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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(SiMe$_3$)$_2$} 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].

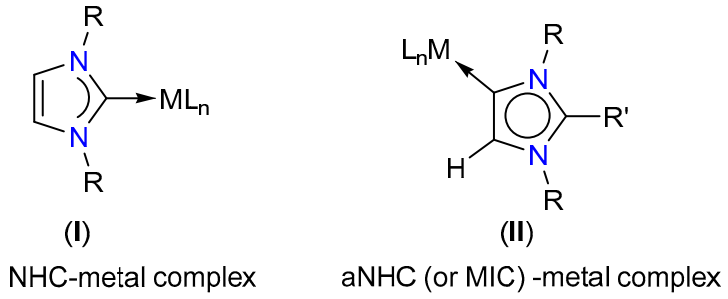


Chart 1. NHC- (**I**) and aNHC- (or MIC) (**II**) complexes.

NHC-Cu(I) complexes have been extensively investigated in CuCAAC reactions [43,44,63,65–71]. Compounds of a general formula Cu(NHC)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 $[Cu(NHC)_2]X$ (**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 [Cu(NHC)(NHC')]X featuring dissimilar Arduengo-type NHCs, but heteroleptic compounds such as [Cu(NHC)(aNHC)]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, $[Cu(aIPr^{Ph})_2]I$ (**3**) and $[Cu(aIPr^{Ph})(IPr)]I$ (**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 $Cu(aIPr^{Ph})I$ (**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.

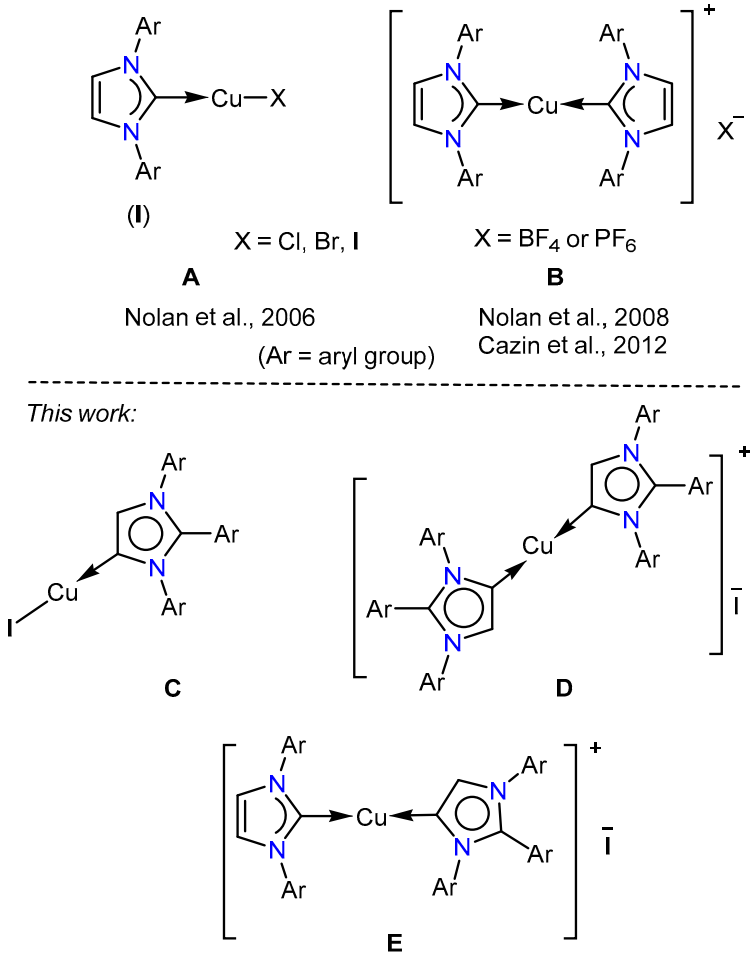


Chart 2. Neutral Cu(NHC)X (**A**) and cationic [Cu(NHC)$_2$]X (**B**) compounds and their aNHC-counterparts (**C**–**E**).

