discussed cycloaddition reaction, we turned our focus to a comparison among all the halide-free complexes **8**–**11** discussed here. The cycloaddition reaction between benzyl azide and phenylacetylene did not offer good insights here, because reactions with all the halide-free catalysts were complete within 15 min. Hence, we turned our attention to the cycloaddition reaction between phenyl azide and phenylacetylene (Scheme 3).



Scheme 3. Test reaction used for probing the efficiency of the halide-free complexes **8**–**11**.

With 0.5 mol-% catalyst loading, the reaction shown in Scheme 3 was monitored for 240 min with **8** and for 250 min with **9**, and conversions of 91% and 49%, respectively, to the corresponding 1,2,3-triazole were observed after the monitored time frame (Figure 3). Under identical conditions, a full conversion was obtained with **10** as well as with **11** as catalyst after a total time of 170 min (Table 4). Thus, the catalysts **10** and **11**, which have phenyl and 2-methylthiophenyl substituents and phenyl and mesityl substituents, respectively, on the triazolylidene rings, are the most potent in the group. This effect is probably related to the steric bulk of the substituents on the 2-methylthiophenyl and mesityl rings, which are missing in the substitu-

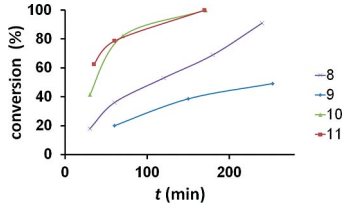


Figure 3. Conversion–time plots for catalysts **8**–**11** for the reaction depicted in Scheme 3.

Table 3. Comparative results of the catalytic efficiency of iodido-containing (**6** and **7**) and iodido-free (**10**) complexes for the reaction shown in Scheme 2.

Catalyst	Time	Conversion [%]
6	2 h	100
7	3 h	100
10	15 min	100
$[Cu(MeCN)_4](BF_4)$	5 h	21

Table 4. Comparison within the iodide-free catalyst series (**8**–**11**) for the test reaction shown in Scheme 3.

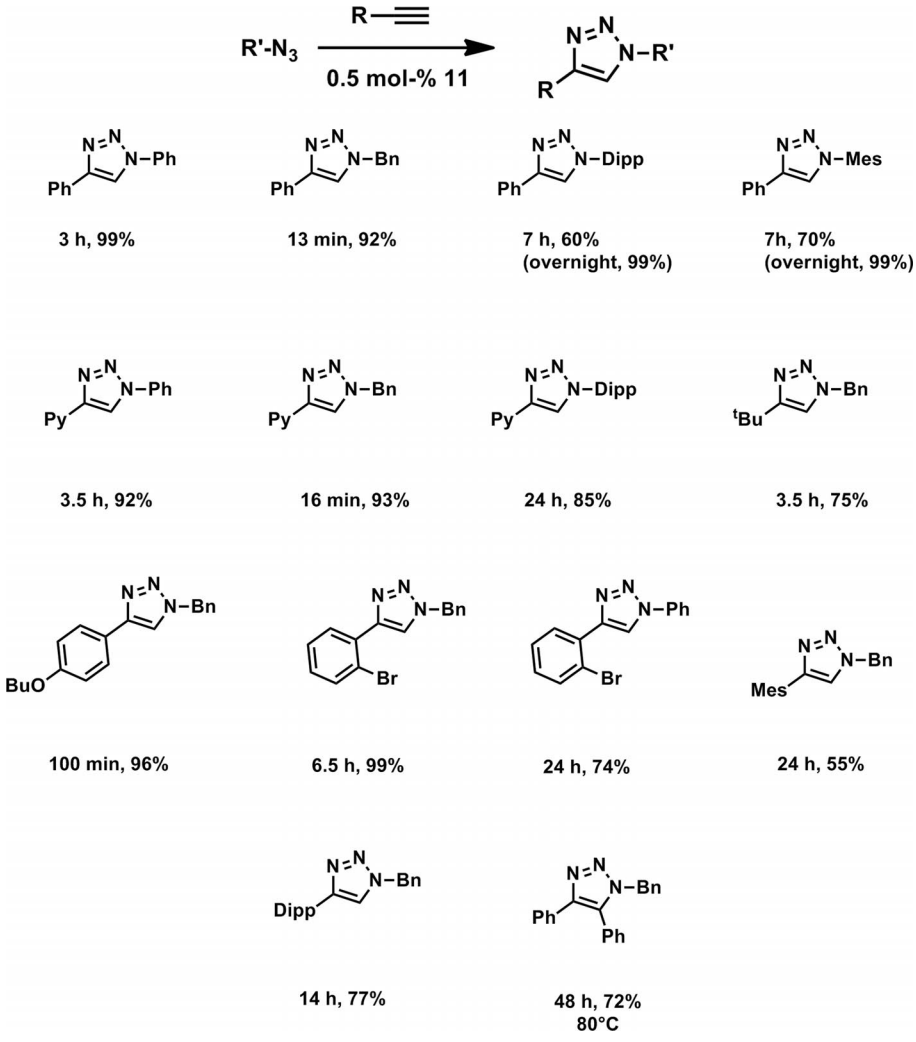
Catalyst	Time	Conversion [%]
8	240 min	91
9	250 min	49
10	170 min	100
11	170 min	100

ents on the triazolylidene rings in **8** and **9** (benzyl and phenyl groups, respectively). A likely effect of these bulky groups is that they increase the solubility of the catalysts and also enhance their stability in air. The comparable efficiencies of **10** and **11** preclude the possibility that additional donor atoms in the ligand backbone (SMe in the case of **10**) are advantageous for catalysis.

