

Article

Expanding the Scope of Cu(I) Catalyzed “Click Chemistry” with Abnormal NHCs: Three-Fold Click to Tris-Triazoles

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Abstract: Cationic copper(I) complexes [Cu(aIPr^{Ph})(IPr)]I (**3**) and [Cu(aIPr^{Ph})₂]I (**4**) featuring an abnormal *N*-heterocyclic carbene (aNHC) (aIPr^{Ph} = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4-ylidene) and/or an NHC (IPr = 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene) ligand(s) are reported. Treatment of Cu(aIPr^{Ph})I (**2**) with IPr affords complex **3**. Reaction of (IPrPh)I (**1**) (IPrPh = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazolium) with CuI in the presence of K{N(SiMe₃)₂} leads to the formation of **4**. Complexes **3** and **4** represent rare examples of mixed aNHC-NHC and bis-aNHC metal complexes, respectively. They are characterized by elemental analysis, NMR spectroscopic, and mass spectrometric studies. The solid-state molecular structures of **3** and **4** have been determined by single crystal X-ray diffraction analyses. The catalytic activity of **2**, **3**, and **4** has been investigated in the [3+2] cycloaddition of alkynes and organic azides, affording triazole derivatives in an almost quantitative yield. Notably, complexes **2**, **3**, and **4** are excellent catalysts for the three-fold cycloaddition of a tris-azide with various alkynes. This catalytic protocol offers a high yield access to tris-triazoles in a shorter reaction time and considerably reduces the experimental work-up compared to the classical synthetic method.

Keywords: abnormal carbene; click reaction; copper; [3+2] cycloaddition; *N*-heterocyclic carbene; tris-triazoles; structure; catalysis

1. Introduction

N-Heterocyclic carbenes (NHCs) are an important class of carbon-donor neutral ligands in organometallic chemistry and catalysis [1–6]. The versatility of NHCs is manifested in a variety of transition metal-mediated chemical transformations [7–13] as well as in the stabilization of a variety of fascinating molecular compounds featuring low-valent main group elements [14–17]. The success of the NHC-metal partnership (**I**, Chart 1) in catalysis and beyond is largely attributed to the strong σ -donor ability of NHCs, resulting in the formation of a rather robust M–C_(NHC) bond. This has also prompted further interests in the development of different types of carbon-donor ligands with improved donor-acceptor properties [18–23]. A new type of NHCs (**II**, Chart 1) that bind to metals at the imidazol-backbone (i.e., at the C4- or C5-atom) is of a special significance [22,24–32] because experimental and theoretical data suggest that these so-called abnormal NHCs (aNHCs) (**II**) are

stronger σ -donors than classical NHCs (**I**) as well as Bertrand's CAACs (cyclic alkyl amino carbenes) [21,33,34]. Classical NHCs (**I**) are also referred as C2-carbenes or Arduengo's carbenes. As no neutral canonical form without the introduction of formal charges can be written, aNHCs (**II**) are sometimes also described as mesoionic carbenes (MICs) [35]. In 2001, Crabtree et al. [32] reported, albeit as a result of serendipitous product, the first aNHC-complex. In 2009, Bertrand and co-workers reported the first stable metal-free aNHC [27]. Though most of the aNHC-metal complexes (**II**) reported so far were isolated as serendipitous products [22,36], they exhibit excellent catalytic activity, which in many cases surpasses that of their normal counterparts under similar experimental conditions [21,22,30,37–42]. Therefore, the development of new synthetic methods to aNHC-complexes [43,44] is highly desired to further foster their applications in catalysis and beyond [36]. We recently reported the direct C2-arylation of an NHC using a palladium catalyst to give C2-arylated imidazolium salts [45,46], which are found to be suitable precursors to different aNHC-metal complexes [45–49].

The copper-catalyzed alkyne-azide cycloaddition (CuCAAC) reaction (also known as Huisgen 1,3-dipolar cycloaddition) [50–54] represents the flagship transformation of "Click Chemistry" that has found remarkable applications in organic synthesis [55,56], coordination chemistry [57,58], and material science [59–62]. In general, any Cu(I) source can be used as a catalyst, however, the application of well-defined Cu(I)-complexes offers several advantages, including the ease with mechanistic studies, selectivity, low-catalyst loading, and milder reaction conditions [63–65].

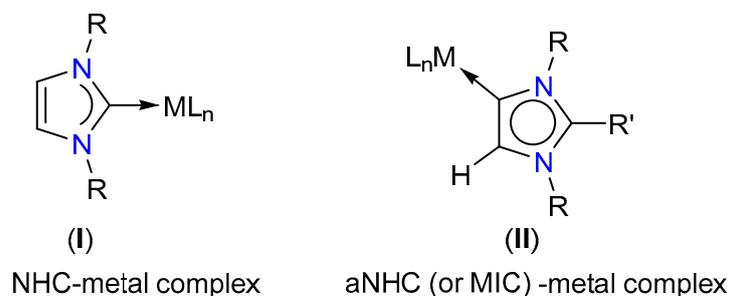


Chart 1. NHC- (**I**) and aNHC- (or MIC) (**II**) complexes.

