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Side-Arm Functionalized Silylene Copper(I) Complexes in Catalysis

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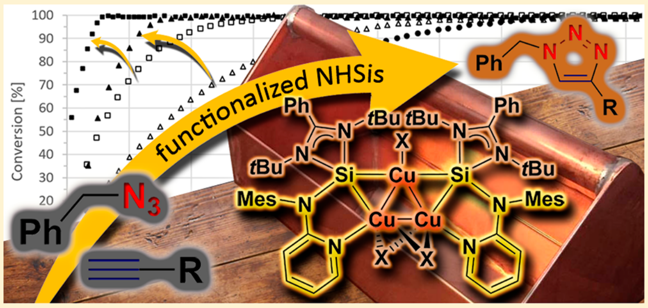
Supporting Information

ABSTRACT: A convenient new method was added to the toolbox of the ligand design of *N*-heterocyclic silylenes and their transition-metal complexes. Herein we report on six novel compounds of two novel classes of copper(I) complexes based on the benzamidinate silylene (Cl)Si(PhC(N*t*Bu)$_2$). By taming the high reactivity of the free electron pair of the Si(II) atom via a preset metalation with a desired metal precursor (in this case copper(I) halides) we can easily introduce novel pyridyl-based groups in the subsequent functionalization of the chloro group and undergo coordination of the metal atom at the same time. The resulting pseudocubane-like tetramer [XCu(I) ← (Cl)Si(PhC(N*t*Bu)$_2$)]$_4$ **2a**−**2c** and the trinuclear dimer [(XCu(I))$_3$(PyNMes)Si(PhC(N*t*Bu)$_2$)] **3a**−**3c** (with X = Cl (**2a**/**3a**), Br (**2b**/**3b**), I (**2c**/**3c**)) were fully characterized via X-ray diffraction analysis, NMR spectroscopy, mass spectrometry, and elemental analysis. Moreover, we took a look into the catalytic potential of the Cu(I) complexes **2b** and **3b** by testing them under the conditions of the renowned copper(I)-catalyzed alkyne−azide cycloaddition and observed an increased activity of the functionalized species.



INTRODUCTION

Over the past decades, *N*-heterocyclic silylenes (NHSi) have been intensively studied and became more and more a suitable alternative for traditional ligands in organometallic chemistry, not only but primarily in their role as strong σ-donors in metal complexes.[1−3] For several years, only group 5−10 transition-metal complexes stood in the focus of research, whereas group 11 or 12 metal complexes were still comparatively rare.[1] Early examples of Frenking and Boehme about theoretical analysis of coinage metal NHSi complexes[4] were followed by single synthetic approaches by Lappert et al., who, for example, published a tetrahedral copper NHSi complex employing the Arduengo type of motif (**I**, Scheme 1).[5] Ten years later the group of Driess started new synthetic approaches on group 11 complexes to further explore the fundamentals of copper NHSi complexes (**II**−**III**).[6] These results were expanded through the very recent work of Khan et al., who published certain reports on group 11 transition-metal complexes and inter alia one of the first gold and silver complexes (**IV**−**VI**).[7−13] Almost all these metal complexes are based on the same core unit, the benzamidinate silylene,[14] which had its breakthrough in 2010, when the group of Roesky was able to publish an improved synthesis of this ligand, which allowed facile access to the high-yield synthesis of the chlorobenzamidinate silylene (NHSiCl, **1**) ligand.[15]

Shortly after, certain groups independently published similar methods on the facile functionalization via simple substitution of the chloro group with seemingly any other monoanionic group bearing nitrogen, phosphor, or even oxygen atoms (Scheme 2A).[16] These achievements boosted the research of the chemistry of *N*-heterocyclic silylenes and are the basis of many following results.

Of course there are also other ways of substituting the chloro group, which appeared in the literature, for example, through rearrangement. Roesky et al. observed the coordination of ZnEt$_2$/Zn(arene)$_2$ and the subsequent rearrangement of the alkyl/aryl group with the chloro group to eventually coordinate ZnCl$_2$.[17] Nevertheless, such methods did not gain broad acceptance in the field of versatile functionalization. The focus was set on the substitution of the chloro group due to the possibility of flexible ligand design.

Herein, we concentrated on the enhanced functionalization of the chlorobenzamidinate ligand by introducing additional donor sites. The idea of functionalizing silylenes for a bi- or tridentate coordination of metal atoms is not new to silylene chemistry but barely applied. In fact, some of the first transition-metal complexes were designed as pincer-like ligands (e.g., **III**, Scheme 1; **VII** & **X**, Scheme 3).[18−23] One of the very few examples that illustrates the possibility to form new NHSi bearing an additional coordination site on a nitrogenous base was published by Tacke et al. (Scheme 2B).[24−26] Referring back to the previous work on the heavier Ge(II) analogues,[27,28] they were using 2 equiv of benzamidinate as building blocks right from the start, whereby one-half can function as the pendent donating side arm. However, alongside the benefits of this synthesis, this method is limited to a symmetrical design of the ligand, and therefore objects our intentions. As we were searching for a suitable route to substitute the chloro group of

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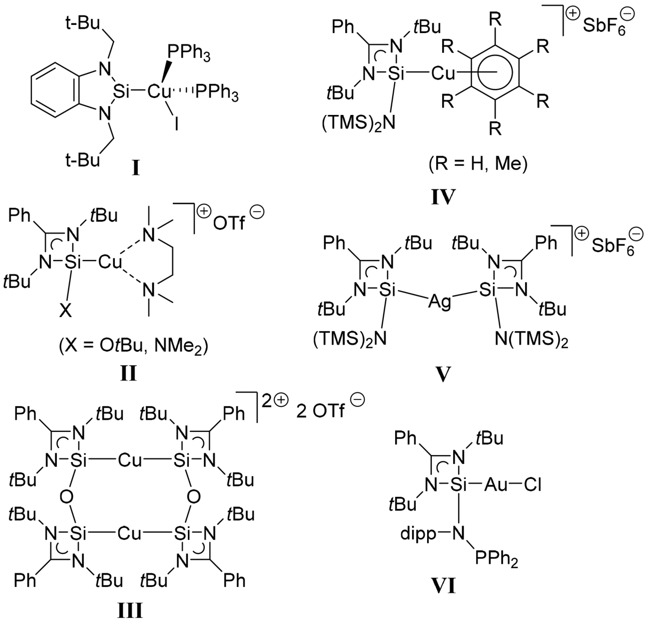
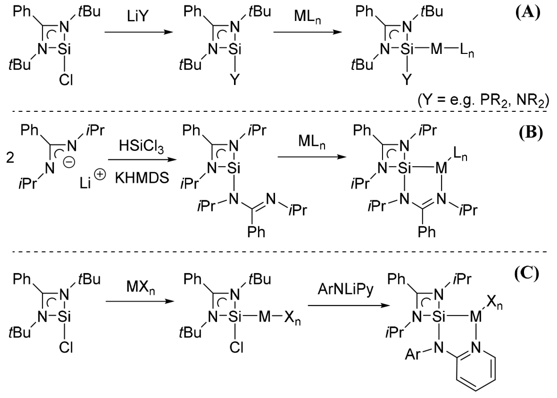
Scheme 1. Overview of Early to Recent *N*-Heterocyclic Silylene Group 11 Transition-Metal Complexes[a]