2. Results and Discussion

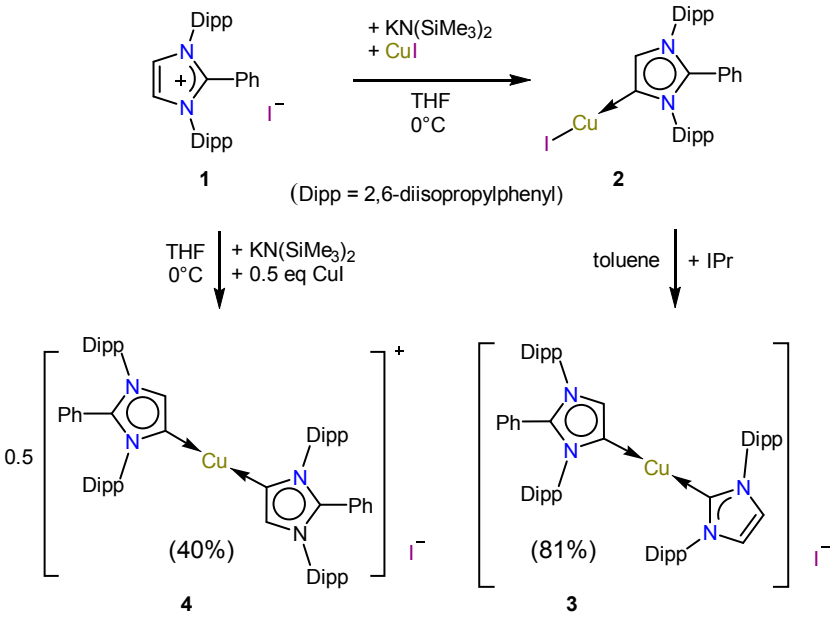
2.1. Synthesis

Treatment of a THF suspension of (IPrPh)I (**1**) and CuI with one eq of potassium hexamehtyldisilazide (KHMDS) (Scheme 1) leads to the formation of complex Cu(aIPr^{Ph})I (**2**) (91%) [45]. Reaction of compound **2** with one equivalent of free IPr cleanly affords the heteroleptic copper complex [Cu(aIPr^{Ph})(IPr)]I (**3**) (81%), containing both aNHC and NHC ligands. Similarly, treatment of a mixture of **1** and CuI in a 2:1 molar ration with two equivalents of KHMDS gives the complex [(aIPr^{Ph})$_2$Cu]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, ^{1}H 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 ^{1}H 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 ^{1}H 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 $HCMe_2$ groups. The imidazol-backbone protons appear as a singlet at δ 7.08 ppm. The ^{13}C NMR spectra of compounds **3** and **4** exhibit corresponding signals for the IPr and aIPr^{Ph} ligands, which are consistent with their ^{1}H NMR resonances. Compound **3** exhibits ^{13}C NMR resonances for the carbene carbon atoms at δ 159.53 ($C_{(aIPrPh)}$–Cu) and 180.99 ($C_{(IPr)}$–Cu) ppm. The ^{13}C NMR spectrum of **4** shows a signal at δ 161. 05 ppm, which can be assigned for the abnormal carbene carbon atom ($C_{(aIPrPh)}$–Cu).



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

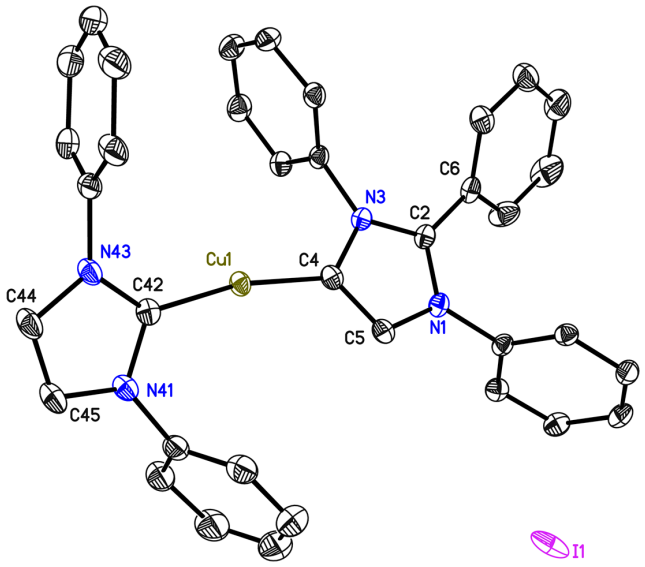


Figure 1. Molecular structure of [Cu(aIPr^{Ph})(IPr)]I (**3**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): C42–Cu1, 1.9041(19); C4–Cu1, 1.9005(19); C4–C5, 1.365(3); 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).

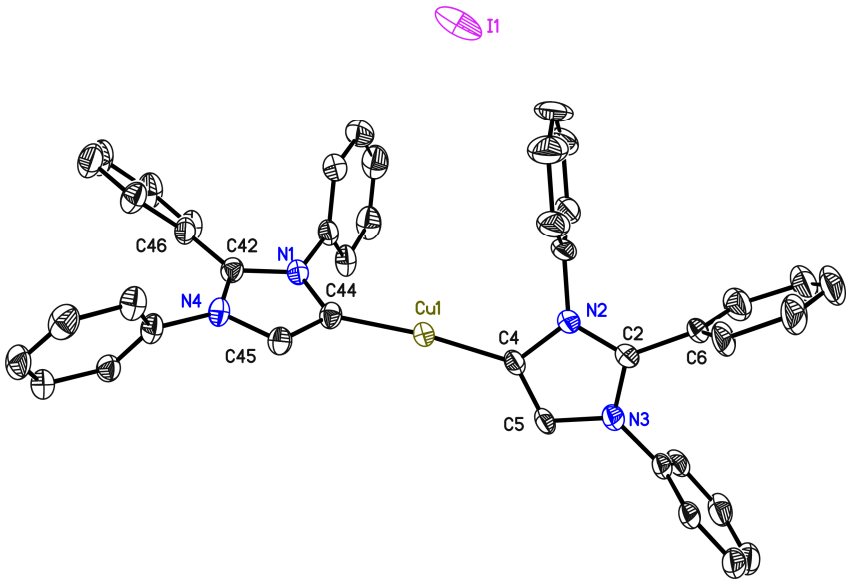


Figure 2. Molecular structure of [Cu(aIPr^{Ph})$_2$]I (**4**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): C44–Cu1, 1.914(3); C4–Cu1, 1.914(3); C4–C5, 1.356(4); 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)°. The C42–Cu1 (1.9041(19) Å) and C4–Cu1 (1.9005(19) Å) bond lengths, respectively for the normal (IPr) and abnormal (aIPr^{Ph}) NHC are comparable. The C4–C5 (1.365(3) Å) bond length of **3** is slightly longer than that of the C44–C45 (1.341(3) Å), indicating the carbene nature of the C4-carbon atom. Similarly, the N3–C4–C5 bond angle (102.99(16)°) is smaller than the corresponding N43–C44–C45 (107.41(18)°) 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)°) and N3–C2–N1 (106.49(16)°) bond angles are compared, where only the former features a carbene carbon atom.