NHC-Cu(I) complexes have been extensively investigated in CuCAAC reactions [43,44,63,65–71]. Compounds of a general formula $\text{Cu}(\text{NHC})\text{X}$ (**A**) (Chart 2) are among the most widely explored Cu(I) catalysts [43,63,69,71,72]. However, analogs compounds featuring a 1,3-imidazol-derived aNHC (**C**) are very scarce [43,44,73–75]. Similarly, only a handful of other transition metal complexes featuring mixed NHC-aNHC ligands are known [76–85]. Nolan et al. reported cationic copper complexes $[\text{Cu}(\text{NHC})_2]\text{X}$ (**B**, Chart 2) which exhibit enhanced activity in the CuCAAC reactions compared to **A** [65], however analogous derivatives such as **D** containing aNHCs have remained so far unknown. Cazin et al. [86,87] investigated heteroleptic Cu(I) complexes $[\text{Cu}(\text{NHC})(\text{NHC}')]\text{X}$ featuring dissimilar Arduengo-type NHCs, but heteroleptic compounds such as $[\text{Cu}(\text{NHC})(\text{aNHC})]\text{X}$ (**E**) featuring a normal as well as an abnormal NHC are remained so far unexplored.

We report herein the synthesis and characterization of two new cationic copper complexes, $[\text{Cu}(\text{aIPr}^{\text{Ph}})_2]\text{I}$ (**3**) and $[\text{Cu}(\text{aIPr}^{\text{Ph}})(\text{IPr})]\text{I}$ (**4**), featuring 1,3-imidazol-derived carbenes (aIPr^{Ph} = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4-ylidene; IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). The catalytic activity of complexes $\text{Cu}(\text{aIPr}^{\text{Ph}})\text{I}$ (**2**) [45], **3**, and **4** has been examined in CuCAAC reactions to yield various triazoles. Tris-triazoles are important ligands in coordination chemistry [57,58,88,89] and serve as building blocks for the preparation of multitopic triazole-based aNHC compounds [90,91]. Interestingly, compounds **2**, **3**, and **4** are also found to be excellent catalysts for the cycloaddition of tris-azides with alkynes, leading to the formation of tris-triazoles in an excellent yield.

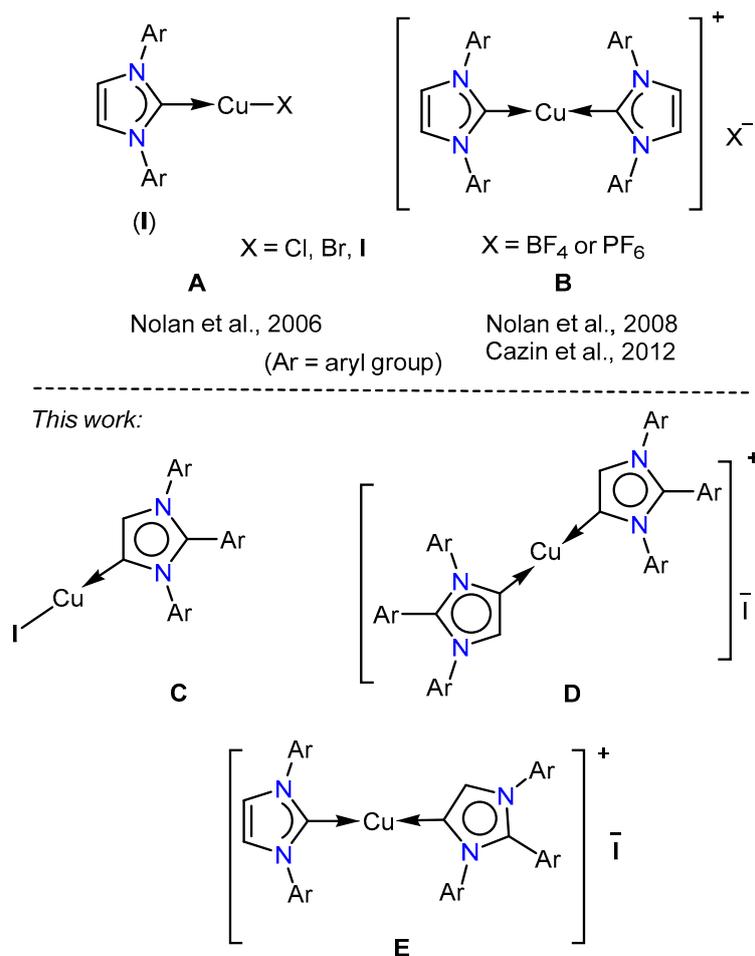


Chart 2. Neutral $\text{Cu}(\text{NHC})\text{X}$ (**A**) and cationic $[\text{Cu}(\text{NHC})_2]\text{X}$ (**B**) compounds and their aNHC-counterparts (**C–E**).