Once we had established that **10** and **11** are the most potent catalysts of all the complexes tested, we decided to perform a substrate screening with one of these complexes. Since both complexes showed identical activity in the test reaction, we chose **11** (with a 0.5 mol-% catalyst loading) for substrate screening. As can be seen from Scheme 4, **11** is capable of catalyzing the cycloaddition reaction between a host of substrates. The electronic and steric properties of the starting alkynes and azides were systematically varied to decipher the effect of these substrate properties on the activity of the catalyst.

As can be seen from the conversion times listed in Scheme 4, the reaction times are the longest for electron-rich alkynes (for example *tert*-butylacetylene) and for electron-poor or sterically demanding azides. The first step of the catalytic cycle is the deprotonation of the alkyne, followed by the binding of the acetylide ligand to the copper(I) center (see Scheme 6 below). An electron-rich alkyne is expected to be more difficult to deprotonate in comparison to an electron-poor one. This difficulty would explain the need for longer reaction times and the worse catalytic efficiency for the reaction with electron-rich alkynes. Substituting the phenyl ring of phenylacetylene also leads to longer reaction times and worse catalytic efficiency (Scheme 4). Internal alkynes, which are considered to be difficult substrates for the CuAAC, could also be converted into the corresponding triazoles with **11** as the catalyst. However, this reaction required 48 h and heating-up to 80 °C.

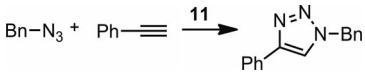
A subsequent step in the catalytic cycle is probably the coordination of the organic azide to the copper(I) center. Because the R group of RN_3 is bound to the same nitrogen atom that coordinates to the copper(I) center, the nature of this group is likely to drastically influence the azide binding



Scheme 4. The range of substrates tested with catalyst **11**.

to the metal center and hence to determine the eventual efficiency of the catalyst. Thus, azides with phenyl substituents, which would decrease the electron density at the nitrogen atom they are bound to, are less reactive than benzyl azides. Azides containing bulky substituents are difficult substrates for the click (CuAAC) reaction, because the bulky groups are likely to interfere with the binding of the organic azide to the copper(I) center. Hence, reactions with bulky azides are slower (Scheme 4). However, with catalyst **11** and stirring the reaction overnight or for 24 h, a nearly quantitative conversion is achieved even with bulky azides. These results display the highly potent nature of the catalysts reported here in comparison to the original click recipe, which employs $CuSO_4$, ascorbate, and tbta.

Finally, we were interested in downscaling the catalyst loading. To do this, we chose **11** as the catalyst and the CuAAC between benzyl azide and phenylacetylene as the model reaction (Scheme 5). The reaction was monitored by following the disappearance and appearance of the ^{1}H NMR signals assigned to the benzylic CH_2 protons of the reactants and products (Figure 4).



Scheme 5. Test reaction used for downscaling the catalyst loading with **11** as the catalyst.

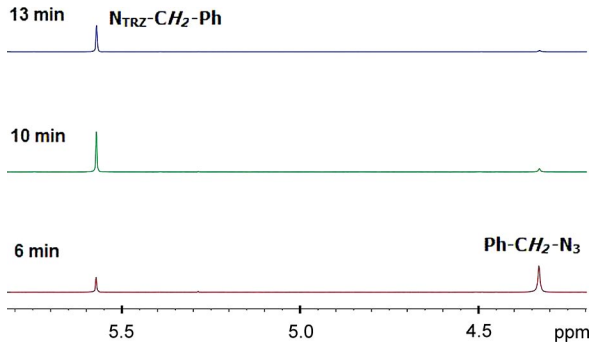


Figure 4. ^{1}H NMR spectra of the benzylic CH_2 protons of reactant and product showing the completion of the reaction shown in Scheme 5.

As stated above, with a catalyst loading of only 0.1 mol-%, a full conversion of the reaction shown in Scheme 5 was achieved within 15 min. Upon lowering the catalyst loading to 0.05 mol-%, a conversion of about 86% was observed after only 30 min (Figure 5 and Table 5). Eventually, we could decrease the catalyst concentration to 0.005 mol-%. In this case, mild heating to 50 °C was necessary to obtain a conversion of about 82% within 180 min. Thus, the catalyst loading can be decreased to extremely small amounts, and its efficiency is still maintained. Hence, catalyst **11** is more efficient for the reaction depicted in Scheme 5 than the [Cu(*a*NHC)I] catalysts we reported previously.[14a]