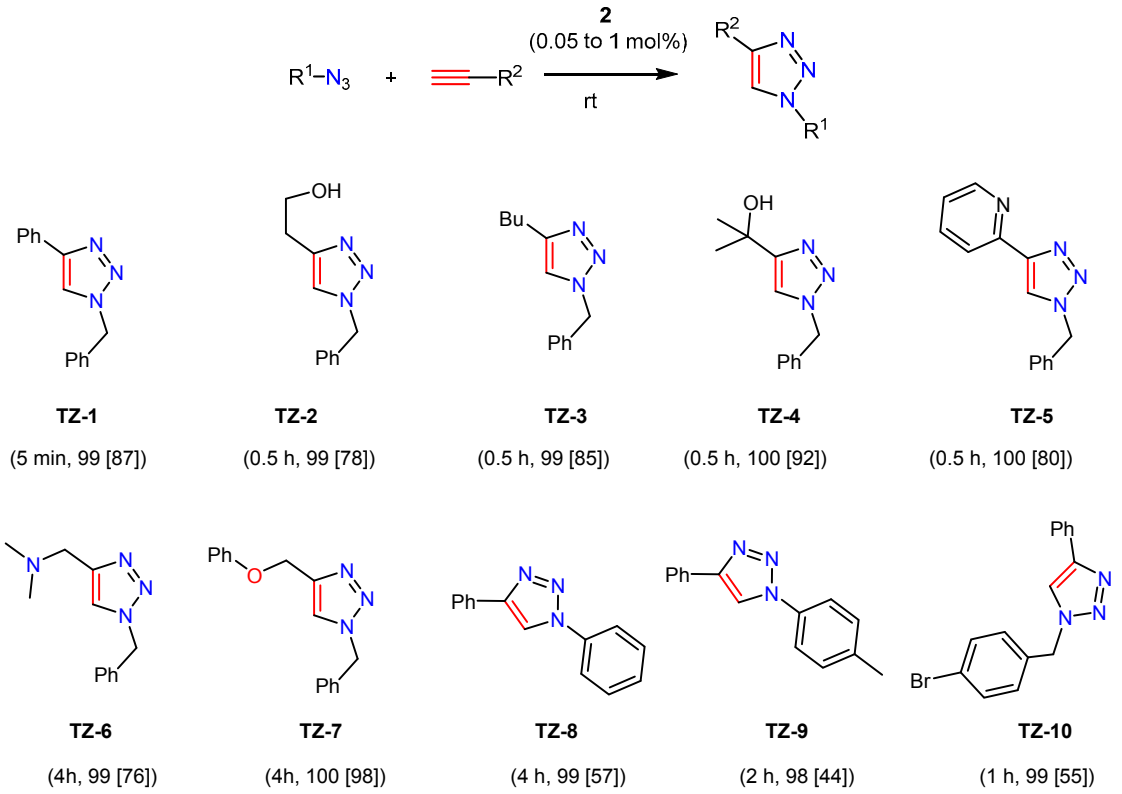
The molecular structure of **4** (Figure 2) features a two-coordinated copper atom with a slightly bent C4–Cu1–C44 bond angle (172.66(12)°). The C4–Cu1 (1.914(3) Å) and C44–Cu1 (1.914(3) Å) bond lengths are slightly longer than that of **3**, whereas other structural features are comparable with compound **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 ^{1}H 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). ^{1}H 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 = BF_4 or PF_6) [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**.

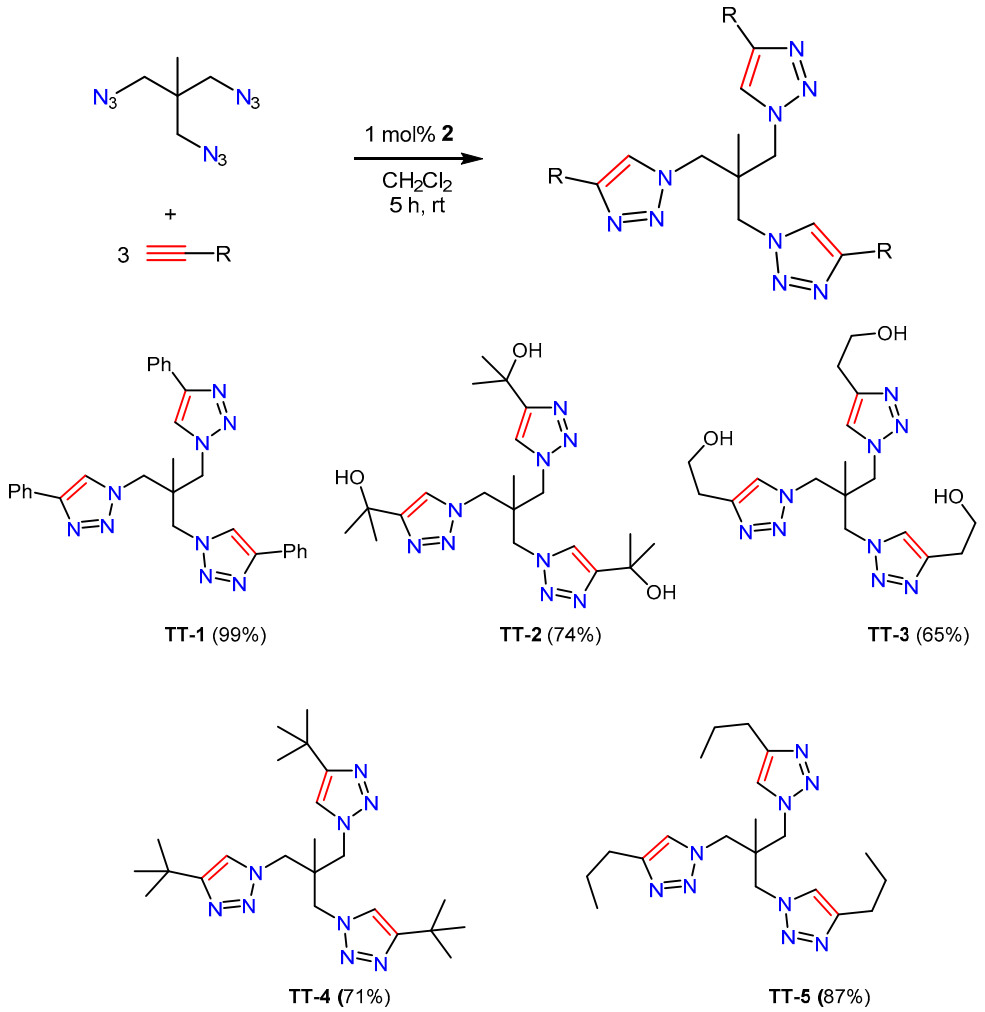
Having recognized the highest activity of **2**, we examined further cycloaddition reactions with different substrates using **2** as a precatalyst. With the lowering of the catalyst loading to 0.5 (entry 2), 0.1 (entry 3), and 0.05 (entry 4) mol %, quantitative conversion was achieved after 5 min, 1 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 ($CuSO_4$) 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. ^{1}H 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_8 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_8 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**, $C_{60}H_{76}N_4CuI$ (1043): C, 69.05; H, 7.34; N, 5.37; found: C, 69.35; H, 7.08; N, 5.02. ^{1}H-NMR (300 MHz, 298 K, THF-d_8): δ 0.69 (d, J = 6.79 Hz, 6H, $CHMe_2$); 0.86 (d, J = 6.86 Hz, 6H, $CHMe_2$); 1.00 (d, J = 6.85 Hz, 6H, $CHMe_2$); 1.13 (t, J = 6.65 Hz, 18H, $CHMe_2$); 1.20 (d, 12H, J = 6.85 Hz, $CHMe_2$); 2.24 (m, 2H, $CHMe_2$); 2.36 (m, 2H, $CHMe_2$); 2.62 (sept, J = 6.85 Hz, 4H, $CHMe_2$); 6.55 (s, 1H, $HNC_{(aIPrPh)}C$); 6.84 (d, J = 7.38 Hz, 2H, o-C_6H_5); 7.11–7.16 (m, 4H, p-C_6H_3), 7.19–7.40 (m, 8H, m-C_6H_3), 7.45–7.55 (m, 3H, m-C_6H_5, p-C_6H_5); 7.78 (s, 2H, NCHCHN) ppm. $^{13}C\{^1H\}$-NMR (75 MHz, 25 °C, THF-d_8): δ 22.81 ($CHMe_2$); 22.94 ($CHMe_2$); 24.48 ($CHMe_2$); 25.34 ($CHMe_2$, $CHMe_2$); 26.29 ($CHMe_2$); 29.73 ($CHMe_2$); 29.83 ($CHMe_2$); 30.05 ($CHMe_2$); 123.67 (o-C_6H_3); 125.20 (p-C_6H_3); 125.58 (p-C_6H_3); 126.05 (m-C_6H_3); 126.08 (NCH); 129.76 (p-C_6H_3); 129.98 (o-C_6H_5); 131.47, 131.81 (m-C_6H_5, p-C_6H_5); 132.09 (NCH); 132.48, 132.57, 136.02 (o-C_6H_3); 136.44, 145.17 (o-C_6H_3); 145.80, 145.89, 146.58 (*ipso*-C_6H_5); 159.53 ($C_{(aIPrPh)}$–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), $KN(SiMe_3)_2$ (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**, $C_{66}H_{80}N_4CuI$ (1119): C, 70.79; H, 7.20; N, 5.00; found: C, 71.21; H, 7.11; N, 4.72. ^{1}H-NMR (500 MHz, 298 K, THF-d_8): δ 1.01 (t, J = 6.9 Hz, 24H, $HCMe_2$); 1.12 (d, J = 6.8 Hz, 12H, $HCMe_2$); 1.22 (d, J = 6.8 Hz, 12H, $HCMe_2$); 2.47–2.61 (m, 8H, $CHMe_2$); 6.91 (d, J = 7.4 Hz, 4H, o-C_6H_3); 7.08 (s, 2H, NCH); 7.18 (t, J = 7.5 Hz, 4H, m-C_6H_5); 7.23 (d, J = 7.8 Hz, 4H, m-C_6H_3); 7.30 (t, J = 7.5 Hz, 2H, p-C_6H_3); 7.38 (m, 6H, m-C_6H_3, p-C_6H_5); 7.54 (t, J = 7.8 Hz, 2H, p-C_6H_3) ppm. $^{13}C\{^1H\}$-NMR (125.76 MHz, 25 °C, THF-d_8): δ 22.89 ($CHMe_2$); 22.95 ($CHMe_2$); 25.90 ($CHMe_2$); 26.38 ($CHMe_2$); 29.91 ($CHMe_2$); 30.08 ($CHMe_2$); 124.07, 125.55, 125.95, 129.68 (m-C_6H_5); 130.10 (o-C_6H_5); 131.51 (p-C_6H_5); 131.73 (NCH); 132.18 (p-C_6H_3); 132.33 (p-C_6H_3); 132.43 (o-C_6H_3); 136.65 (o-C_6H_3); 145.84 (*ipso*-C_6H_5); 146.01 (*ipso*-C_6H_5); 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 ^{1}H 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 ^{1}H 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; ^{1}H and ^{13}C 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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References