2. Results and Discussion

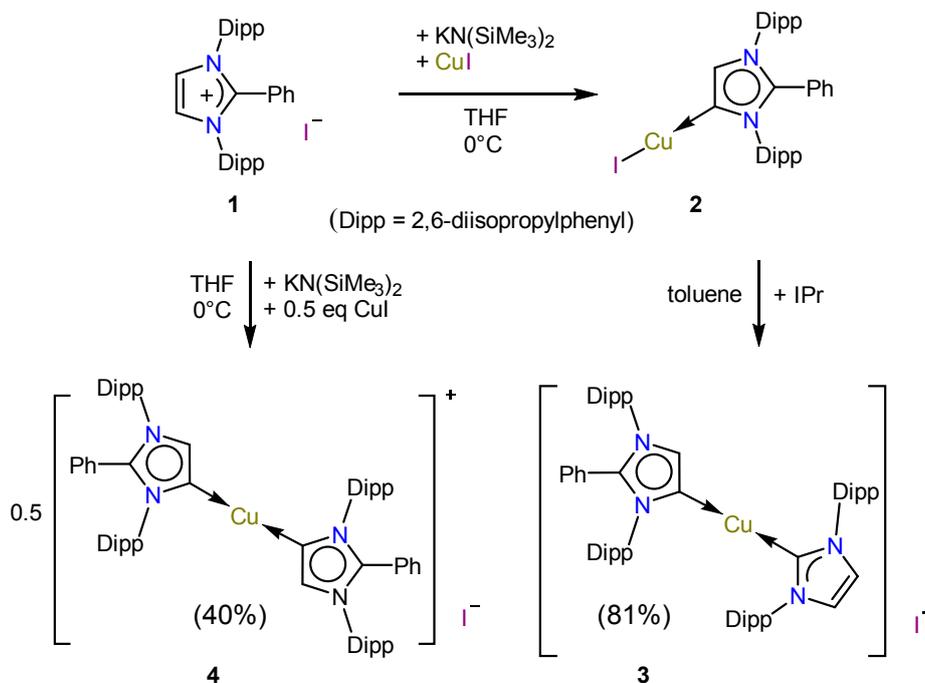
2.1. Synthesis

Treatment of a THF suspension of $(\text{IPrPh})\text{I}$ (**1**) and CuI with one eq of potassium hexamethyldisilazide (KHMDs) (Scheme 1) leads to the formation of complex $\text{Cu}(\text{aIPr}^{\text{Ph}})\text{I}$ (**2**) (91%) [45]. Reaction of compound **2** with one equivalent of free IPr clearly affords the heteroleptic copper complex $[\text{Cu}(\text{aIPr}^{\text{Ph}})(\text{IPr})]\text{I}$ (**3**) (81%), containing both aNHC and NHC ligands. Similarly, treatment of a mixture of **1** and CuI in a 2:1 molar ratio with two equivalents of KHMDs gives the complex $[(\text{aIPr}^{\text{Ph}})_2\text{Cu}]\text{I}$ (**4**) (40%). Compounds **2**, **3**, and **4** are colorless crystalline solids that are stable under an inert gas atmosphere.

2.2. Characterization

Compounds **3** and **4** have been characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. In addition, the solid-state molecular structures of **3** (Figure 1) and **4** (Figure 2) have been unequivocally determined by single crystal X-ray diffraction analyses. The ESI mass spectrum of each of **3** (915.5 amu) and **4** (991.6 amu) shows the molecular ion peak that corresponds to the respective cationic moiety. As expected, the ^1H NMR spectrum of **3** exhibit two doublets and one septet for the isopropyl groups of IPr ligand. However, due to the lack of the C2-symmetry, the isopropyl groups of aIPr^{Ph} ligand show four doublets, one of them overlaps with a doublet of IPr ligand, and two septets. The imidazol-backbone protons can be identified as a singlet at δ 6.54 (for aIPr^{Ph}) and 7.78 (for IPr) ppm. Similarly, the ^1H NMR spectrum of **4** exhibits one pseudo-

triplet, which arises due to two overlapping doublets, and two doublets for methyl groups along with a multiplet for the methine protons of HCMe₂ groups. The imidazol-backbone protons appear as a singlet at δ 7.08 ppm. The ¹³C NMR spectra of compounds **3** and **4** exhibit corresponding signals for the IPr and aIPr^{Ph} ligands, which are consistent with their ¹H NMR resonances. Compound **3** exhibits ¹³C NMR resonances for the carbene carbon atoms at δ 159.53 (*C*_{(aIPr^{Ph})-Cu}) and 180.99 (*C*_{(IPr)-Cu}) ppm. The ¹³C NMR spectrum of **4** shows a signal at δ 161.05 ppm, which can be assigned for the abnormal carbene carbon atom (*C*_{(aIPr^{Ph})-Cu}).



Scheme 1. Synthesis of aNHC-Cu(I) complexes **2**, **3**, and **4**.