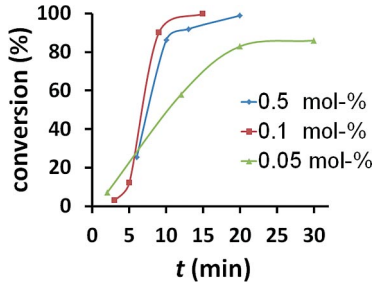


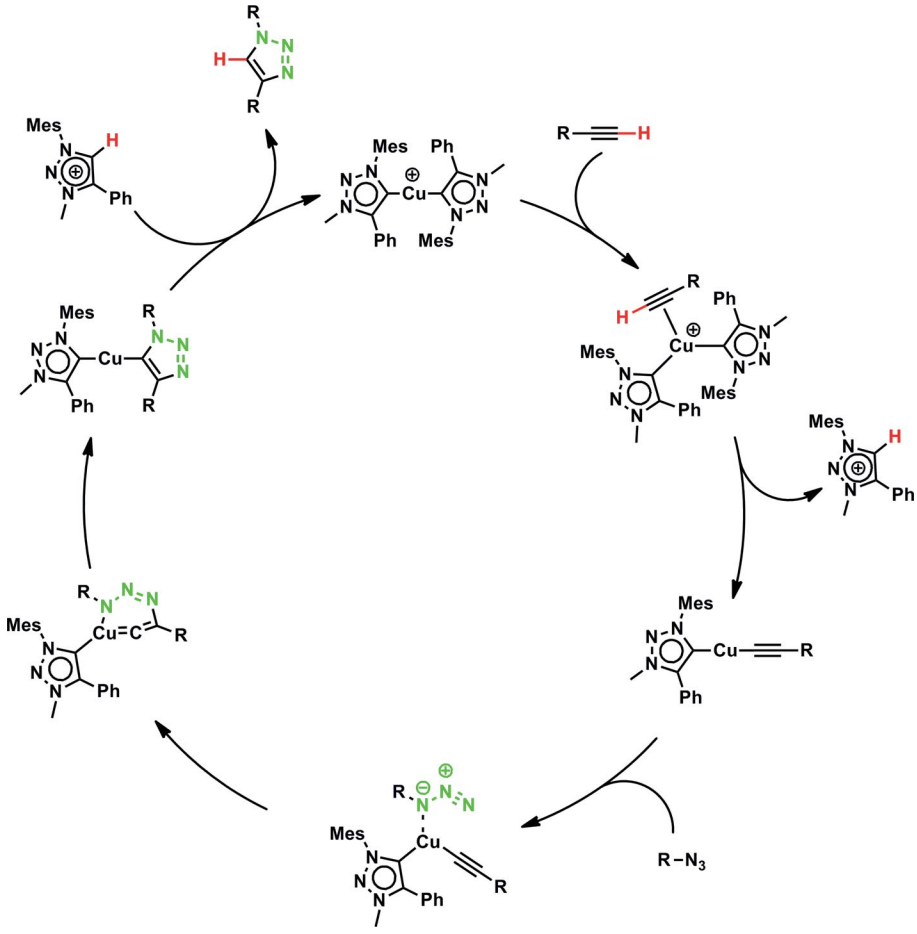
Figure 5. Conversion–time plot for the downscaling of the reactions with **11** as the catalyst.

Table 5. Results of downscaling experiments for the reaction shown in Scheme 5 with **11** as the catalyst.

Loading [mol-%]	Time	Conversion [%]
0.5	13 min	92
0.1	15 min	100
0.05	30 min	86
0.005	180 min	82

The catalytic mechanism of the processes described here is likely the same as that described for analogous bis-carbene–copper(I) complexes recently described in the literature (Scheme 6). Most likely, the initial step here is the deprotonation of the alkyne by one of the copper-bound triazolylidene ligands and the subsequent formation of a triazolium salt. The thus formed acetylide ligand then binds to the copper(I) center to form a copper–acetylide complex. The organic azide then binds to the copper–acetylide complex, and the cycloaddition reaction takes place at the copper center to yield a copper-bound triazolide ligand. The eventual protonation of the triazolide by the triazolium salt (formed in the first step) leads to the release of the 1,2,3-triazole molecule and the regeneration of the copper(I)–carbene catalyst. Proof that such a mechanism is operational in the present case came from noncatalytic studies, for which we added phenylacetylene to the complex **11** in an NMR experiment (Figure S3). The addition of phenylacetylene leads to the appearance of a downfield-shifted ^{1}H NMR signal, which corresponds to the ring C–H proton of the triazolium salt that is formed through deprotonation of phenylacetylene and protonation of the copper-bound triazolylidene ligand. Additional signals of the released triazolium salt and the corresponding copper-acetylide complex were also observed in the ^{1}H NMR spectrum (Figure S3).

This mechanism would explain the lower efficiencies of the iodide-containing catalysts **6** and **7** in comparison to the halide-free complexes **8**–**11**. It also explains the observed trends in catalytic efficiency as a function of the steric and electronic properties of the substrates, as has been discussed above.