1. Hopkinson, M.N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485–496. [CrossRef] [PubMed]
2. Diez-Gonzalez, S.; Marion, N.; Nolan, S.P. N-Heterocyclic carbenes in late transition metal catalysis. *Chem. Rev.* **2009**, *109*, 3612–3676. [CrossRef] [PubMed]
3. Glorius, F. *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Springer: Berlin/Heidelberg, Germany, 2007; Volume 21.
4. Herrmann, W.A. N-Heterocyclic Carbenes: A new concept in organometallic catalysis. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309. [CrossRef]
5. Nolan, S.P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH Verlag GmbH & Co., KGaA: Weinheim, Germany, 2006.
6. Nolan, S.P. *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*; Wiley-VCH Verlag GmbH & Co., KGaA: Weinheim, Germany, 2014.
7. Lazreg, F.; Nahra, F.; Cazin, C.S.J. Copper–NHC complexes in catalysis. *Coord. Chem. Rev.* **2015**, *293*, 48–79. [CrossRef]
8. Enders, D.; Balensiefer, T. Nucleophilic Carbenes in Asymmetric Organocatalysis. *Acc. Chem. Res.* **2004**, *37*, 534–541. [CrossRef] [PubMed]
9. Cesar, V.; Bellemin-Laponnaz, S.; Gade, L.H. Chiral N-heterocyclic carbenes as stereodirecting ligands in asymmetric catalysis. *Chem. Soc. Rev.* **2004**, *33*, 619–636. [CrossRef] [PubMed]
10. Boeda, F.; Nolan, S.P. N-Heterocyclic carbene-containing complexes in catalysis. *Annu. Rep. Prog. Chem. Sect. B Org. Chem.* **2008**, *104*, 184–210. [CrossRef]
11. Fortman, G.C.; Nolan, S.P. N-Heterocyclic carbene (NHC) ligands and palladium in homogeneous cross-coupling catalysis: A perfect union. *Chem. Soc. Rev.* **2011**, *40*, 5151–5169. [CrossRef] [PubMed]