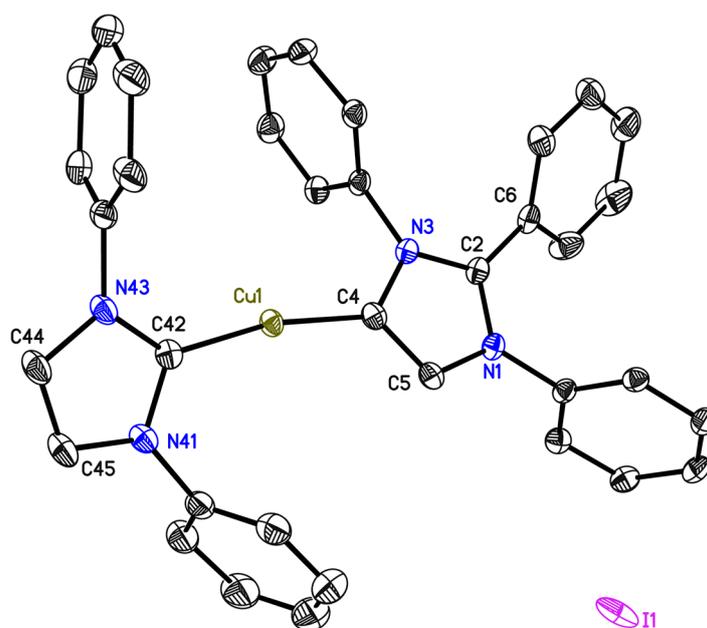


Figure 1. Molecular structure of [Cu(aIPr^{Ph})(IPr)]I (**3**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): C42–Cu1, 1.9041(19); C4–Cu1, 1.9005(19); C4–C5, 1.365(3); C44–C45, 1.341(3); C42–Cu1–C4, 168.45(9); N43–C42–N41, 104.06(16); N43–C44–C45, 107.44(18); N3–C4–C5, 102.99(16); N3–C2–N1, 106.49(16).

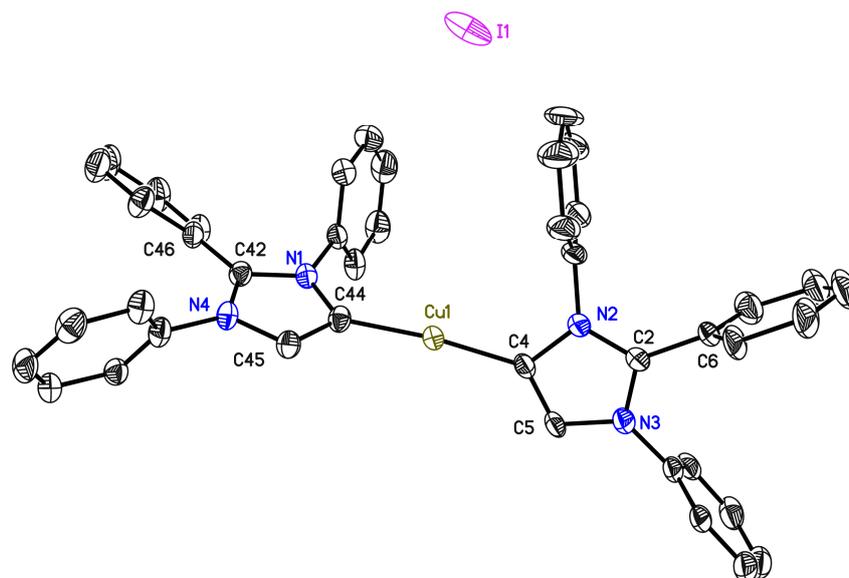


Figure 2. Molecular structure of $[\text{Cu}(\text{aIPr}^{\text{Ph}})_2]\text{I}$ (**4**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (\AA) and bond angles ($^\circ$): C44–Cu1, 1.914(3); C4–Cu1, 1.914(3); C4–C5, 1.356(4); C44–C45, 1.363(4); C44–Cu1–C4, 172.66(12); N1–C42–N4, 106.3(2); N2–C4–C5, 102.7(2); N3–C2–N2, 107.4(3).

The molecular structure of **3** (Figure 1) features a two-fold coordinated copper atom with a considerably bent C4–Cu1–C42 bond angle of $168.45(9)^\circ$. The C42–Cu1 ($1.9041(19) \text{\AA}$) and C4–Cu1 ($1.9005(19) \text{\AA}$) bond lengths, respectively for the normal (IPr) and abnormal (aIPr^{Ph}) NHC are comparable. The C4–C5 ($1.365(3) \text{\AA}$) bond length of **3** is slightly longer than that of the C44–C45 ($1.341(3) \text{\AA}$), indicating the carbene nature of the C4-carbon atom. Similarly, the N3–C4–C5 bond angle ($102.99(16)^\circ$) is smaller than the corresponding N43–C44–C45 ($107.41(18)^\circ$) bond angle, highlighting the impact of the position of the carbene carbon (C4) atom on the structural coordinates. This becomes more obvious when N43–C42–N41 ($104.06(16)^\circ$) and N3–C2–N1 ($106.49(16)^\circ$) bond angles are compared, where only the former features a carbene carbon atom.