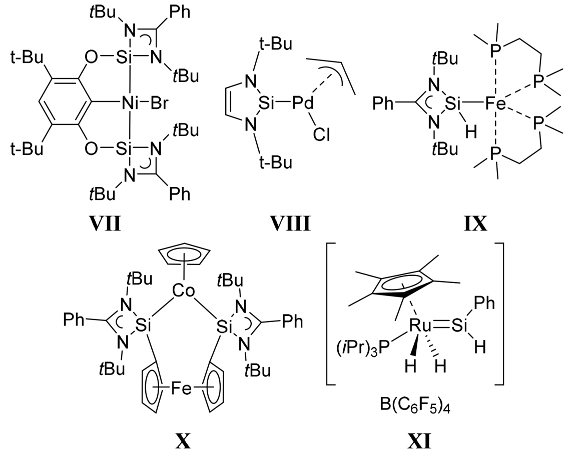
[a]By Lappert et al. (I),[5] Driess et al. (II, III),[6] and Khan et al. (IV–VI).[7,8,10]

Scheme 2. Comparison of Different Methods of Functionalization and Metalation[a]



[a](A) Preset substitution of the free chloro benzamidinate silylene, followed by the coordination of the metal precursor; (B) direct functionalization and generation of the free silylene with subsequent metalation; (C) preset metalation with simple metal precursors and subsequent substitution of the chloro group and accompanied metal coordination.

Scheme 3. Examples of Silylene Transition-Metal Complexes in Catalysis[a]



[a]VII: Driess et al., Sonogashira cross coupling;[20] VIII: Roesky et al., Heck coupling;[37] IX: Driess et al., ketone hydrosilylation;[44] X: Driess et al., [2 + 2 + 2] cyclotrimerization;[22] XI: Tilley et al., hydrosilylation of alkenes.[36].

NHSiCl with pyridyl-based groups, we were inspired to investigate alternative methods for the functionalization. Because of the high reactivity of the free electron pair of the silicon(II) atom we changed the conventional synthetic route described above to an early metalation of the neat chloro silylene, and therefore tame the lone pair through the coordination of transition-metal atoms and postpone the functionalization (Scheme 2C). Of course there are already numerous reports on NHSiCl transition-metal complexes (e.g., Co,[29] Cr,[30] Mo,[30] W,[30] Mn,[31] Fe,[32] Cu,[6] Ni[33]) but never under the aspect to perform further reactions with it like functionalization. With these metal complexes in hand, we were able to concentrate on the substitution of the chloro group with more complex features. In this work we will report our results of this method featuring copper(I) halide precursors.

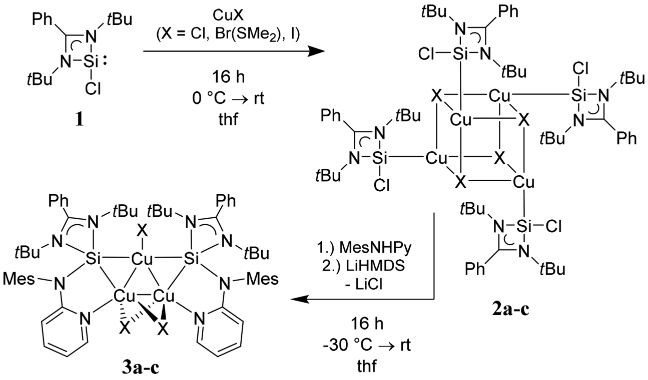
Simultaneous to our investigations, the group of Li and Sun reported their work on a similar structure motif, featuring a functional group of the type MeNPy instead but employing the conventional route via previous isolation of the free silylene and following metalation.[34] Within their work they investigated the catalytical properties of corresponding iron hydride complexes in hydroboration reactions, thus further illustrating the potential of such bidentate NHSis.

Besides new synthetic approaches, it was always our intention to investigate the reactivity of new NHSi transition-metal complexes. In direct comparison with their lighter homologue, the ubiquitous *N*-heterocyclic carbenes (NHCs), their applications in catalysis are still comparatively rare, yet emerging in various fields (e.g., Co,[22] Rh,[35,36] Ir,[18,35] Fe,[32] Pd,[19,37] and Ni[21,23]). The group of Tilley not only made a significant contribution to the elucidation of early transition-metal silylene complexes in the early 1990s[38,39] but has also contributed to a large number of investigations of catalytic applications over the past decades.[36,40,41] Likewise, Driess and his co-workers illustrated the potential of NHSi transition-metal complexes in certain reviews and were able to show that, in some cases, the catalytic activity and even selectivity can be increased and consequently prove that silylenes are not only isoelectronic replacements for classical phosphines or NHCs.[42,43] For these reasons we analyzed the catalytical potential of our newly characterized NHSi copper(I) complexes by checking their reactivity in the field of the renowned "Click" chemistry with a scope of commonly used azides and acetylenes at ambient temperature.