Scheme 6. Possible mechanism of catalytic action. Adapted from ref.[12c,f]

Conclusions

In conclusion, we have reported here on iodido-containing as well as halide-free copper(I) complexes containing two triazolylidene ligands. The structural characterization shows that the iodide-containing copper(I) complexes are tricoordinated with a coordination geometry in between that of a trigonal planar and a T-shaped structure. The halide-free complexes contain copper centers that are linearly coordinated through the carbon atoms of the two triazolylidene rings. Both kinds of complexes are efficient catalysts for the [3+2] cycloaddition reaction between azides and alkynes. The cationic, halide-free complexes are more efficient than their neutral iodide-containing counterparts. A substrate screening was performed by choosing the most potent complex as the catalyst. The screening showed that these copper–*a*NHC complexes are capable of catalyzing the reaction of electron-poor, electron-rich, and bulky azides with electronically diverse alkynes. In downscaling experiments, it could be shown that the catalysts remain active, even when their loading is decreased to 0.005 mol-%. Our results illustrate the high efficiency of copper(I) complexes with *a*NHC ligands of the triazolylidene type as catalysts for the click (CuAAC) reaction. Such catalysts are also capable of catalyzing reactions with bulky azides (a class of substrates considered difficult for the original click recipe) under mild conditions. Thus, these results establish the use of the emerging class of triazolylidene compounds as efficient ligands for homogeneous catalysis.[4h]

Experimental Section

Materials and Physical Methods: Potassium *tert*-butoxide, copper iodide, $[Cu(CH_3CN)_4](BF_4)$ and trimethyloxonium tetrafluoroborate (Meerwein salt) were purchased from Sigma–Aldrich. All reagents were used as supplied. The solvents used for metal-complex synthesis and methylations with Meerwein salt were dried and distilled under argon and degassed by common techniques prior to use.

The ^1H and ^{13}C NMR spectra were recorded with a Jeol ECS 400 spectrometer. Elemental analyses were performed with the Perkin–Elmer Analyzer 240 and with a Elementar Vario EL III. Mass spectrometry was performed with an Agilent 6210 ESI-TOF.

Synthesis of Ligands: Ligands **1**,[11b,14a] **2**,[14a] and **3**[14b] and were synthesized according to the methods described in the literature.

3-Methyl-1-[2-(methylthio)phenyl]-4-phenyl-1*H*-1,2,3-triazol-3-ium Tetrafluoroborate (4): The corresponding triazole **4a**[14a] (1 equiv., 2 mmol) and Meerwein salt (1.5 equiv., 3 mmol) were dissolved in dichloromethane (15 mL) under inert gas atmosphere and stirred overnight. Afterwards, the reaction was quenched by the addition of methanol (3 mL) and stirred under air for another 30 min. The reaction mixture was then poured into ethyl ether (200 mL), and

the white precipitate was filtered off, washed several times with ethyl ether, and dried under air to give a white powder in a good yield of 81%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.42 (s, 1 H, triazole-5-H), 7.86–7.82 (m, 2 H, aryl-H), 7.73–7.69 (m, 2 H, aryl-H), 7.62–7.51 (m, 4 H, aryl-H), 7.48–7.44 (m, 1 H, aryl-H), 7.37–7.31 (m, 1 H, aryl-H), 4.33 (s, 3 H, N-CH_3), 2.48 (s, 3 H, S-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 143.7 (triazole-5-C), 134.9, 133.2, 133.1, 132.8, 132.1, 129.9, 129.8, 129.6, 128.1, 128.0, 127.1, 121.7 (all aryl-C), 39.1 (N-CH_3), 16.5 (S-CH_3) ppm. MS (ESI): *m*/*z* = calcd. for [$C_{16}H_{16}N_3S_1^+$] 282.1059; found 282.1063. $C_{16}H_{16}BF_4N_3S{\cdot}0.3CH_2Cl_2$: calcd. C 49.35, H 4.23, N 10.57; found C 49.28, H 3.69, N 10.66.

1-Mesityl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium Tetrafluoroborate (5): The corresponding triazole **5a**[11i] (1 equiv., 2 mmol) and Meerwein salt (1.5 equiv., 3 mmol) were dissolved in dichloromethane (15 mL) under inert gas atmosphere and stirred overnight. Afterwards, the reaction was quenched by the addition of methanol (3 mL) and stirred under air for another 30 min. The reaction mixture was then poured into ethyl ether (200 mL), and the white precipitate was filtered off and washed several times with ethyl ether and dried in air to give a white powder in of 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.32 (s, 1 H, triazole-5-H), 7.78–7.73 (m, 2 H, aryl-H), 7.57–7.50 (m, 3 H, aryl-H), 7.02 (s, 2 H, mesityl-H), 4.37 (s, 3 H, N-CH_3), 2.35 (s,3 H, *para*-mesityl-CH_3), 2.09 (s, 6 H, *ortho*-mesityl-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 144.5 (triazole-5-C), 142.6, 134.7, 132.1, 131.4, 130.0, 129.9, 129.8, 129.6, 121.6 (all aryl-C), 39.2 (N-CH_3), 21.3 (*para*-mesityl-CH_3), 17.3 (*ortho*-mesityl-CH_3) ppm. MS (ESI): *m*/*z* = calcd. for [$C_{18}H_{20}N_3^+$] 278.1657; found 278.1655. $C_{18}H_{20}N_3BF_4{\cdot}0.16CH_2Cl_2$: calcd. C 57.20, H 5.38, N 11.00; found C 57.20, H 6.03, N 11.07.