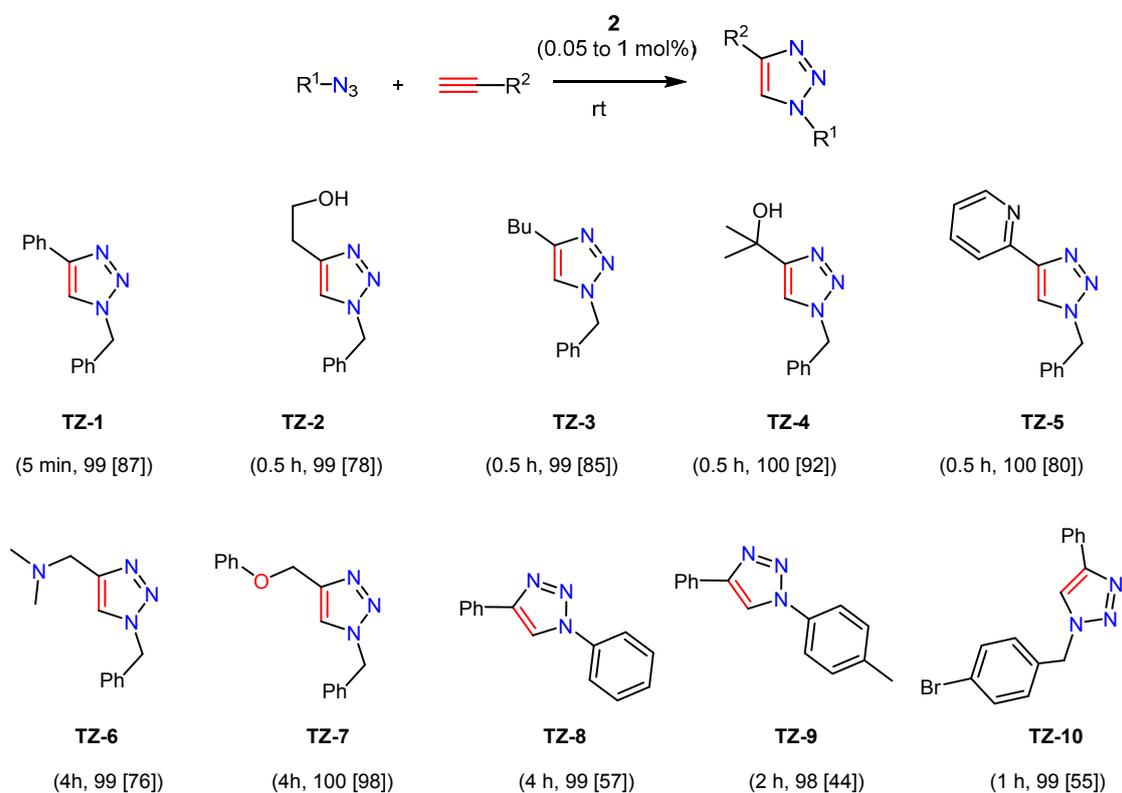
The molecular structure of **4** (Figure 2) features a two-coordinated copper atom with a slightly bent C4–Cu1–C44 bond angle ($172.66(12)^\circ$). The C4–Cu1 ($1.914(3) \text{\AA}$) and C44–Cu1 ($1.914(3) \text{\AA}$) bond lengths are slightly longer than that of **3**, whereas other structural features are comparable with compound **3**.

2.3. Catalysis

The reaction of phenyl acetylene and benzyl azide was chosen as a benchmark reaction for assessing the catalytic activity of compounds **2**, **3**, and **4**. The progress of the reaction was monitored by ^1H NMR spectroscopic analysis. A neat solution of benzyl azide (1 mmol) and phenyl acetylene (1.1 mmol) and an appropriate amount of the catalyst was stirred at room temperature. The details of catalysts screening are provided in the supporting information. Compound **2** is highly active and quantitative conversion was observed after 5 min with a catalyst loading of 1 mol % (Table S1, entry 1). However, under similar experimental conditions no conversion was seen with compound **3** or **4** even after 1 h (Table S1, entries 5 and 6). ^1H NMR analysis after 5 h indicated 99% conversion with **3** (Table S1, entry 7), however compound **4** required 15 h to achieve 80% conversion (Table S1, entry 8). This indicates that all three compounds are active catalysts; however, **3** and **4** need a higher induction period. In order to further compare the catalytic activity of **2**, **3**, and **4**, different alkyne substrates were treated with benzyl azide at room temperature using 1 mol % of the catalyst loading. The findings clearly suggest the following reactivity order $2 > 3 > 4$. Recent studies have shown that dinuclear copper species are the active catalysts in the CuCAAC reactions, which can be readily generated with **2** as it features a iodide ligand as an easy leaving group [52,56,64]. Cationic

[(NHC)₂Cu]X (B) (X = BF₄ or PF₆) [65] complexes are also active catalysts as one carbene ligand can easily undergo exchange reaction with an azide to afford the desired active catalyst. In view of the strong σ -donor ability of aNHC (aIPr^{Ph}), the generation of mono-ligated (aIPr^{Ph})Cu species from **4** seems demanding, and therefore rationalizes its slow reactivity due to a longer induction period in comparison with **2** and **3**.