■ RESULTS AND DISCUSSION

For the synthesis of $[(XCu(I))_3 \leftarrow (PyNMes)Si(PhC(N\textit{t}Bu)_2)]$ **3a–c** we started with the metalation of the chlorinated silylene $PhC(N\textit{t}Bu)_2SiCl$ **1**. Treatment of a tetrahydrofuran (thf) suspension of the metal halide precursors (CuCl, $CuBr(SMe_2)$, CuI) with 1 equiv of NHSiCl **1** at ambient temperature leads to the formation of the pseudocubane $Cu_4(\mu_3\text{-}X)_4$ $[XCu(I) \leftarrow (Cl)Si(PhC(NtBu)_2)]_4$ **2a−c** in the form of slightly yellowish crystals after storage at −30 °C for 1 d. Compounds **2a−2c** (Scheme 4) have been characterized by elemental analysis, ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (XRD) analysis. The latter confirms the compounds in their pseudocubane nature. Each copper(I) atom of this alternating tetramer is coordinated by an unsubstituted silylene ligand **1**. The formation of such pseudocubanes is not uncommon for $[MX]_4L_n$ complexes with M = Cu, Ag; X = Cl, Br, I; and L = neutral donor ligands.[45,46] Nevertheless, until now there are no reports on such tetramers bearing silylenes and especially the well-known chlorosilylene benzamidinate ligand. However, looking at the higher homologue germanium, there are a few recent reports about the synthesis and characterization of such tetramers by Polo et al. using germylene benzamidinate ligands or six-membered germylenes by Mak et al.[47,48] The molecular structures of **2a−2c** (shown in Figure 1; see also Table 1) crystallize in the monoclinic space groups $C2/c$. The bond lengths and angles of M−X and M−X−M, respectively, correlate to the respective halides and therefore lay in a typical range of such pseudocubanes. The Si−M bond lengths (2.1889(9)−2.2306(13) Å) are comparable to cubane systems with common phosphine ligands (e.g., $[CuX]_4Ln$; L = PPh_3, X = Br; Cu−P = 2.209 Å).[46,49]

Scheme 4. Synthesis of 2a−2c and 3a−3c via Reaction of the Chlorosilylene Benzamidinate 1 and the Respective Copper(I) Precursors[a]



[a] Reaction of the chlorosilylene benzamidinate **1** and the respective copper(I) precursors, and the subsequent functionalization to the complexes **3a−3c** via the in situ deprotonation of the amine MesNHPy using LiHMDS.

Contrary to the XRD experiments, diffusion-ordered spectroscopy (DOSY) analysis indicates the presence of a dimeric structure in solution. With the help of the external calibration curve method to determine the molecular weight of compounds and intermediates via DOSY experiments, which was established in our group by Neufeld, we were able to detect a molecular weight in the area of a dimeric structure accompanied by thf molecules.[50,51] The ^1H and ^{13}C NMR spectra show one set of slightly shifted signals characteristic for the benzamidinate-like ligand. But more importantly, the ^{29}Si NMR show one broadened singlet at 27.73, 26.09, and 22.62 ppm, respectively. In 2014 Driess et al. published the first heteroleptic NHSi-Cu(I) complexes containing the first chlorosilylene copper complex $[Cu(I)(tmeda) \leftarrow (Cl)Si(PhC(NtBu)_2)][OTf]$ (**II**, Scheme 2) with a similar ^{29}Si shift of 32.9 ppm.[6]

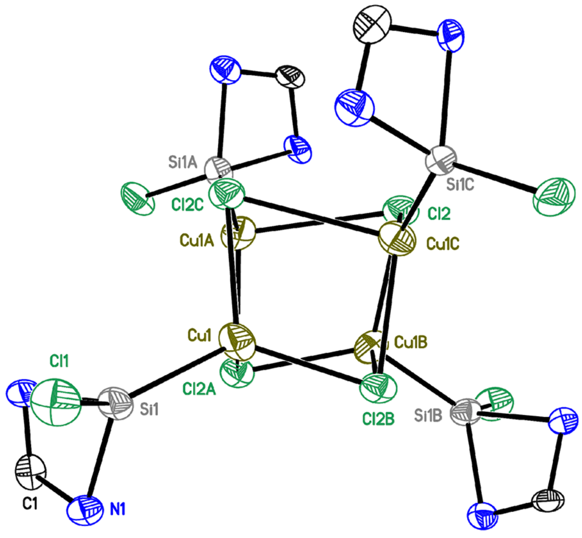


Figure 1. Molecular structure of **2a**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms, *tert*-butyl, phenyl groups, and solvent molecules are omitted for clarity. Structural data and selected bond lengths [Å] and angles [deg] are given in the Experimental Section and in Table 1, respectively (The molecular structures and full lists of bond lengths and angles of **2b**, **2c**, and **2a** are listed in the Supporting Information).

To further investigate the structure of **2a−2c** we tried various mass spectrometry techniques (LIFDI, ESI, MALDI, and EI) but were unable to obtain any informative mass spectrum of these compounds. We assume that, as a result of the comparatively high molecular weight, the neutral charge of the complex, and the air and moisture sensitivity of the tetramers **2a−2c** they decomposed during the processes. However, it was possible to identify a side product containing the characteristic pseudocubane core unit. A reaction of **2b** with a slight excess of $NaSbF_6$ led to the oxidized product $[(NHSiCl)_4(Cu(I))_2(Cu(II))_2Br_3(SbF_6)_2]^+$. Even though this structure contains oxidized copper(II) atoms the matching isotope pattern of m/z = 2144.78 compared to the simulated spectrum confirms the presence of the core moiety known by XRD experiments.

In the following functionalization steps, the corresponding complexes **2a−2c** were dissolved in thf, and 4 equiv of the amine MesNHPy were added. At a temperature of −30 °C the mixture was treated with LiHMDS to gain the target compounds as bright yellow crystals. Likewise, compounds **3a−3c** were characterized by elemental analysis, ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, mass spectrometry, and single-crystal XRD analysis. The most prominent feature of the resulting dimeric structure, the triple copper(I) core unit, was initially illustrated by XRD experiments (see Figure 2). The silicon(II) atoms of both ligands are coordinating not one but two copper(I) atoms, whereby one copper atom (the "tip" of the Cu_3 triangle) is mutually coordinated by both silylenes at a time in a Si−Cu−Si fashion, and the additional copper atoms (the "base" of the Cu_3 triangle) are supported by the coordination of the corresponding pyridyl group of the newly introduced functional group. The tip of the triangle bears a terminal halide, whereas the two base copper(I) atoms are μ-bridged by two halide atoms in a $Cu_2(\mu_2\text{-}X)_2$ manner.

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Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complexes 2a−2c[a]

	2a	2b	2c
Si−Cu	2.1889(8)−2.1930(9)	2.2068(7)−2.2085(7)	2.2285(13)−2.2306(13)
Cu−X	2.3097(8)−2.7844(10)	2.4632(8)−2.7860(10)	2.5993(9)−2.8559(8)
Cu−X−Cu	69.96(2)−90.07(3)	68.02(2)−85.16(2)	65.48(3)−78.57(4)
X−Cu−X	84.81(3)−111.93(3)	88.59(2)−114.22(2)	93.21(4)−116.56(3)

[a] The Cu−X bond lengths show wide ranges caused by the distortion of the pseudocubane-like structure.