12. Bantreil, X.; Nolan, S.P. Synthesis of N-heterocyclic carbene ligands and derived ruthenium olefin metathesis catalysts. *Nat. Protoc.* **2011**, *6*, 69–77. [CrossRef] [PubMed]
13. Grossmann, A.; Enders, D. N-Heterocyclic carbene catalyzed domino reactions. *Angew. Chem. Int. Ed.* **2012**, *51*, 314–325. [CrossRef] [PubMed]
14. Soleilhavoup, M.; Bertrand, G. Cyclic (alkyl)(amino)carbenes (CAACs): Stable carbenes on the rise. *Acc. Chem. Res.* **2015**, *48*, 256–266. [CrossRef] [PubMed]
15. Wang, Y.; Robinson, G.H. N-heterocyclic carbene-main-group chemistry: A rapidly evolving field. *Inorg. Chem.* **2014**, *53*, 11815–11832. [CrossRef] [PubMed]
16. Martin, C.D.; Soleilhavoup, M.; Bertrand, G. Carbene-stabilized main group radicals and radical ions. *Chem. Sci.* **2013**, *4*, 3020–3030. [CrossRef] [PubMed]
17. Ghadwal, R.S.; Azhakar, R.; Roesky, H.W. Dichlorosilylene: A high temperature transient species to an indispensable building block. *Acc. Chem. Res.* **2013**, *46*, 444–456. [CrossRef] [PubMed]
18. Bidal, Y.D.; Santoro, O.; Melaimi, M.; Cordes, D.B.; Slawin, A.M.Z.; Bertrand, G.; Cazin, C.S.J. Generalization of the copper to late-transition-metal transmetallation to carbenes beyond N-heterocyclic carbenes. *Chem. Eur. J.* **2016**, *22*, 9404–9409. [CrossRef] [PubMed]
19. Ghadwal, R.S. Carbon-based two electron sigma-donor ligands beyond classical N-heterocyclic carbenes. *Dalton Trans.* **2016**, *45*, 16081–16095. [CrossRef] [PubMed]
20. Lepetit, C.; Maraval, V.; Canac, Y.; Chauvin, R. On the nature of the dative bond: Coordination to metals and beyond. The carbon case. *Coord. Chem. Rev.* **2016**, *308*, 59–75. [CrossRef]
21. Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Stable cyclic carbenes and related species beyond diaminocarbenes. *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849. [CrossRef] [PubMed]
22. Schuster, O.; Yang, L.; Raubenheimer, H.G.; Albrecht, M. Beyond conventional N-heterocyclic carbenes: Abnormal, remote and other classes of NHC ligands with reduced heteroatom stabilization. *Chem. Rev.* **2009**, *109*, 3445–3478. [CrossRef] [PubMed]
23. Ghadwal, R.S.; Rottschäfer, D.; Blomeyer, S.; Neumann, B.; Stammler, H.-G. Silylene-functionalized N-heterocyclic carbene (Si-NHC). *Chem. Eur. J.* **2017**. [CrossRef] [PubMed]
24. Schnee, G.; Nieto Faza, O.; Specklin, D.; Jacques, B.; Karmazin, L.; Welter, R.; Silva López, C.; Dagorne, S. Normal-to-abnormal NHC rearrangement of AlIII, GaIII, and InIII trialkyl complexes: Scope, mechanism, reactivity studies, and H2 activation. *Chem. Eur. J.* **2015**, *21*, 17959–17972. [CrossRef] [PubMed]
25. Poulain, A.; Iglesias, M.; Albrecht, M. Abnormal NHC palladium complexes: Synthesis, structure, and reactivity. *Curr. Org. Chem.* **2011**, *15*, 3325–3336. [CrossRef]
26. Xu, X.; Xu, B.; Li, Y.; Hong, S.H. Abnormal N-heterocyclic carbene promoted Suzuki−Miyaura coupling reaction: A comparative study. *Organometallics* **2010**, *29*, 6343–6349. [CrossRef]
27. Aldeco-Perez, E.; Rosenthal, A.J.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. Isolation of a C5-deprotonated imidazolium, a crystalline "Abnormal" N-heterocyclic carbene. *Science* **2009**, *326*, 556–559. [CrossRef] [PubMed]
28. Crittall, M.R.; Ellul, C.E.; Mahon, M.F.; Saker, O.; Whittlesey, M.K. Abnormal coordination of Arduengo's carbene upon reaction with M3 (CO) 12 (M = Ru, Os). *Dalton Trans.* **2008**, 4209–4211. [CrossRef] [PubMed]
29. Cooke, C.E.; Jennings, M.C.; Pomeroy, R.K.; Clyburne, J.A.C. Normal and abnormal NHC coordination in [Os4(μ-H)4(CO)11(IMes)] and exhaustive dehydrogenation of an IMes methyl group. *Organometallics* **2007**, *26*, 6059–6062. [CrossRef]
30. Arnold, P.L.; Pearson, S. Abnormal N-heterocyclic carbenes. *Coord. Chem. Rev.* **2007**, *251*, 596–609. [CrossRef]
31. Chianese, A.R.; Kovacevic, A.; Zeglis, B.M.; Faller, J.W.; Crabtree, R.H. Abnormal C5-bound N-heterocyclic carbenes: Extremely strong electron donor ligands and their iridium(I) and iridium(III) complexes. *Organometallics* **2004**, *23*, 2461–2468. [CrossRef]
32. Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J.W.; Crabtree, R.H. Abnormal binding in a carbene complex formed from an imidazolium salt and a metal hydride complex. *Chem. Commun.* **2001**, 2274–2275. [CrossRef]
33. Droge, T.; Glorius, F. The measure of all rings-N-heterocyclic carbenes. *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952. [CrossRef] [PubMed]
34. Nelson, D.J.; Nolan, S.P. Quantifying and understanding the electronic properties of N-heterocyclic carbenes. *Chem. Soc. Rev.* **2013**, *42*, 6723–6753. [CrossRef] [PubMed]

35. Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. Crystalline 1H-1,2,3-triazol-5-ylidenes: New stable mesoionic carbenes (MICs). *Angew. Chem. Int. Ed.* **2010**, *49*, 4759–4762. [CrossRef] [PubMed]
36. Crabtree, R.H. Abnormal, mesoionic and remote N-heterocyclic carbene complexes. *Coord. Chem. Rev.* **2013**, *257*, 755–766. [CrossRef]
37. Heckenroth, M.; Kluser, E.; Neels, A.; Albrecht, M. Neutral ligands with exceptional donor ability for palladium-catalyzed alkene hydrogenation. *Angew. Chem. Int. Ed.* **2007**, *46*, 6293–6296. [CrossRef] [PubMed]
38. Albrecht, M. C4-bound imidazolylidenes: From curiosities to high-impact carbene ligands. *Chem. Commun.* **2008**, 3601–3610. [CrossRef] [PubMed]
39. Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. A brief survey of our contribution to stable carbene chemistry. *Organometallics* **2011**, *30*, 5304–5313. [CrossRef] [PubMed]
40. Prades, A.; Viciano, M.; Sanau, M.; Peris, E. Preparation of a series of "Ru(p-cymene)" complexes with different N-heterocyclic carbene ligands for the catalytic β-alkylation of secondary alcohols and dimerization of phenylacetylene. *Organometallics* **2008**, *27*, 4254–4259. [CrossRef]
41. Saha, S.; Ghatak, T.; Saha, B.; Doucet, H.; Bera, J.K. Steric control at the wingtip of a bis-N-heterocyclic carbene ligand: Coordination behavior and catalytic responses of its ruthenium compounds. *Organometallics* **2012**, *31*, 5500–5505. [CrossRef]
42. Keitz, B.K.; Bouffard, J.; Bertrand, G.; Grubbs, R.H. Protonolysis of a ruthenium-carbene bond and applications in olefin metathesis. *J. Am. Chem. Soc.* **2011**, *133*, 8498–8501. [CrossRef] [PubMed]
43. Bidal, Y.D.; Lesieur, M.; Melaimi, M.; Nahra, F.; Cordes, D.B.; Athukorala Arachchige, K.S.; Slawin, A.M.Z.; Bertrand, G.; Cazin, C.S.J. Copper(I) complexes bearing carbenes beyond classical N-heterocyclic carbenes: Synthesis and catalytic activity in "Click chemistry". *Adv. Synth. Catal.* **2015**, *357*, 3155–3161. [CrossRef]
44. Sau, S.C.; Roy, S.R.; Sen, T.K.; Mullangi, D.; Mandal, S.K. An abnormal N-heterocyclic carbene-copper(I) complex in click chemistry. *Adv. Synth. Catal.* **2013**, *355*, 2982–2991. [CrossRef]
45. Ghadwal, R.S.; Reichmann, S.O.; Herbst-Irmer, R. Palladium-catalyzed direct C2-arylation of an N-heterocyclic carbene: An atom-economic route to mesoionic carbene ligands. *Chem. Eur. J.* **2015**, *21*, 4247–4251. [CrossRef] [PubMed]
46. Ghadwal, R.S.; Ho, N.K.; Neumann, B.; Stammler, G.; Menezes da Silva, V.H.; Watanabe, D.; Braga, A.A.C. Nickel-catalysed direct C2-arylation of N-heterocyclic carbene. *Dalton Trans.* **2017**. [CrossRef]
47. Rottschäfer, D.; Schürmann, C.J.; Lamm, J.-H.; Paesch, A.N.; Neumann, B.; Ghadwal, R.S. Abnormal-NHC palladium(II) complexes: Rational synthesis, structural elucidation, and catalytic activity. *Organometallics* **2016**, *35*, 3421–3429. [CrossRef]
48. Ghadwal, R.S.; Rottschäfer, D.; Schürmann, C.J. Expedient access to normal- and abnormal- N-heterocyclic carbene (NHC) magnesium compounds from imidazolium salts. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1236–1240. [CrossRef]
49. Ghadwal, R.S.; Lamm, J.-H.; Rottschafer, D.; Schurmann, C.J.; Demeshko, S. Facile routes to abnormal-NHC-cobalt(II) complexes. *Dalton Trans.* **2017**, *46*, 7664–7667. [CrossRef] [PubMed]
50. Meldal, M.; Tornøe, C.W. Cu-catalyzed azide−alkyne cycloaddition. *Chem. Rev.* **2008**, *108*, 2952–3015. [CrossRef] [PubMed]
51. Finn, M.G.; Fokin, V.V. Click chemistry: Function follows form. *Chem. Soc. Rev.* **2010**, *39*, 1231–1232. [CrossRef] [PubMed]
52. Berg, R.; Straub, B.F. Advancements in the mechanistic understanding of the copper-catalyzed azide–alkyne cycloaddition. *Beilstein J. Org. Chem.* **2013**, *9*, 2715–2750. [CrossRef] [PubMed]
53. Himo, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V.V.; Noodleman, L.; Sharpless, K.B.; Fokin, V.V. Copper(I)-catalyzed synthesis of azoles. DFT study predicts unprecedented reactivity and intermediates. *J. Am. Chem. Soc.* **2005**, *127*, 210–216. [CrossRef] [PubMed]
54. Kolb, H.C.; Finn, M.G.; Sharpless, K.B. Click chemistry: Diverse chemical function from a few good reactions. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021. [CrossRef]
55. Schulze, B.; Schubert, U.S. Beyond click chemistry—Supramolecular interactions of 1,2,3-triazoles. *Chem. Soc. Rev.* **2014**, *43*, 2522–2571. [CrossRef] [PubMed]
56. Straub, B.; Holm, S.; Siegle, A.; Loos, C.; Rominger, F. Preparation and N-alkylation of 4-aryl-1,2,4-triazoles. *Synthesis* **2010**, *2010*, 2278–2286. [CrossRef]
57. Wang, C.; Wang, D.; Yu, S.; Cornilleau, T.; Ruiz, J.; Salmon, L.; Astruc, D. Design and applications of an efficient amphiphilic "Click" CuI catalyst in water. *ACS Catal.* **2016**, *6*, 5424–5431. [CrossRef]