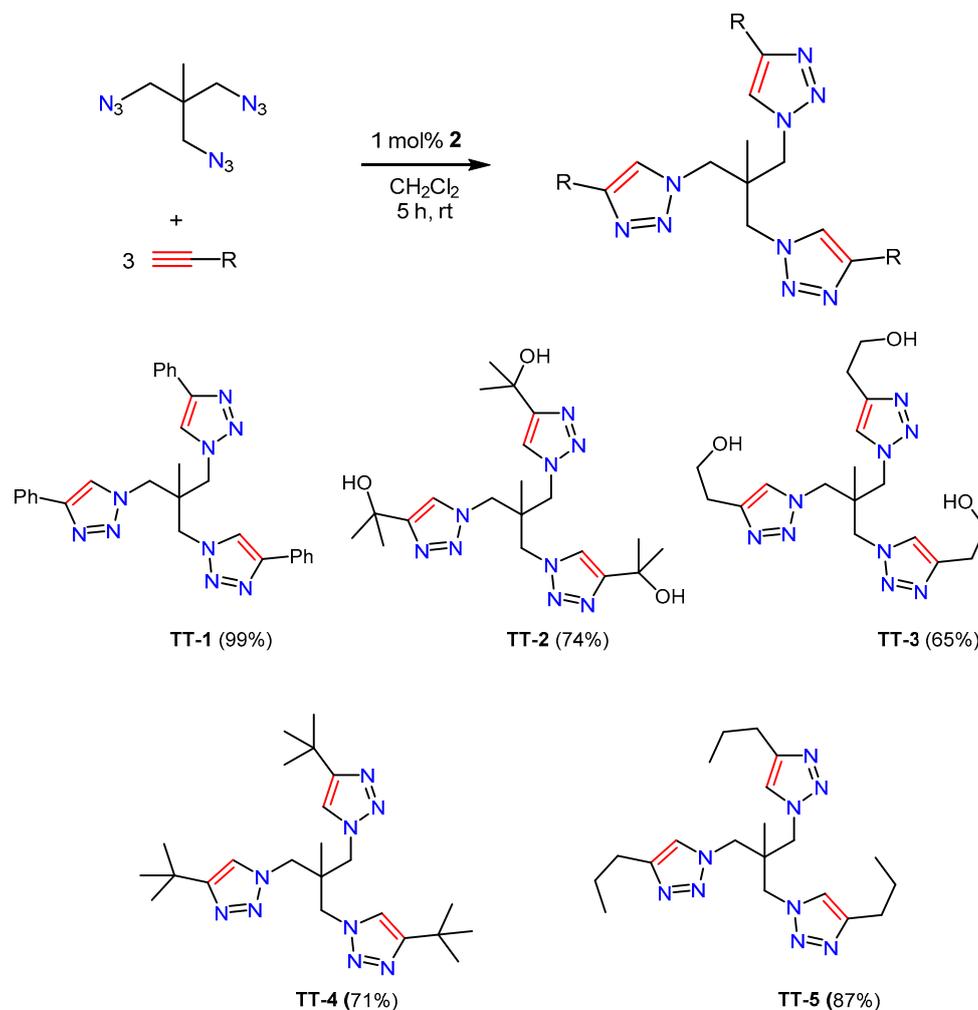
Having recognized the highest activity of **2**, we examined further cycloaddition reactions with different substrates using **2** as a precatalyst. With the lowering of the catalyst loading to 0.5 (entry 2), 0.1 (entry 3), and 0.05 (entry 4) mol %, quantitative conversion was achieved after 5 min, 1 h, and 3 h, respectively (Table S1). However, only 56% conversion was reached after 4 h when 0.01 mol % of **2** was employed, indicating diminished reactivity at further lowering of the catalyst loading. The scope of **2** with other substrates were investigated with 0.5 (TZ-1–TZ-5) and 0.05 (TZ-6–TZ-10) mol % of the loading at room temperature (Scheme 2).



Scheme 2. Scope of the [3+2] cycloaddition of azides and alkynes with compound **2**. Reaction conditions: azide (1 mmol), alkyne (1.1 mmol), **2** (1, 0.5, or 0.05 mol %), rt (25 °C), solvent-free. Reaction time, NMR yield [Isolated yield] for triazoles **TZ-1** to **TZ-10**.

Tris-triazoles are important building blocks in materials science and offer significant promises as ligands in coordination chemistry and catalysis [57]. Note that, in comparison with simple triazoles such as **TZ-1–TZ-10**, synthetic protocols to tris-triazoles are quite demanding [92,93]. In general, copper sulphate (CuSO₄) is used as a pre-catalyst in the synthesis of tris-triazoles and a mixture of water and *tert*-butanol is the solvent of choice [58]. In the presence of a base, this reaction leads to the formation of tris-triazoles. A major drawback of this classical procedure is the elaborate experimental work-up that is required for the complete removal of residual copper contents from the product [50,94]. Excellent solubility and stability of **2–4** in dichloromethane, coupled with their high catalytic activity in standard “Click Reactions” (Scheme 2) encouraged us to probe their utility in the synthesis of tris-triazoles via the CuCAAC reaction. Interestingly, all compounds **2**, **3**, and **4** are active catalysts and affords tris-triazoles via three-fold click reactions of a tris-azide with a variety of alkynes (Scheme 3). This facile procedure is more atom-economic (three-clicks with 0.5 to 1 mol % of the

catalyst loading) and shortens the experimental work-up without compromising the reaction outcome. The products show a negative test for the presence of copper. In a general procedure, a dichloromethane solution of a tris-azide and an alkyne is loaded with 1 mol % of the catalyst and stirred at room temperature for 5 h. With the catalyst loading of 0.5 mol % (Table S2, entry 2), only a slight lowering of the yield (91%) was observed. The product precipitated out on addition of cold pentane and was isolated by filtration. Five different acetylenes were successfully employed to prepare tris-triazoles **TT-1**–**TT-5**. The highest yield was obtained with phenylacetylene (Table S2, entry 1) and compound **2** afforded the best results.