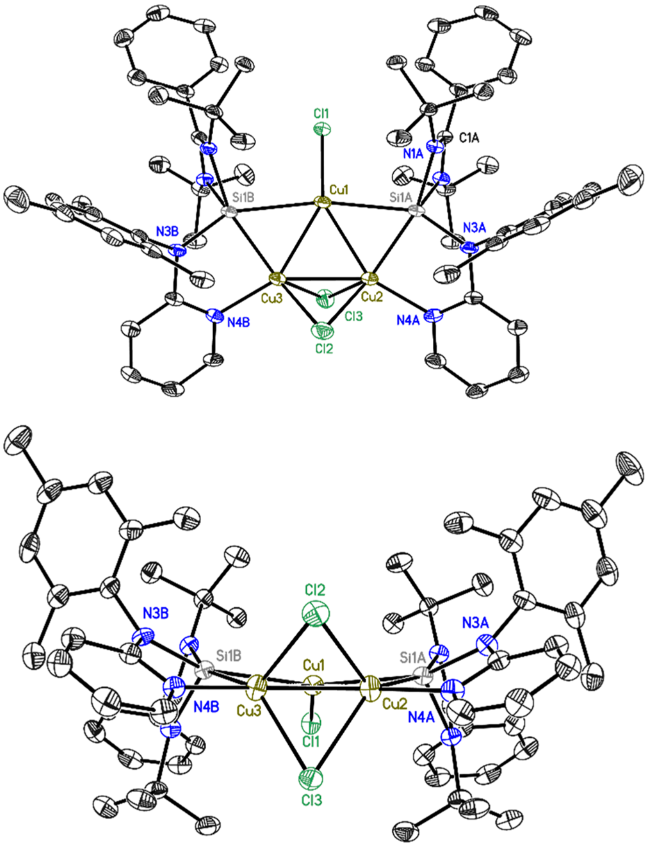


Figure 2. Molecular structure of **3a**. Central view at the Cu triangle (top); view along the triangle Cu2/3 → Cu1 (bottom). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Structural data and selected bond lengths [Å] and angles [deg] are given in the Experimental Section and in Table 2, respectively (The molecular structures and full lists of bond lengths and angles of **3b**, **3c**, and **3a** are listed in the Supporting Information.).

To the best of our knowledge, there is no previous report on such a $[(XCu)(Cu_2(\mu_2\text{-}X)_2)]$ moiety. The formation of copper triangles itself, however, is not new in coordination chemistry, yet rarely observed, especially in low-valent compounds like carbenes, silylenes, or germylenes. Recently Lu et al. and Chen et al. published certain structures with pyridyl-functionalized NHCs that bind to a copper triangle in a similar fashion.[52−54]

In both cases the copper triangle is fully coordinated by the carbene carbon and pyridyl nitrogen atoms, whereas the carbon atoms are also coordinating two copper atoms at a time. Because of their C_3-like composition, it is no surprise that the triangles are nearly isosceles (e.g., 60 ± 0.25°, 2.490 ± 0.007 Å).[52] The C_2-symmetric structure of compounds **3a**−**3c** shows a slightly distorted triangle, with a shortened bond length to the tip (e.g., **3a**, 2.4305(10)−2.4399(10) Å) and an elongated bond length of the base (e.g., **3a**, 2.5078(7) Å), which also results in diverging angles (e.g., **3a**, 61.98(2)° (tip), 59.19(3)°/58.82(3)° (base)). Furthermore, it is to emphasize that the Si−Cu1 bond length is significantly longer in comparison to the Si−Cu2/3 bond length (e.g., **3a**, 2.5427(13)/2.5569(14) Å vs 2.2564(14)/2.2647(15) Å). The aforementioned and closely related copper(I) complexes by Khan et al.[8,9] and Driess et al.[6] show a narrow range of Si−Cu (2.199−2.231 Å) and N4−Si (1.710−1.737 Å) bond lengths, for which the shorter Si−Cu bond fits quite well, and the substituted amine is slightly elongated in the case of **3a**−**3c** (1.813(4)−1.828(4) Å). The range of the Si−Cu1 bond lengths (2.5427(13)−2.6063(8) Å; Table 2) is more comparable to bridging silyl groups, like in dimeric NHC copper(I) complexes reported by Romero et al. and Kleeberg et al.[55,56] They illustrate a variety of dimeric structures, whereby bulky silyl groups (e.g., $Si(TMS)_2(Et)$) (TMS = tetramethylsilane) are bridging Cu−Cu bonds in a wide range from 2.385 to 2.618 Å. The wide range is caused due to the asymmetric bonding nature of silyl groups, which is often observed in $M_2(\mu_2\text{-}SiR_3)$ moieties and is pursued in **3a**−**3c**. Noteworthy, in comparison to other five-coordinated silicon atoms coordinating two Cu(I) atoms in the same manner, here the Si−Cu bonds are significantly elongated. We characterized certain multinuclear copper halide complexes earlier on, showing μ-bridging $Si(TMS)_3$ groups with bond lengths from 2.406(2) to 2.283(2) Å and from 2.348(3) to 2.334(3) Å, respectively.[57,58]

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complexes 3a−3c

	3a	3b	3c
Si−Cu1	2.5427(13)/ 2.5569(14)	2.5806(14)/ 2.5812(14)	2.5985(8)/ 2.6063(8)
Si−Cu2/3	2.2564(14)/ 2.2647(15)	2.2678(15)/ 2.2689(15)	2.2819(11)/ 2.2838(11)
Cu1−Cu2/3	2.4305(10)/ 2.4399(10)	2.4289(11)/ 2.4323(11)	2.4227(9)/ 2.4333(9)
Cu2−Cu3	2.5078(7)	2.5350(9)	2.5458(5)
N4−Cu2/3	1.995(4)/ 1.998(4)	2.005(4)/ 2.014(4)	2.009(2)/ 2.014(2)
N3−Si	1.813(4)/ 1.828(4)	1.814(4)/ 1.823(4)	1.815(2)/ 1.821(2)
Cu−X	2.2240(11)	2.307(5)	2.550(5)
Cu−(μ^2-X)	2.3699(13)− 2.4333(13)	2.5043(10)− 2.5308(9)	2.6629(6)− 2.6698(8)
Cu2−Cu1−Cu3	61.98(2)	62.86(3)	63.24(2)
Cu1−Cu2/3−Cu3/2	58.82(3)/ 59.19(3)	58.50(3)/ 58.63(3)	58.18(3)/ 58.59(3)
Cu1−Si−Cu2/3	60.41(4)/ 60.53(4)	59.71(4)/ 59.78(4)	59.08(3)/ 59.26(3)
Si−Cu−N4	85.82(12)/ 85.94(12)	85.39(11)/ 85.59(12)	84.83(7)/ 84.92(7)
Cu−(μ^2-X)−Cu	62.64(3)/ 63.31(3)	60.25(2)/ 60.69(2)	56.986(16)/ 57.039(12)