Syntheses of the Halogenated Biscarbene-Complexes

General Procedure: Tetrakis(acetonitrile)copper(I) tetrafluoroborate and the respective triazolium iodide were suspended in dichloromethane (20 mL) and cooled to –78 °C. After that, potassium *tert*-butoxide suspended in dichloromethane (5 mL) was slowly added to the suspension, and the reaction mixture was stirred overnight and was slowly warmed to room temperature. The reaction mixture was filtered through a pad of Celite, and the volatiles were removed under high vacuum until only about 15% of the solvent was left. The remaining dichloromethane solution was layered with hexanes and allowed to stand at –5 °C for several hours to induce crystallization of the product. The complexes were then obtained as colorless crystals in good yields.

Bis(1-benzyl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene)copper(I) Iodide (6): Synthesized from tetrakis(acetonitrile)copper(I) tetrafluoroborate (1 equiv., 0.15 mmol, 47 mg), triazolium salt **1** (2 equiv., 0.3 mmol, 113 mg), and potassium *tert*-butoxide (3 equiv., 0.45 mmol, 51 mg). The desired product was obtained in 85% yield. (0.127 mmol, 88 mg). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 7.53–7.47 (m, 4 H, aryl-H), 7.42–7.37 (m, 2 H, aryl-H), 7.36–7.30 (m, 4 H, aryl-H), 7.27–7.16 (m, 10 H, aryl-H), 5.56 (s, 4 H, N-CH_2-Ph), 4.04 (s, 6 H, N-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ = 165.1, 148.4, 134.9, 129.8, 129.5, 129.0, 128.9, 128.7, 128.5, 127.8 (all aryl-C), 58.8 (N-CH_2-Ph), 37.5 (N-CH_3) ppm. MS (ESI): *m*/*z* = calcd. for [$C_{32}H_{30}N_6Cu^+$] 561.1822; found 561.1835. $C_{32}H_{30}CuIN_6{\cdot}0.3CH_2Cl_2$: calcd. C 53.36, H 4.27, N 11.49; found C 53.78, H 4.67, N 11.01.

Bis{3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazol-5-ylidene}copper(I) Iodide (7): Synthesized from tetrakis(acetonitrile)-copper(I) tetrafluoroborate (1 equiv., 0.15 mmol, 0.047 g), triazolium salt **2** (2 equiv., 0.3 mmol, 0.123 g), and potassium *tert*-butoxide (3 equiv., 0.45 mmol, 0.051 g). The desired product was obtained in of 79% yield. (0.118 mmol, 89 mg). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 7.53–7.30 (m, 14 H, aryl-H), 7.26–7.26 (m, 4 H, aryl-H), 4.15 (s, 6 H, N-CH_3), 2.18 (s, 6 H, S-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ = 166.1 (carbene-C), 148.3, 137.2, 134.6, 130.8, 130.1, 129.4, 129.1, 127.1, 126.9, 126.6, 125.6 (all aryl-C), 37.9 (N-CH_3), 15.9 (S-CH_3) ppm. MS (ESI): *m*/*z* = calcd. for [$C_{32}H_{30}N_6S_2Cu^+$] 625.1269; found 625.1268. $C_{32}H_{30}N_6S_2CuI$: calcd. C 51.03, H 4.01, N 11.16; found C 50.97, H 4.33, N 10.87.

Syntheses of the Halide-Free Biscarbene Complexes

General Procedure: Tetrakis(acetonitrile)copper(I) tetrafluoroborate and the respective triazolium tetrafluoroborate salt were suspended in dichloromethane (20 mL) and cooled to –78 °C. After that, potassium *tert*-butoxide suspended in dichloromethane (5 mL) was slowly added to the suspension, and the reaction mixture was stirred overnight and was slowly warmed to room temperature. The reaction mixture was filtered through a pad of Celite and the volatiles were removed under high vacuum until only about 15% of the solvent was left. The remaining dichloromethane solution was layered with hexanes and allowed to stand at –5 °C for several hours to induce crystallization of the product. The complexes were obtained as colorless crystals in good yields.

Bis(1-benzyl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene)copper(I) Tetrafluoroborate (8): Synthesized from tetrakis(acetonitrile)copper(I) tetrafluoroborate (1 equiv., 0.15 mmol, 47 mg), triazolium tetrafluoroborate salt **1** (2 equiv., 0.3 mmol, 113 mg), and potassium *tert*-butoxide (3 equiv., 0.45 mmol, 51 mg). The desired product was obtained in 71% yield (0.108 mmol, 69 mg). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 7.51–7.17 (m, 20 H, aryl-H), 5.43 (s, 4 H, N-CH_2-Ph), 4.03 (s, 6 H, N-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ = 162.6 (Carbene-C), 149.1, 134.5, 130.1, 129.4, 129.1, 129.0, 128.6, 127.4 (all aryl-C), 59.1 (N-CH_2-Ph), 37.4 (N-CH_3) ppm. MS (ESI): *m*/*z* = calcd. for [$C_{32}H_{30}N_6Cu^+$] 561.1822; found 561.1823. $C_{32}H_{30}N_6CuBF_4{\cdot}3CH_2Cl_2$: calcd. C 46.51, H 4.01, N 9.30; found C 46.19, H 3.75, N 9.67.