Scheme 3. Synthesis of tris-triazoles **TT-1**–**TT-5** via the [3+2] cycloaddition of a tris-azide with alkynes catalyzed by **2**.

3. Materials and Methods

Unless stated otherwise, all syntheses and manipulations were carried out under an inert atmosphere of dry argon or nitrogen gas using *Schlenk* line techniques or a glove box. All solvents were dried over appropriate drying agents, distilled, and stored over 3 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 300 or a Bruker Avance I 500 spectrometer (Bruker Corporation, Billerica, MA, USA) using the residual solvent peak as reference [95]: δ_{H} [C_6D_6 7.16, CDCl_3 7.26 (Deutero GmbH, Kastellaun, Germany); CD_2Cl_2 5.35 (Carl Roth GmbH + Co. KG, Karlsruhe, Germany); THF-*d*₅ 3.58, 1.73 (Sigma-Aldrich, St. Louis, MO, USA)] ppm and δ_{C} [C_6D_6 128.06, CDCl_3 77.16, CD_2Cl_2 53.84, THF-*d*₅ 61.50, 126.28] ppm at 298 K. EI-mass spectra were recorded with a Finnigan MAT 95 (70 eV) (Thermo Finnigan MAT GmbH, Bremen, Germany). Organic azides were prepared by literature methods [43]. All alkynes were purchased from commercial suppliers (Sigma-Aldrich, St. Louis, MO, USA or Acros Organics, Thermo Fisher Scientific, Geel, Belgium) and

used without further purification. Compounds (IPrPh)I (**1**) and Cu(aIPr^{Ph})I (**2**) were synthesized according to the reported procedure [45].

3.1. Synthesis of Complexes **3** and **4**

[Cu(aIPr^{Ph})(IPr)]I (3**):** To a 100 mL Schlenk flask equipped with Cu(aIPr^{Ph})I (**2**) (1.0 g, 1.53 mmol) and IPr (594 mg, 1.53 mmol) was added 20 mL of toluene. The reaction mixture was stirred overnight at room temperature. Filtration through a plug of Celite® (Carl Roth GmbH + Co. KG, Karlsruhe, Germany) afforded a clear solution. The volatiles were removed under vacuum to obtain the desired compound **3** as a colorless solid (1.29 g, 81%). Elemental analysis (%) calcd. for **3**, C₆₀H₇₆N₄CuI (1043): C, 69.05; H, 7.34; N, 5.37; found: C, 69.35; H, 7.08; N, 5.02. ¹H-NMR (300 MHz, 298 K, THF-*d*₈): δ 0.69 (d, *J* = 6.79 Hz, 6H, CHMe₂); 0.86 (d, *J* = 6.86 Hz, 6H, CHMe₂); 1.00 (d, *J* = 6.85 Hz, 6H, CHMe₂); 1.13 (t, *J* = 6.65 Hz, 18H, CHMe₂); 1.20 (d, 12H, *J* = 6.85 Hz, CHMe₂); 2.24 (m, 2H, CHMe₂); 2.36 (m, 2H, CHMe₂); 2.62 (sept, *J* = 6.85 Hz, 4H, CHMe₂); 6.55 (s, 1H, HNC_(aIPr^{Ph})C); 6.84 (d, *J* = 7.38 Hz, 2H, *o*-C₆H₅); 7.11–7.16 (m, 4H, *p*-C₆H₃), 7.19–7.40 (m, 8H, *m*-C₆H₃), 7.45–7.55 (m, 3H, *m*-C₆H₅, *p*-C₆H₅); 7.78 (s, 2H, NCHCHN) ppm. ¹³C{¹H}-NMR (75 MHz, 25 °C, THF-*d*₈): δ 22.81 (CHMe₂); 22.94 (CHMe₂); 24.48 (CHMe₂); 25.34 (CHMe₂, CHMe₂); 26.29 (CHMe₂); 29.73 (CHMe₂); 29.83 (CHMe₂); 30.05 (CHMe₂); 123.67 (*o*-C₆H₅); 125.20 (*p*-C₆H₃); 125.58 (*p*-C₆H₃); 126.05 (*m*-C₆H₃); 126.08 (NCH); 129.76 (*p*-C₆H₅); 129.98 (*o*-C₆H₅); 131.47, 131.81 (*m*-C₆H₅, *p*-C₆H₅); 132.09 (NCH); 132.48, 132.57, 136.02 (*o*-C₆H₃); 136.44, 145.17 (*o*-C₆H₅); 145.80, 145.89, 146.58 (*ipso*-C₆H₅); 159.53 (C_(aIPr^{Ph})-Cu); 180.99 (C_(IPr)-Cu) ppm. ESI-MS *m/z* [%]: 915.5 [(M-I)]⁺.