58. Wang, D.; Deraedt, C.; Salmon, L.; Labrugère, C.; Etienne, L.; Ruiz, J.; Astruc, D. A tris(triazolate) ligand for a highly active and magneticall recoverable palladium catalyst of selective alcohol oxidation using air at atmospheric pressure. *Chem. Eur. J.* **2015**, *21*, 6501–6510. [CrossRef] [PubMed]
59. He, C.; Shreeve, J.N.M. Energetic materials with promising properties: Synthesis and characterization of 4,4′-bis(5-nitro-1,2,3-2H-triazole) derivatives. *Angew. Chem. Int. Ed.* **2015**, *54*, 6260–6264. [CrossRef] [PubMed]
60. Dippold, A.A.; Klapötke, T.M. A study of dinitro-bis-1,2,4-triazole-1,1′-diol and derivatives: Design of high-performance insensitive energetic materials by the introduction of N-oxides. *J. Am. Chem. Soc.* **2013**, *135*, 9931–9938. [CrossRef] [PubMed]
61. Brantley, J.N.; Wiggins, K.M.; Bielawski, C.W. Unclicking the click: Mechanically facilitated 1,3-dipolar cycloreversions. *Science* **2011**, *333*, 1606–1609. [CrossRef] [PubMed]
62. Juricek, M.; Kouwer, P.H.J.; Rowan, A.E. Triazole: A unique building block for the construction of functional materials. *Chem. Commun.* **2011**, *47*, 8740–8749. [CrossRef] [PubMed]
63. Diez-Gonzalez, S.; Escudero-Adan, E.C.; Benet-Buchholz, J.; Stevens, E.D.; Slawin, A.M.Z.; Nolan, S.P. [(NHC)CuX] complexes: Synthesis, characterization and catalytic activities in reduction reactions and click chemistry. On the advantage of using well-defined catalytic systems. *Dalton Trans.* **2010**, *39*, 7595–7606. [CrossRef] [PubMed]
64. Makarem, A.; Berg, R.; Rominger, F.; Straub, B.F. A fluxional copper acetylide cluster in CuAAC catalysis. *Angew. Chem. Int. Ed.* **2015**, *54*, 7431–7435. [CrossRef] [PubMed]
65. Diez-Gonzalez, S.; Nolan, S.P. [(NHC)2Cu]X Complexes as efficient catalysts for azide-alkyne click chemistry at low catalyst loadings. *Angew. Chem. Int. Ed.* **2008**, *47*, 8881–8884. [CrossRef] [PubMed]
66. Diaz Velazquez, H.; Ruiz Garcia, Y.; Vandichel, M.; Madder, A.; Verpoort, F. Water-soluble NHC-Cu catalysts: Applications in click chemistry, bioconjugation and mechanistic analysis. *Org. Biomol. Chem.* **2014**, *12*, 9350–9356. [CrossRef] [PubMed]
67. Hohloch, S.; Sarkar, B.; Nauton, L.; Cisnetti, F.; Gautier, A. Are Cu(I)-mesoionic NHC carbenes associated with nitrogen additives the best Cu-carbene catalysts for the azide-alkyne click reaction in solution? A case study. *Tetrahedron Lett.* **2013**, *54*, 1808–1812. [CrossRef]
68. Nakamura, T.; Terashima, T.; Ogata, K.; Fukuzawa, S. Copper(I) 1,2,3-triazol-5-ylidene complexes as efficient catalysts for click reactions of azides with alkynes. *Org. Lett.* **2011**, *13*, 620–623. [CrossRef] [PubMed]
69. Diez-Gonzalez, S.; Stevens, E.D.; Nolan, S.P. A [(NHC)CuCl] complex as a latent click catalyst. *Chem. Commun.* **2008**, 4747–4749. [CrossRef] [PubMed]
70. Diez-Gonzalez, S.; Nolan, S.P. N-heterocyclic carbene-copper(I) complexes in homogeneous catalysis. *Synlett* **2007**, *2007*, 2158–2167. [CrossRef]
71. Diez-Gonzalez, S.; Correa, A.; Cavallo, L.; Nolan, S.P. (NHC)copper(I)-catalyzed [3+2] cycloaddition of azides and mono- or disubstituted alkynes. *Chem. Eur. J.* **2006**, *12*, 7558–7564. [CrossRef] [PubMed]
72. Bidal, Y.D.; Lesieur, M.; Melaimi, M.; Cordes, D.B.; Slawin, A.M.; Bertrand, G.; Cazin, C.S. A simple access to transition metal cyclopropenylidene complexes. *Chem. Commun.* **2015**, *51*, 4778–4781. [CrossRef] [PubMed]
73. Sau, S.C.; Roy, S.R.; Mandal, S.K. One-pot consecutive catalysis by integrating organometallic catalysis with organocatalysis. *Chem. Asian. J.* **2014**, *9*, 2806–2813. [CrossRef] [PubMed]
74. Roy, S.R.; Sau, S.C.; Mandal, S.K. Chemoselective reduction of the carbonyl functionality through hydrosilylation: Integrating click catalysis with hydrosilylation in one pot. *J. Org. Chem.* **2014**, *79*, 9150–9160. [CrossRef] [PubMed]
75. Hu, X.; Castro-Rodriguez, I.; Meyer, K. A bis-carbene alkenyl copper(I) complex from a tripodal tris-carbene ligand. *Organometallics* **2003**, *22*, 3016–3018. [CrossRef]
76. Filonenko, G.A.; Cosimi, E.; Lefort, L.; Conley, M.P.; Coperet, C.; Lutz, M.; Hensen, E.J.M.; Pidko, E.A. Lutidine-derived Ru-CNC hydrogenation pincer catalysts with versatile coordination properties. *ACS Catal.* **2014**, *4*, 2667–2671. [CrossRef]
77. Bitzer, M.J.; Pothig, A.; Jandl, C.; Kühn, F.E.; Baratta, W. Ru-Ag and Ru-Au dicarbene complexes from an abnormal carbene ruthenium system. *Dalton Trans.* **2015**, *44*, 11686–11689. [CrossRef] [PubMed]
78. Krueger, A.; Albrecht, M. Rhodium carbene complexes as versatile catalyst precursors for Si-H bond activation. *Chem. Eur. J.* **2012**, *18*, 652–658. [CrossRef] [PubMed]