Bis(3-methyl-1,4-diphenyl-1,2,3-triazol-5-ylidene)copper(I) Tetrafluoroborate (9): Synthesized from tetrakis(acetonitrile)copper(I) tetrafluoroborate (1 equiv., 0.15 mmol, 47 mg), triazolium tetrafluoroborate salt **3** (2 equiv., 0.3 mmol, 97 mg), and potassium *tert*-butoxide (3 equiv., 0.45 mmol, 51 mg). The desired product was obtained in 86% yield (0.13 mmol, 82 mg). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 7.87–7.75 (m, 4 H, aryl-H), 7.56–7.49 (m, 6 H, aryl-H), 7.47–7.38 (m, 6 H, aryl-H), 7.35–7.24 (m, 4 H, aryl-H), 4.17 (s, 6 H, N-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ = 162.0 (carbene-C), 149.4, 139.6, 130.3, 130.2, 129.5, 129.2, 123.0 (all aryl-C), 37.7 (N-CH_3) ppm. MS (ESI): *m*/*z* = calcd. for [$C_{30}H_{26}N_6Cu^+$] 533.1509; found 533.1502. $C_{30}H_{26}N_6CuBF_4$: calcd. C 58.03, H 4.22, N 13.53; found C 58.51, H 4.34, N 13.19.

Bis{3-methyl-1-[2-(methylthio)phenyl]-4-phenyl-1,2,3-triazol-5-ylidene}copper(I) Tetrafluoroborate (10): Synthesized from tetrakis(acetonitrile)copper(I) tetrafluoroborate (1 equiv., 0.15 mmol, 47 mg), triazolium salt **4** (2 equiv., 0.3 mmol, 110 mg), and potassium *tert*-butoxide (3 equiv., 0.45 mmol, 51 mg). The desired product was obtained in 78% yield (0.117 mmol, 83 mg). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 7.52–7.31 (m, 15 H, aryl-H), 7.24–7.18 (m, 3 H, aryl-H), 4.13 (s, 6 H, N-CH_3), 2.18 (s, 6 H, S-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ = 166.0 (carbene-C), 148.3, 137.2, 134.6, 130.8, 130.1, 129.4, 129.1, 127.2, 126.9, 126.6, 125.6 (all aryl-C), 37.6 (N-CH_3), 15.8 (S-CH_3) ppm.

Table 6. Crystallographic details.

	4	**5**	**6**·CH_2Cl_2	**11**·CH_2Cl_2
Formula	$C_{16}H_{16}N_3SBF_4$	$C_{18}H_{20}N_3BF_4$	$C_{33}H_{32}N_6ICuCl_2$	$C_{37}H_{40}N_6CuBF_4Cl_2$
M_r	369.19	365.18	773.99	790.00
Crystal system	monoclincic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	10.730(3)	7.9155(17)	14.0666(8)	11.493(3)
b [Å]	15.643(4)	10.153(2)	14.3507(9)	13.516(4)
c [Å]	11.467(3)	21.707(5)	17.3045(10)	13.775(4)
α [°]	90	90	90	103.323(6)
β [°]	116.946(5)	92.726(5)	111.519(2)	94.257(6)
γ [°]	90	90	90	111.738(6)
V [Å^3]	1715.7(8)	1742.6(6)	3249.7(3)	1903.7(9)
Z	4	4	4	2
Densitiy [g cm^{-3}]	1.429	1.392	1.582	1.378
F(000)	760	760	1552	816
Radiation type	Mo-K_α	Mo-K_α	Cu-K_α	Mo-K_α
μ [mm^{-1}]	0.233	0.113	10.176	0.769
Crystal size	0.20 × 0.15 × 0.15	0.38 × 0.10 × 0.10	0.22 × 0.10 × 0.08	0.25 × 0.20 × 0.08
Meas. reflections	16019	13389	20267	21920
Indep. reflections	3130	2969	5482	7381
Obsvd. [$I > 2\sigma(I)$] refl.	2360	2247	4963	5943
R_{int}	0.0522	0.0378	0.0475	0.0462
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$, S	0.589, 0.1603, 1.049	0.0356, 0.909, 1.025	0.0340, 0.0872, 1.060	0.0572, 0.1613, 1.050
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.558, –0.418	0.228, –0.226	1.110, –0.645	0.991, –0.643

MS (ESI): m/z = calcd. for [$C_{32}H_{30}N_6S_2Cu^+$] 625.1269; found 625.1266. $C_{32}H_{30}N_6S_2CuBF_4$·0.3CH_2Cl_2: calcd. C 51.66, H 4.14, N 10.06; found C 51.91, H 4.26, N 10.29.

Bis(1-mesityl-3-methyl-4-phenyl-1,2,3-triazol-5-ylidene)copper(I) Tetrafluoroborate (11): Synthesized from tetrakis(acetonitrile)copper(I) tetrafluoroborate (1 equiv., 0.15 mmol, 47 mg), triazolium salt **5** (2 equiv., 0.3 mmol, 110 mg), and potassium *tert*-butoxide (3 equiv., 0.45 mmol, 0.051 g). The desired product was obtained in 85% yield (0.12 mol, 84.6 mg). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 7.64–7.48 (m, 4 H, aryl-H), 7.45–7.38 (m, 6 H, aryl-H), 6.94 (s, 4 H, mesityl-H), 4.16 (s, 6 H, N-CH_3), 2.40 (s, 6 H, *para*-mesityl-CH_3), 1.83 (s, 12 H, *ortho*-mesityl-CH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ = 165.0 (carbene-C), 149.2, 140.3, 136.1, 134.0, 130.1, 129.3, 129.2, 129.1, 127.0 (all aryl-C), 37.7 (N-CH_3), 21.1 (*ortho*-mesityl-CH_3), 17.1 (*para*-mesityl-CH_3) ppm. MS (ESI): m/z = calcd. for [$C_{36}H_{38}N_6Cu^+$] 617.2454; found 617.2452. $C_{36}H_{38}N_6CuBF_4$·2CH_2Cl_2: calcd. C 52.16, H 4.84, N 9.61; found C 52.23, H 4.65, N 9.80.