Synthesis of [Cu(aIPr^{Ph})₂]I (4**):** To a 100 mL Schlenk flask equipped with (IPrPh)I (**1**) (1.0 g, 1.69 mmol), KN(SiMe₃)₂ (337 mg, 1.69 mmol), and CuI (161 mg, 0.84 mmol) was added 30 mL of pre-cooled THF at 0 °C. The reaction mixture was brought to room temperature and further stirred overnight. Filtration through a plug of Celite® afforded a clear solution. The volatiles were removed under vacuum to obtain an off-white solid, which was washed with 20 mL of *n*-pentane and dried to yield compound **4** (0.75 g, 40%). Elemental analysis (%) calcd for **4**, C₆₆H₈₀N₄CuI (1119): C, 70.79; H, 7.20; N, 5.00; found: C, 71.21; H, 7.11; N, 4.72. ¹H-NMR (500 MHz, 298 K, THF-*d*₈): δ 1.01 (t, *J* = 6.9 Hz, 24H, HCMe₂); 1.12 (d, *J* = 6.8 Hz, 12H, HCMe₂); 1.22 (d, *J* = 6.8 Hz, 12H, HCMe₂); 2.47–2.61 (m, 8H, CHMe₂); 6.91 (d, *J* = 7.4 Hz, 4H, *o*-C₆H₃); 7.08 (s, 2H, NCH); 7.18 (t, *J* = 7.5 Hz, 4H, *m*-C₆H₃); 7.23 (d, *J* = 7.8 Hz, 4H, *m*-C₆H₃); 7.30 (t, *J* = 7.5 Hz, 2H, *p*-C₆H₃); 7.38 (m, 6H, *m*-C₆H₃, *p*-C₆H₃); 7.54 (t, *J* = 7.8 Hz, 2H, *p*-C₆H₃) ppm. ¹³C{¹H}-NMR (125.76 MHz, 25 °C, THF-*d*₈): δ 22.89 (CHMe₂); 22.95 (CHMe₂); 25.90 (CHMe₂); 26.38 (CHMe₂); 29.91 (CHMe₂); 30.08 (CHMe₂); 124.07, 125.55, 125.95, 129.68 (*m*-C₆H₃); 130.10 (*o*-C₆H₃); 131.51 (*p*-C₆H₃); 131.73 (NCH); 132.18 (*p*-C₆H₃); 132.33 (*p*-C₆H₃); 132.43 (*o*-C₆H₃); 136.65 (*o*-C₆H₃); 145.84 (*ipso*-C₆H₃); 146.01 (*ipso*-C₆H₃); 161.05 (C-Cu) ppm. ESI-MS *m/z* [%]: 991.6 [(M-I)]⁺.

3.2. Crystal Structure Determinations

The data of structures **3**, **4** (Table S3), **TZ-2**, and **TZ-4** (Table S4) were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a microfocus source [96] and for structure **TZ-3** (Table S4) on a Bruker D8 TXS-Mo-rotating anode. All data were integrated with SAINT [97]. A multi-scan absorption correction for all structures and a 3λ correction [98] for structures **3**, **4**, **TZ-2**, and **TZ-4** were applied using SADABS [99]. The structures were solved by SHELXT [100] and refined on *F*² using SHELXL [101] in the graphical user interface ShelXle [102].

3.3. General Procedure for Catalysis

Method A. A reaction vessel was charged with the azide (1 mmol), alkyne (1.1 mmol), and the appropriate catalyst and stirred without any added solvent (neat) at rt (25 °C) for the appropriate period. The conversion was monitored by the ¹H NMR spectroscopic analysis.

Method B. To a reaction vessel containing the azide (1 mmol), alkyne (1.1 mmol), and the appropriate catalyst was added 5 mL dichloromethane and stirred at rt for the appropriate period. The conversion was monitored by the ¹H NMR spectroscopic analysis.

4. Conclusions

In conclusion, the synthesis and characterization of two new aNHC-copper complexes **3** and **4** featuring a 1,3-imidazol-4-ylidene type carbene(s) are reported. The catalytic activity of compounds **2**, **3**, and **4** has been explored for the [3+2] cycloaddition reactions of alkynes with azides. Compound **2** has been found to be extremely reactive, leading to a high TON value of 2000 (entry 4 Table S1) and a TOF value of 2400 h⁻¹ (entry 2, Table S1). These compounds are also very efficient for the “three-fold [3+2] cycloaddition” of tris-azides with alkynes, enabling very facile access to tris-triazole derivatives.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/9/262/s1. Synthesis and characterization details of copper complexes **3** and **4** and catalysis products; ¹H and ¹³C NMR spectra of complexes **3**, **4**, and triazoles, and tris-triazoles; experimental details of catalytic procedures; and details of single crystal X-ray diffraction studies are provided in the supporting information. Single crystal X-ray crystallographic data of **3**, **4**, **TZ-2**, **TZ-3**, and **TZ-4** can also be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif, CCDC number: 1560171-1560175.

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