The dimeric structure holding the trinuclear copper(I) core of **3a**–**3c** could also be verified by LIFDI mass spectrometry by identifying the ion peaks corresponding to the cationic moieties of $[M-X]^+$ (X = Cl, Br, I) with m/z = 1117.2, 1291.2 and 1385.3, respectively. The ^1H NMR spectra of **3a**–**3c** show the expected additional aromatic signals of the pyridyl and mesityl group. Although the solid-state structure shows a butterfly-like structure the NMR spectra show one set of signals, which indicates that the structure must be flattened under the NMR time scale in solution and therefore symmetric. The usually sharp multiplets of the pyridyl hydrogens are partially broadened and upfield-shifted caused by the functionalization and metal coordination (e.g., 8.09 → 8.72 ppm or 6.26 → 6.80 ppm). The ^{13}C NMR spectra of **3a**–**3c** exhibit corresponding signals, which are consistent with their ^1H NMR resonances. Unfortunately, under no circumstances were we able to detect any ^{29}Si NMR signals. It is assumed that the low natural abundance of ^{29}Si in combination with the already broadened signals known from **2a**–**2c** got further broadened due to the functionalization and enhanced metal coordination, therefore making it nearly impossible to detect any ^{29}Si signals. Broadened signals are often accompanied by fluctuating effects of compounds in solution. It is possible that the N^{Py}–Cu coordination opens up along with a transformation of the bridging halide to a terminal one. Thus, conceiving this scenario as a dynamic complexation and decomplexation in solution the signal could be heavily broadened. Nevertheless, the remaining analyses confirm the presence of the silicon atoms.

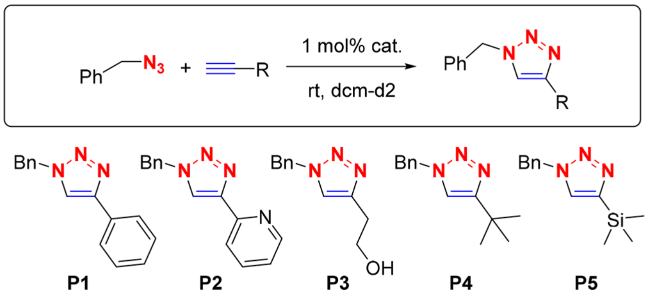
Catalysis. After the full characterization of our newly designed NHSi: → copper(I) complexes via the alternative functionalization we wanted to further investigate its behavior by checking possible catalytic activity. Former publications of low-valent silicon chemistry have illustrated the great potential of silylenes as new and improved ligands and also found various applications in catalysis.[42,59–61] However, in the field of silylene copper(I) chemistry there has been only one report on catalytic applications yet. In 2013 Driess and Hartwig characterized a novel silylene nickel(II) complex and investigated its reactivity and copper(I) intermediates toward the Sonogashira coupling.[20]

Our overall idea was to test and compare possible catalytic behavior toward renowned reactions. Therefore, we chose the copper(I)-catalyzed alkyne–azide cycloaddition (CuAAC) also known as the Huisgen 1,3-dipolar cycloaddition.[62,63] It is one of the most established and investigated transformations of the so-called Click chemistry and has noteworthy applications in nearly every field of chemistry.[64–67] The analogous NHC-Cu(I) complexes have been extensively investigated in Click chemistry and illustrate the great potential in this field of catalysis.[68,69]

Putting Click chemistry in simple terms, any Cu(I) source can be used as a catalyst; however, well-designed Cu(I) complexes can increase the selectivity, decrease catalyst loadings, or establish milder reaction conditions.[68–70] When Fokin and Finn revealed crucial details of the CuAAC mechanism in 2005[71] and therefore the mandatory role of copper(I), following studies increasingly concentrated on dinuclear copper species as the active species and illustrated their potential.[62,65,70,72,73]

Following these examples, we wanted to test and compare the catalytic activity of our new multinuclear complexes **2b** and **3b** in certain CuAAC reactions (the details of catalysts screening are provided in the Supporting Information). Thereby it must be considered that the catalytic application within the context of this work was not intended to offer a comprehensive comparison to other literature-known applications of copper(I) based catalysts, nor was it intended to provide a wide-ranging scope of subjected substrates or reaction conditions. The subjected complexes **2b** and **3b** should rather demonstrate the potential of the silylene ligands in a currently uncharted area and, above all, the influence of the functionalization on the reactivity among the two complexes. The progress of the reactions was monitored by ^1H NMR spectroscopy at ambient temperature. To a solution of benzyl azide (1.00 equiv), the appropriate alkyne (1.00 equiv), and adamantane as an internal standard in deuterated dichloromethane (dcm) complex **2b**/**3b** was added (Scheme 5). For the alkyne scope we chose commonly used small alkynes like phenylacetylene, 2-ethynylpyridine, and 3-butyn-1-ol and sterically more demanding ones like *tert*-butylacetylene and ethynyltrimethylsilane. The results of our time-resolved measurements are depicted in Chart 1 and summarized in Table 3, respectively. Within the framework of these catalytic investigations, blank tests were performed for cross-checking to ensure that the determined conversion rates did not originate from possible traces of neat Cu(I)Br (see Supporting Information for further details).

Scheme 5. General Synthesis of the Triazoles P1-5 via the CuAAC Conducted Here[a]



[a]Catalyst = **2b**/**3b**; R = Ph–CCH, Py-CCH, 3-butyn-1-ol, *t*Bu-CCH, TMS-CCH.