General Procedure for Catalytic Experiments: For catalytic experiments, the respective alkynes and azides (1:1) were mixed in a small vial, and the catalyst (0.5–0.005 mol-%) was added. (***Caution:*** *reactions on a large scale, with more than 5 mmol, under neat conditions are highly exothermic!*) The reaction was stirred at room temperature. In the case 0.005 mol-% catalyst loading, the mixture was heated up to 50 °C. The reaction was monitored by ^{1}H NMR spectroscopy until full consumption of the alkyne was achieved or no further reaction was taking place. Conversions were determined by using ^{1}H NMR spectroscopy.

X-ray Crystallography: Data were collected by using either a Bruker Kappa Apex 2 duo or a Bruker Smart AXS diffractometer (Table 6). The measurements were carried out at 100 K by using 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.[15]

CCDC-913981 (for **4**), -911943 (for **5**), -906190 (for **6**), and -906191 (for **11**) 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.

Supporting Information (see footnote on the first page of this article): ORTEP plots for compounds **4** and **5** and NMR spectrum showing the formation of the triazolium salt upon adding phenylacetylene to complex **11**.

Acknowledgments

The authors are grateful to the Fonds der Chemischen Industrie (FCI) for financial support. Paul Kubella is very kindly acknowledged for experimental help.

[1] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.

[2] a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; b) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; c) V. Cesar, S. B.-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; d) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122; e) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18; f) F. A. Glorius, *Top. Organomet. Chem.* **2007**, *21*, 1; g) S. D.-Gonzalez, S. P. Nolan, *Aldrichim. Acta* **2008**, *41*, 43.

[3] a) D. M. Khramov, E. L. Rosen, V. M. Lynch, C. W. Bielawski, *Angew. Chem.* **2008**, *120*, 2299; *Angew. Chem. Int. Ed.* **2008**, *47*, 2267; b) T. Ramnial, I. Mckenzie, B. Gorodetzki, E. M. W. Tsang, J. A. C. Clyburne, *Chem. Commun.* **2004**, 1054; c) U. Siemeling, C. Faerber, C. Bruhn, *Chem. Commun.* **2009**, 98; d) U. Siemeling, C. Faerber, M. Leibold, C. Bruhn, P. Muecke, R. F. Winter, B. Sarkar, M. v. Hopffgarten, G. Frenking, *Eur. J. Inorg. Chem.* **2009**, 4607; e) N. Deibel, D. Schweinfurth, S. Hohloch, B. Sarkar, *Inorg. Chim. Acta* **2012**, *380*, 296.

[4] a) P. Mathew, A. Neels, M. Albrecht, *J. Am. Chem. Soc.* **2008**, *130*, 13534; b) S. Gruendemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473; c) Y. Han, H. V. Huynh, G. K. Tan, *Organometallics* **2007**, *26*, 6581; d) O. Schuster, L. Yang, H. G. Raubenheimer,

M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445; e) E. A. Perez, A. M. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556; f) G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 4869; *Angew. Chem. Int. Ed.* **2010**, *49*, 4759; g) R. H. Crabtree, *Coord. Chem. Rev.* **2013**, *257*, 755; h) K. F. Donnelly, A. Petronilho, M. Albrecht, *Chem. Commun.* **2013**, *49*, 1145; i) J. D. Crowley, A. Lee, K. J. Kiplin, *Aust. J. Chem.* **2011**, *64*, 1118; j) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596.

[5] a) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596; b) C. W. Tornoe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057.

[6] a) L. Liang, D. Astruc, *Coord. Chem. Rev.* **2011**, *255*, 2933; b) H. Struthers, T. L. Mindt, R. Schibli, *Dalton Trans.* **2010**, *39*, 675; c) J. D. Crowley, D. McMorran, in: *Topics in Heterocyclic Chemistry Vol. 22* (Ed.: J. Kosmrlj), Springer, Berlin/Heidelberg, **2012**, pp. 31; d) D. Schweinfurth, N. Deibel, F. Weisser, B. Sarkar, *Nachr. Chem.* **2011**, *59*, 937; e) G. Aromi, L. A. Barrios, O. Roubeau, P. Gamez, *Coord. Chem. Rev.* **2011**, *255*, 485.

[7] a) Y. Li, J. C. Huffman, A. H. Flood, *Chem. Commun.* **2007**, 2692; b) W. W. Yang, L. Wang, Y. W. Zhong, Y. Yao, *Organometallics* **2011**, *30*, 2236; c) D. G. Brown, N. Sanguantrakun, B. Schulz, U. S. Schubert, C. P. Berlinguette, *J. Am. Chem. Soc.* **2012**, *134*, 12354; d) D. Schweinfurth, R. Pattacini, S. Strobel, B. Sarkar, *Dalton Trans.* **2009**, 9291; e) D. Schweinfurth, S. Strobel, B. Sarkar, *Inorg. Chim. Acta* **2011**, *374*, 253.