79. Kruger, A.; Haller, L.J.L.; Muller-Bunz, H.; Serada, O.; Neels, A.; Macgregor, S.A.; Albrecht, M. Smooth C(alkyl)-H bond activation in rhodium complexes comprising abnormal carbene ligands. *Dalton Trans.* **2011**, *40*, 9911–9920. [CrossRef] [PubMed]
80. Zuo, W.; Braunstein, P. N-Heterocyclic dicarbene iridium(III) pincer complexes featuring mixed NHC/abnormal NHC ligands and their applications in the transfer dehydrogenation of cyclooctane. *Organometallics* **2012**, *31*, 2606–2615. [CrossRef]
81. Tang, C.Y.; Smith, W.; Vidovic, D.; Thompson, A.L.; Chaplin, A.B.; Aldridge, S. Sterically encumbered Iridium bis(N-heterocyclic carbene) systems: Multiple C-H activation processes and isomeric normal/abnormal carbene complexes. *Organometallics* **2009**, *28*, 3059–3066. [CrossRef]
82. Tan, K.V.; Dutton, J.L.; Skelton, B.W.; Wilson, D.J.D.; Barnard, P.J. Nickel(II) and palladium(II) complexes with chelating N-heterocyclic carbene amidate ligands: Interplay between normal and abnormal coordination modes. *Organometallics* **2013**, *32*, 1913–1923. [CrossRef]
83. Lebel, H.; Janes, M.K.; Charette, A.B.; Nolan, S.P. Structure and reactivity of "unusual" N-heterocyclic carbene (NHC) palladium complexes synthesized from imidazolium salts. *J. Am. Chem. Soc.* **2004**, *126*, 5046–5047. [CrossRef] [PubMed]
84. Danopoulos, A.A.; Tsoureas, N.; Wright, J.A.; Light, M.E. N-Heterocyclic pincer dicarbene complexes of iron(II): C-2 and C-5 Metalated carbenes on the same metal center. *Organometallics* **2004**, *23*, 166–168. [CrossRef]
85. Varonka, M.S.; Warren, T.H. Three-coordinate N-heterocyclic carbene nickel nitrosyl complexes. *Organometallics* **2010**, *29*, 717–720. [CrossRef]
86. Santoro, O.; Lazreg, F.; Cordes, D.B.; Slawin, A.M.Z.; Cazin, C.S.J. Homoleptic and heteroleptic bis-NHC Cu(I) complexes as carbene transfer reagents. *Dalton Trans.* **2016**, *45*, 4970–4973. [CrossRef] [PubMed]
87. Lazreg, F.; Slawin, A.M.Z.; Cazin, C.S.J. Heteroleptic bis(N-heterocyclic carbene) Copper(I) complexes: Highly efficient systems for the [3+2] cycloaddition of azides and alkynes. *Organometallics* **2012**, *31*, 7969–7975. [CrossRef]
88. Weisser, F.; Stevens, H.; Klein, J.; van der Meer, M.; Hohloch, S.; Sarkar, B. Tailoring Ru(II) pyridine/triazole oxygenation catalysts and using photoreactivity to probe their electronic properties. *Chem. Eur. J.* **2015**, *21*, 8926–8938. [CrossRef] [PubMed]
89. Schweinfurth, D.; Sommer, M.G.; Atanasov, M.; Demeshko, S.; Hohloch, S.; Meyer, F.; Neese, F.; Sarkar, B. The ligand field of the azido ligand: Insights into bonding parameters and magnetic anisotropy in a Co(II)-azido complex. *J. Am. Chem. Soc.* **2015**, *137*, 1993–2005. [CrossRef] [PubMed]
90. Maity, R.; van der Meer, M.; Hohloch, S.; Sarkar, B. Di- and trinuclear iridium(III) complexes with poly-mesoionic carbenes synthesized through selective base-dependent metalation. *Organometallics* **2015**, *34*, 3090–3096. [CrossRef]
91. Maity, R.; van der Meer, M.; Sarkar, B. Redox-active multinuclear Pd(II) complexes with bis- and tris-mesoionic carbenes. *Dalton Trans.* **2015**, *44*, 46–49. [CrossRef] [PubMed]
92. Etayo, P.; Ayats, C.; Pericas, M.A. Synthesis and catalytic applications of C3-symmetric tris(triazolyl)methanol ligands and derivatives. *Chem. Commun.* **2016**, *52*, 1997–2010. [CrossRef] [PubMed]
93. Chan, T.R.; Hilgraf, R.; Sharpless, K.B.; Fokin, V.V. Polytriazoles as copper(I)-stabilizing ligands in catalysis. *Org. Lett.* **2004**, *6*, 2853–2855. [CrossRef] [PubMed]
94. Hein, J.E.; Fokin, V.V. Copper-catalyzed azide-alkyne cycloaddition (CuAAC) and beyond: New reactivity of copper(I) acetylides. *Chem. Soc. Rev.* **2010**, *39*, 1302–1315. [CrossRef] [PubMed]
95. Fulmer, G.R.; Miller, A.J.M.; Sherden, N.H.; Gottlieb, H.E.; Nudelman, A.; Stoltz, B.M.; Bercaw, J.E.; Goldberg, K.I. NMR chemical shifts of trace impurities: Common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist. *Organometallics* **2010**, *29*, 2176–2179. [CrossRef]
96. Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G.M.; Stalke, D. A comparison of a microfocus X-ray source and a conventional sealed tube for crystal structure determination. *J. Appl. Cryst.* **2009**, *42*, 885–891. [CrossRef]
97. Bruker AXS Inc. *In Bruker Apex CCD, SAINT v8.30C*; Bruker AXS Inst. Inc.: Madison, WI, USA, 2013.
98. Krause, L.; Herbst-Irmer, R.; Stalke, D. An empirical correction for the influence of low-energy contamination. *J. Appl. Cryst.* **2015**, *48*, 1907–1913. [CrossRef]
99. Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* **2015**, *48*, 3–10. [CrossRef] [PubMed]

100. Sheldrick, G. SHELXT—Integrated space-group and crystal-structure determination. *Acta Cryst. A* **2015**, *71*, 3–8. [CrossRef] [PubMed]
101. Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3–8. [CrossRef] [PubMed]
102. Hubschle, C.B.; Sheldrick, G.M.; Dittrich, B. ShelXle: A Qt graphical user interface for SHELXL. *J. Appl. Cryst.* **2011**, *44*, 1281–1284. [CrossRef] [PubMed]