Both complexes show catalytic activity toward the formation of triazoles in CuAAC reactions. A more detailed look at the smaller triazoles **P1**–**P3** reveals that the trinuclear complex **3b** shows significantly improved conversion times than the tetrameric complex **2b**. The quantitative conversion of **P2** and **P3** was already achieved after 1.5 and 0.5 h, respectively, and was therefore 3 to 8 times faster as with **2b**. The formation of **P1** shows a half-conversion time of ~8.5 h using **2b**. Changing to complex **3b** leads to a full conversion within 8 h. At this point, it must be noted that conversion times in this area can still not fully compete when compared to the literature, but they illustrate the potential of silylenes and more important functionalized silylenes as active catalysts. Moreover, the decrease in conversion times between complex **2b** and **3b** shows how the ligand design can increase the reactivity. Dimeric NHC-Cu(I) systems most likely tend to undergo decomplexation in solution during CuAAC reactions to form more reactive species.[70] It is questionable if the tetrameric pseudocubane **2b** undergoes similar transformations. However, the increased activity of the trinuclear complex **3b** indicates an improved ligand design. The above-mentioned possibility to

Chart 1. Time−Conversion Diagram of the CuAAC Reactions of Benzyl Azide with the Corresponding Alkynes (right) in the Presence of 1 mol % 2b (hollow icons) or 3b (full icons) under Inert Conditions, in dcm-d_2 at Ambient Temperature

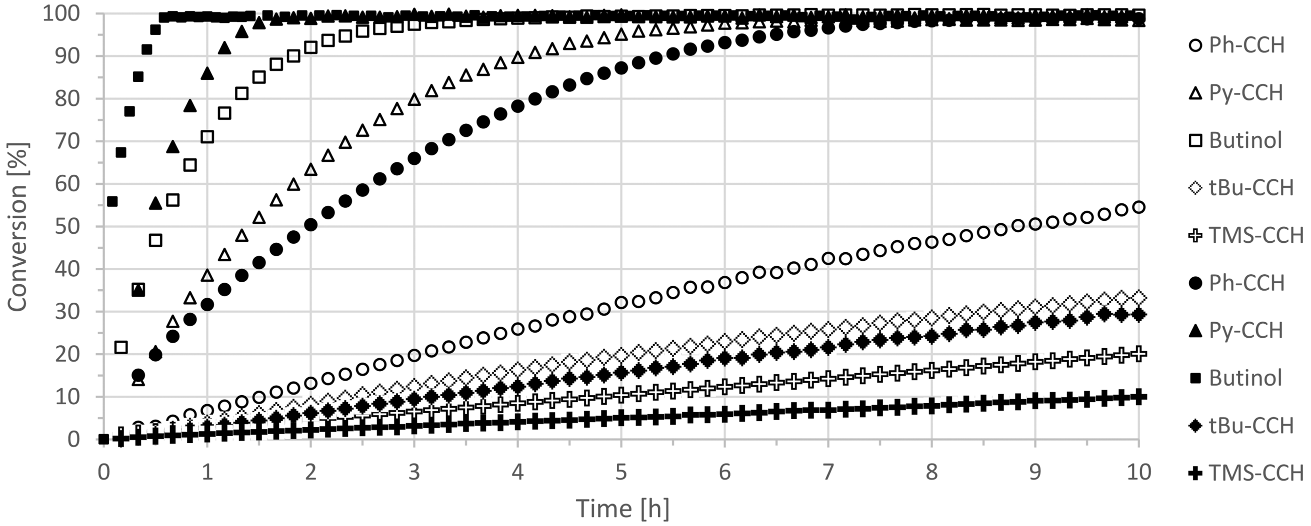


Table 3. Yields and Conversion Times of the Triazoles P1−P5, Monitored by ^{1}H NMR Spectroscopic Analysis[a]

	2b	3b
P1 (R = Ph)	∼46% (8 h)	>99% (8 h)
P2 (R = Py)	>99% (6 h)	>99% (1.5 h)
P3 (R = C_2H_6OH)	>99% (4 h)	>99% (0.5 h)
P4 (R = *t*Bu)	∼33% (10 h)	∼29% (10 h)
P5 (R = TMS)	∼20% (10 h)	∼10% (10 h)

[a] Yields were determined by the integration of the corresponding ^{1}H NMR spectra normalized on the internal standard (adamantane).

cleave the copper nitrogen coordination of the pyridyl groups to form reaction intermediates could be a reason for this observation.

The rather sterically demanding substrates (**P4**, **P5**) showed significantly longer conversion times in both cases. We suggest that the steric bulk of the *tert*-butyl and TMS group hinders the substrates from forming the reactive intermediates and therefore the products. Especially since complex **3b** shows even slightly slower conversion times it is logical to assume that the more complex design of the trinuclear compound hinders the substrate from reacting or that the reaction intermediates are more shielded toward substrates.

■ CONCLUSIONS

In this work, we present the successful synthesis of six novel *N*-heterocyclic silylene group 11 transition-metal complexes **2a**−**2c** and **3a**−**3c**, respectively. These complexes were obtained by applying a new synthetic approach of a preset metalation of the neat chlorobenzamidinate silylene **1** resulting in the pseudocubane-like compounds **2a**−**2c** followed by the subsequent functionalization via the substitution of the chloro group with the lithiated *N*-mesityl-*N*-(2-pyridyl)amine to isolate the complexes **3a**−**3c**. Each of the resulting complexes $[XCu(I) \leftarrow (Cl)Si(PhC\text{-}(NtBu)_2)]_4$ **2a**−**2c** and $[(XCu(I))_3 \leftarrow (PyNMes)Si(PhC(NtBu)_2)]$ **3a**−**3c** (with X = Cl (**2a**/**3a**), Br (**2b**/**3b**), I (**2c**/**3c**)) was characterized in solid state via XRD analysis and in solution via different NMR techniques as well as via mass spectrometry and elemental analysis. The increase of the catalytic activity from compound **2b** to **3b**, which is accompanied with the introduction of the pyridyl-based group and therefore the advanced coordination of the new metal atom, illustrates the potential of functionalized bidentate *N*-heterocyclic silylene copper(I) complexes.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an atmosphere of N_2 and Ar by Schlenk techniques.[74] All solvents were distilled from Na or K before used for synthesis. Starting materials were purchased commercially and used without further purification. MesNHPy and $PhC(NtBu)_2SiCl$ were synthesized according to literature procedures.[14,15,75,76] ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data were recorded on a Bruker Avance 401 MHz and a Bruker Avance 300 MHz spectrometer and referenced to the deuterated solvent (benzene-d_6, dcm-d_2, thf-d_8). Deuterated solvents were dried over activated molecular sieves (3 Å) and stored in an argon drybox. Elemental analyses (C, H, N) were performed on a Vario EL3 at the Mikroanalytisches Labor, Institut für Anorganische Chemie, University of Göttingen. LIFDI-MS spectra were measured on a Jeol AccuTOF spectrometer.