[8] a) M. Ostermeier, M.-A. Berlin, R. M. Meudtner, S. Demeshko, F. Meyer, C. Limberg, S. Hecht, *Chem. Eur. J.* **2010**, *16*, 10202; b) P. M. Guha, H. Phan, J. S. Kinyon, W. S. Brotherton, K. Sreenath, J. T. Simmons, Z. Wang, R. J. Clark, N. S. Dalal, M. Shatruk, L. Zhu, *Inorg. Chem.* **2012**, *51*, 3465; c) D. Schweinfurth, F. Weisser, D. Bubrin, L. Bogani, B. Sarkar, *Inorg. Chem.* **2011**, *50*, 6114.

[9] a) J. D. Crowley, P. H. Bandeen, *Dalton Trans.* **2010**, *39*, 612; b) D. Urankar, A. Pevec, J. Kosmrlj, *Cryst. Growth Des.* **2010**, *10*, 4920; c) K. A. Stevenson, C. F. C. Melan, O. Fleischel, R. Wang, A. Petitjean, *Cryst. Growth Des.* **2012**, *12*, 5169; d) S.-Q. Bai, S. Leelasubcharoen, X. Chen, L. L. Koh, J.-L. Juo, T. S. A. Hor, *Cryst. Growth Des.* **2010**, *10*, 1715.

[10] a) D. Schweinfurth, C.-Y. Su, S.-C. Wei, P. Braunstein, B. Sarkar, *Dalton Trans.* **2012**, *41*, 12984; b) D. Schweinfurth, S. Demeshko, M. M. Khusniyarov, S. Dechert, V. Gurram, M. R. Buchmeiser, F. Meyer, B. Sarkar, *Inorg. Chem.* **2012**, *51*, 7592.

[11] a) R. Lalrempuia, N. D. McDaniel, H. Müller-Bunz, S. Bernhard, M. Albrecht, *Angew. Chem.* **2010**, *122*, 9959; *Angew. Chem. Int. Ed.* **2010**, *49*, 9765; b) K. J. Kilpin, U. S. D. Paul, A.-L. Lee, J. D. Crowley, *Chem. Commun.* **2011**, *47*, 328; c) R. Saravanakumar, V. Ramkumar, S. Sankararaman, *Organometallics* **2011**, *30*, 1689; d) E. M. Schuster, M. Botoshansky, M. Gandelman, *Dalton Trans.* **2011**, *40*, 8764; e) J. Cai, X. Yang, K. Arumugam, C. W. Bielawski, J. L. Sessler, *Organometallics* **2011**, *30*, 5033; f) E. C. Keske, O. V. Zenkina, R. Wang, C. M. Crudden, *Organometallics* **2012**, *31*, 456; g) B. K. Keitz, J. Bouffard, G. Bertrand, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 8498; h) M. T. Zamora, M. L. Ferguson, R. McDonald, M. Cowie, *Organometallics* **2012**, *31*, 5463; i) D. Canseco-Gonzalez, A. Gniewek, M. Szulmanowicz, H. Müller-Bunz, A. M. Trzeciak, M. Albrecht, *Chem. Eur. J.* **2012**, *18*, 6055.

[12] a) S. Diez-Gonzalez, A. Correa, L. Cavallo, S. P. Nolan, *Chem. Eur. J.* **2006**, *12*, 7558; b) S. Diez-Gonzalez, E. D. Stevens, S. P. Nolan, *Chem. Commun.* **2008**, 4747; c) S. Diez-Gonzalez, S. P. Nolan, *Angew. Chem.* **2008**, *120*, 9013; *Angew. Chem. Int. Ed.* **2008**, *47*, 8881; d) G. M. Pawar, B. Bantu, J. Weckesser, S. Blechert, K. Wurst, M. R. Buchmeiser, *Dalton Trans.* **2009**, 9043; e) P. Li, L. Wang, Y. Zhang, *Tetrahedron* **2008**, *64*, 10825; f) F. Lazreg, A. M. Z. Slawin, C. J. Cazin, *Organometallics* **2012**, *31*, 7969.

[13] M.-L. Teyssot, A. Chevry, M. Traikia, M. El-Ghozzi, D. Avignaut, A. Gautier, *Chem. Eur. J.* **2009**, *15*, 6322.

[14] a) S. Hohloch, C.-Y. Su, B. Sarkar, *Eur. J. Inorg. Chem.* **2011**, 3067; b) T. Nakamura, T. Terashima, K. Ogata, S. Fukuzawa, *Org. Lett.* **2011**, *13*, 620; c) S. Hohloch, B. Sarkar, L. Nauton, F. Cisnetti, A. Gautier, *Tetrahedron Lett.* 2013, DOI: 10.1016/j.tetlet.2013.01.054.

[15] G. M. Sheldrick, *SHELX-97*, *Program for Crystal Structure Refinement*, Göttingen, Germany, **1997**.

Received: January 30, 2013
Published Online: ■