Shock-cooled crystals were selected from a Schlenk flask under argon atmosphere using the X-TEMP2 device.[77−79] The data were collected with a Mo−I*μ*S microfocus source.[80] All data were integrated with SAINT,[81] and a multiscan absorption correction (SADABS)[82] was applied. For structures **2b**, **3a**, and **3b**, a 3λ correction was applied.[82] The structures were solved by direct methods (SHELXT)[83] and refined on F^2 using the full-matrix least-squares methods of SHELXL[84] within the SHELXLE GUI.[85] The Crystallographic Information Files (CIF) can be obtained free of charge as indicated in the Supporting Information.

General Procedure for the Preparation of 2. The copper precursor (1.00 equiv) was dissolved in thf (2 mL) to form a white suspension and was subsequently cooled to 0 °C. The chlorosilylene $PhC(NtBu)_2SiCl$ **1** (1.00 equiv) was separately dissolved in thf (5 mL) and slowly added under vigorous stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. After filtration the yellow filtrate was concentrated and stored at −35 °C for 1 d to gain the target compounds in the form of crystals suitable for X-ray analysis.

*Preparation of **2a**.* Following the general procedure described above CuCl (168 mg, 1.70 mmol) and $PhC(NtBu)_2SiCl$ **1** (500 mg, 1.70 mmol) were used and resulted in pale yellow crystals (448.8 mg, 0.285 mmol, 67%).

^{1}H NMR (300.13 MHz, dcm-d_2, ppm): 7.72−7.69 (m, 1H, C*Ph*), 7.60−7.49 (m, 4H, C*Ph*), 1.26 (s, 18H, N^t*Bu*). ^{13}C{^{1}H} NMR (75.48

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MHz, dcm-d_2, ppm): 172.11 (CPh), 131.21 (C*Ph*), 130.59 (C*Ph*), 128.68 (C*Ph*), 128.38 (C*Ph*), 128.07 (C*Ph*), 54.33 (NC(CH$_3$)$_3$), 30.53 (N^t*Bu*). ^{29}Si{^{1}H} NMR (79.49 MHz, dcm-d_2, ppm): 27.73. Elemental analysis (%) calcd for $C_{60}H_{92}N_8Si_4Cl_8Cu_4$: C, 45.74; H, 5.89; N, 7.11; found C, 45.44; H, 5.65; N, 7.31.

*Preparation of **2b**.* Following the general procedure described above CuBr(SMe$_2$) (348 mg, 1.70 mmol) and PhC(N*t*Bu)$_2$SiCl **1** (500 mg, 1.70 mmol) were used and resulted in yellowish crystals (550 mg, 0.302 mmol, 71%).

^{1}H NMR (400.13 MHz, benzene-d_6, ppm): 7.35 (d, *J* = 8.1 Hz, 1H, C*Ph*), 7.13−6.98 (m, 4H, C*Ph*), 1.21 (s, 18H, N^t*Bu*). ^{13}C{^{1}H} NMR (100.62 MHz, benzene-d_6, ppm): 171.52 (CPh), 131.08 (C*Ph*), 130.09 (C*Ph*), 128.35 (C*Ph*), 128.32 (C*Ph*), 127.66 (C*Ph*), 54.29 (NC(Me)$_3$), 30.75 (N^t*Bu*). ^{29}Si{^{1}H} NMR (79.49 MHz, benzene-d_6, ppm): 26.09. MS (ESI[+], thf): *m*/*z* = 2144.78 (<5) [M-Br$^-$+2SbF$_6$]$^+$. Elemental analysis (%) calcd for $C_{60}H_{92}N_8Si_4Br_4Cl_4Cu_4(C_7H_8)$: C, 43.60; H, 5.46; N, 6.07; found C, 43.00; H, 5.40; N, 5.96.

*Preparation of **2c**.* Following the general procedure described above CuI (323 mg, 1.70 mmol) and PhC(N*t*Bu)$_2$SiCl **1** (500 mg, 1.70 mmol) were used and resulted in yellow crystals (454 mg, 0.234 mmol, 55%).

^{1}H NMR (300.13 MHz, dcm-d_2, ppm): 7.66−7.48 (m, 5H, C*Ph*), 1.30 (s, 18H, N^t*Bu*). ^{13}C{^{1}H} NMR (75.48 MHz, dcm-d_2, ppm): 172.14 (CPh), 130.87 (C*Ph*), 130.63 (C*Ph*), 128.63 (C*Ph*), 128.50 (C*Ph*), 128.16 (C*Ph*), 54.58 (NC(CH$_3$)$_3$), 31.11 (N^t*Bu*). ^{29}Si{^{1}H} NMR (79.49 MHz, dcm-d_2, ppm): 22.62. Elemental analysis (%) calcd for $C_{60}H_{92}N_8Si_4I_4Cl_4Cu_4(C_7H_8)$: C, 39.57; H, 4.96; N, 5.51; found C, 38.92; H, 4.61; N, 5.42.

General Procedure for the Preparation of 3. The compound **2** (1.00 equiv) and the amine MesNHPy (4.00 equiv) were dissolved in a mixture of toluene (3 mL) and thf (3 mL) in a ratio of 1:1 and cooled to −30 °C. A separately prepared solution of LiHMDS (4.00 equiv) in thf (2 mL) was added dropwise and subsequently allowed to warm to ambient temperature under constant stirring for ∼16 h. The resulting suspension was concentrated, until a yellow solid precipitated, which was filtered off and dissolved in dcm to fully remove the LiCl salt in a further filtration step. The concentrated solution was stored at −35 °C for 1 d. The target compounds were isolated in form of yellow crystals suitable for X-ray analysis.

*Preparation of **3a**.* Following the general procedure described above, **2a** (213 mg, 0.135 mmol), MesNHPy (115 mg, 0.540 mmol), and LiHMDS (90.4 mg, 0.540 mmol) were used and resulted in yellow crystals (183 mg, 0.148 mmol, 55%).

^{1}H NMR (300.13 MHz, dcm-d_2, ppm): 8.39 (br s, 1H, N*Py*), 7.61−7.42 (m, 5H, C*Ph*), 7.45 (ddd, *J* = 8.8 Hz, 6.2, 1.9 Hz, 1H, N*Py*), 7.06 (s, 2H, N*Mes*), 6.80 (t, *J* = 6.2 Hz, 1H, N*Py*), 6.01 (dt, *J* = 8.5, 1.0 Hz, 1H, N*Py*), 2.39−2.35 (m, 9H, Mes*CH$_3$*), 1.11 (br s, 18H, N^t*Bu*). ^{13}C{^{1}H} NMR (75.48 MHz, dcm-d_2, ppm): 172.09 (CPh), 160.05 (N*Py*), 146.05 (N*Py*), 138.71 (N*Mes*), 137.92 (N*Mes*), 137.24 (N*Mes*), 136.46 (N*Mes*), 130.57 (N*Py*), 129.62 (C*Ph*), 128.96 (N*Mes*), 128.38 (C*Ph*), 128.15 (C*Ph*), 128.00 (C*Ph*), 114.42 (N*Py*), 108.16 (N*Py*), 54.73 (NC(CH$_3$)$_3$), 31.32 (N^t*Bu*), 20.66 (Mes*Me*), 19.38 (Mes*Me*). MS (LIFDI[+], thf): *m*/*z* = 1117.2 (5) [M-Cl]$^+$, 919.4 (100) [M-Cu$_2$Cl$_3$]$^+$. Elemental analysis (%) calcd for $C_{58}H_{76}N_8Si_2Cl_3Cu_3(C_7H_8)_2$: C, 60.78; H, 6.52; N, 7.88; found C, 61.38; H, 6.33; N, 7.70.

*Preparation of **3b**.* Following the general procedure described above, **2b** (234.0 mg, 0.134 mmol), MesNHPy (114 mg, 0.535 mmol), and LiHMDS (89.5 mg, 0.535 mmol) were used and resulted in yellow crystals (77.8 mg, 0.0567 mmol, 42%).

^{1}H NMR (300.13 MHz, dcm-d_2, ppm): 8.27−8.17 (m, 1H, N*Py*), 7.66−7.49 (m, 3H, C*Ph*), 7.45 (ddd, *J* = 8.8, 7.1, 1.9 Hz, 1H, N*Py*), 7.42−7.35 (m, 2H, C*Ph*), 7.06 (s, 2H, N*Mes*), 6.68 (ddd, *J* = 6.6, 5.3, 1.1 Hz, 1H, N*Py*), 6.17 (d, *J* = 8.5 Hz, 1H, N*Py*), 2.35 (s, 3H, Mes*CH$_3$*), 2.31 (s, 6H, Mes*CH$_3$*), 1.05 (s, 18H, N^t*Bu*). ^{13}C{^{1}H} NMR (75.48 MHz, dcm-d_2, ppm): 170.81 (CPh), 162.30 (N*Py*), 148.10 (N*Py*), 139.35 (NMes), 138.74 (N*Py*), 136.20 (N*Mes*), 136.10 (N*Mes*), 131.63 (C*Ph*), 130.74 (C*Ph*), 129.81 (N*Mes*), 128.38 (C*Ph*), 127.83 (C*Ph*), 114.16 (N*Py*), 111.45 (N*Py*), 54.16 (NC(CH$_3$)$_3$), 31.06 (N^t*Bu*), 20.54 (Mes*Me*), 19.70 (Mes*Me*). MS (LIFDI[+], thf): *m*/*z* = 1435.0 (100) [M-Br+2thf]$^+$, 1291.2 (5) [M-Br]$^+$. Elemental analysis (%) calcd for $C_{58}H_{76}N_8Si_2Br_3Cu_3(C_7H_8)_2$: C, 55.57; H, 5.96; N, 7.20; found C, 58.26; H, 5.71; N, 7.19.

*Preparation of **3c**.* Following the general procedure described above, **2c** (334 mg, 0.172 mmol), MesNHPy (146 mg, 0.688 mmol), and LiHMDS (115 mg, 0.688 mmol) were used and resulted in yellow crystals (159 mg, 0.105 mmol, 31%).

^{1}H NMR (300.13 MHz, dcm-d_2, ppm): 8.72 (br s, 1H, N*Py*), 7.59−7.40 (m, 5H, C*Ph*), 7.48−7.42 (m, 1H, N*Py*), 7.08 (s, 2H, N*Mes*), 6.79 (ddd, *J* = 6.8, 5.4, 1.1 Hz, 1H, N*Py*), 6.00 (d, *J* = 8.5 Hz, 1H, N*Py*), 2.41−2.37 (m, 9H, Mes*CH$_3$*), 1.04 (s, 18H, N^t*Bu*). ^{13}C{^{1}H} NMR (75.48 MHz, dcm-d_2, ppm): 172.68 (CPh), 161.13 (N*Py*), 148.57 (N*Py*), 139.93 (N*Mes*), 138.96 (N*Py*), 137.93 (N*Mes*), 137.34 (N*Mes*), 131.68 (C*Ph*), 130.47 (C*Ph*), 129.82 (N*Mes*), 128.96 (C*Ph*), 128.15 (C*Ph*), 114.46 (N*Py*), 110.31 (N*Py*), 54.68-(NC(CH$_3$)$_3$), 31.28 (N^t*Bu*), 20.60 (Mes*Me*), 20.12 (Mes*Me*). MS (LIFDI[+], thf): *m*/*z* = 1385.3 (10) [M-I]$^+$, 1003.6 (<5) [M-Cu$_2$I$_3$]$^+$. Elemental analysis (%) calcd for $C_{58}H_{76}N_8Si_2I_3Cu_3(C_7H_8)$: C, 48.64; H, 5.28; N, 6. 98; found C, 53.53; H, 5.21; N, 7.11.

General Procedure for Catalysis. A NMR Young tube was charged with benzyl azide (1.00 equiv), the appropriate alkyne (1.00 equiv), adamantane as an internal standard, and deuterated dichloromethane. After an initial measurement of the neat reactants, the complex **2b**/**3b** was added. The progress of the reaction was monitored via ^{1}H NMR spectroscopic measurements in 10 min steps for at least 10 h.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00629.

> Discussion of experimental details, X-ray crystallographic and NMR spectroscopic analyses, additional references (PDF)

Accession Codes

CCDC 1898639−1898644 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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