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Copper(I) Heteroleptic Bis(NHC) and Mixed NHC/Phosphine Complexes: Syntheses and Catalytic Activities in the One-Pot Sequential CuAAC Reaction of Aromatic Amines

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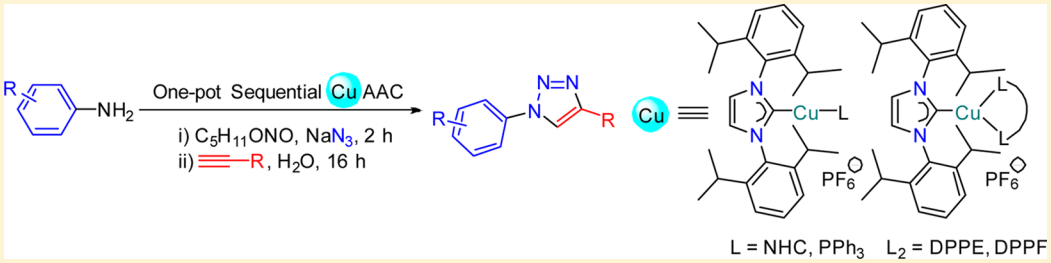
Supporting Information



ABSTRACT: A series of 2-coordinate heteroleptic Cu(I) complexes of the general formula $[Cu(IPr)(L)]PF_6$ (**2**–**5**, L = NHC or phosphine) have been synthesized via either (i) chlorido substitution by phosphine or in situ generated free NHC or (ii) the Ag–NHC transfer protocol using [CuCl(IPr)] (**1**) as a precursor (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene). The reactions of precursor **1** with diphosphine ligands afforded 3-coordinate heteroleptic Cu(I) complexes of the type $[Cu(IPr)(L_2)]PF_6$ (**6** and **7**, L_2 = diphosphine). Complexes **1**–**7** have been subjected to a catalytic one-pot sequential CuAAC study, in which aromatic amines serve as the precursors to aryl azides. Hetero-bis(NHC) complexes **2**–**4** proved to be generally superior compared to their mixed NHC/phosphine counterparts **5**–**7**. Overall, complex $[Cu(Bn_2\text{-imy})(IPr)]PF_6$ (**2**), bearing the Bn_2-imy (Bn_2-imy = 1,3-dibenzyl-imidazolin-2-ylidene) coligand, showed the best catalytic performance.

INTRODUCTION

N-heterocyclic carbenes (NHCs) have become ubiquitous ligands in organometallic chemistry, and since the pioneering work of Arduengo et al.,[1] the interest in Cu(I)–NHC complexes[2] has surged due to their widespread applications, especially in homogeneous catalysis.[3] Despite numerous reports on Cu(I)–NHCs, cationic heteroleptic Cu(I) complexes of the general formula $[Cu(NHC)(L)]^+Y^-$ (L = NHC′ or phosphine, Y = noncoordinating anion) have received little attention.[4] In addition, the reported examples mainly focus on classical imidazolin-2-ylidenes, and the scope of various other NHC types remains largely unexplored in Cu(I) chemistry.

Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) has become a powerful approach for the construction of 1,4-disubstituted 1,2,3-triazoles.[3b−d,5] Most of the previous studies employed preformed azides, while there are only a few scattered examples using in situ generated azides.[6] The latter is clearly more advantageous, as additional intermediate isolation is circumvented, and the handling of potentially hazardous azides can be minimized. A few one-pot CuAAC methodologies using aromatic amines as precursors of aryl azides have been disclosed.[6a−c] However, and to the best of our knowledge, the catalytic activities of Cu(I)–NHCs in such one-pot sequential CuAAC reactions are still unknown. Thus, we herein report a series of new heteroleptic Cu(I) complexes of the type $[Cu(IPr)(L)]PF_6$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, L = NHC or phosphine) and $[Cu(IPr)(L_2)]PF_6$ (L_2 = diphosphine). A one-pot sequential CuAAC study using these complexes as precatalysts, and exploiting aryl azides in situ generated from aromatic amines, is described as well.

RESULTS AND DISCUSSION

Syntheses and Characterization of Cu(I) Hetero-bis(NHC) Complexes. Au(I) hetero-bis(NHC) complexes of the general formula [Au(NHC)(NHC′)]Y (Y = noncoordinating anion) can be synthesized by reacting a mono-NHC precursor [AuX(NHC)] (X = halido ligand) with the respective azolium salts and a base under in situ generation of the free NHC.[7] However, it should also be noted that, in a few cases, this protocol reportedly led to the formation of Au(I) homo-bis(NHC) complexes of the formulas $[Au(NHC)_2]Y$ and $[Au(NHC')_2]Y$.[7b,8]

Nevertheless and as an initial attempt, this convenient route was tested for the preparation of hetero-bis(NHC) congeners of Cu(I). The mono-NHC precursor [CuCl(IPr)] (**1**) was prepared via a modified procedure involving direct cupration of the respective salt precursor with Cu_2O (Scheme 1).[9] When complex **1** was treated with the azolium salts $Bn_2\text{-imy}\cdot H^+PF_6^-$

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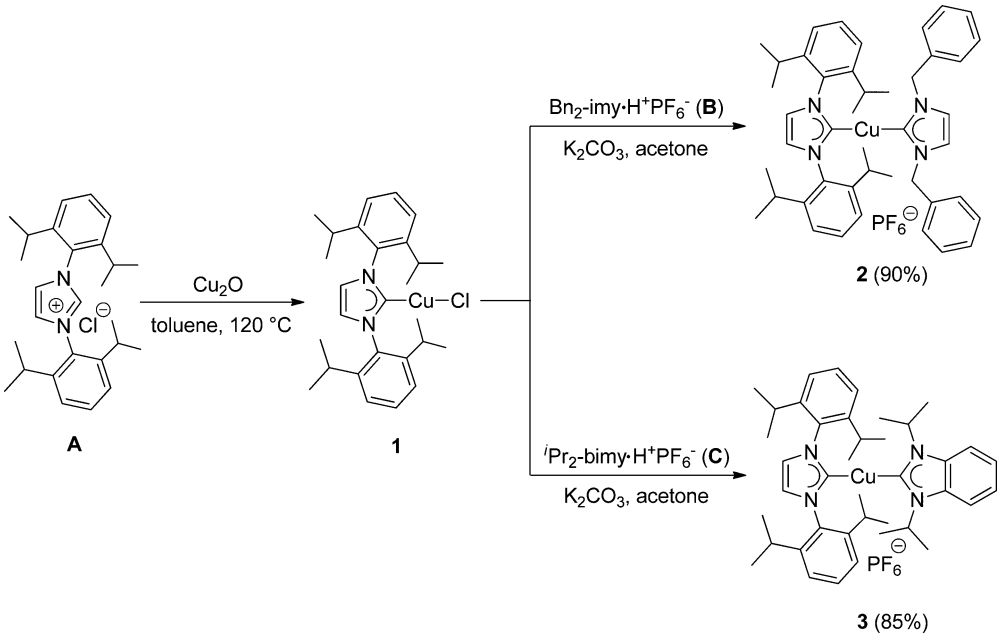
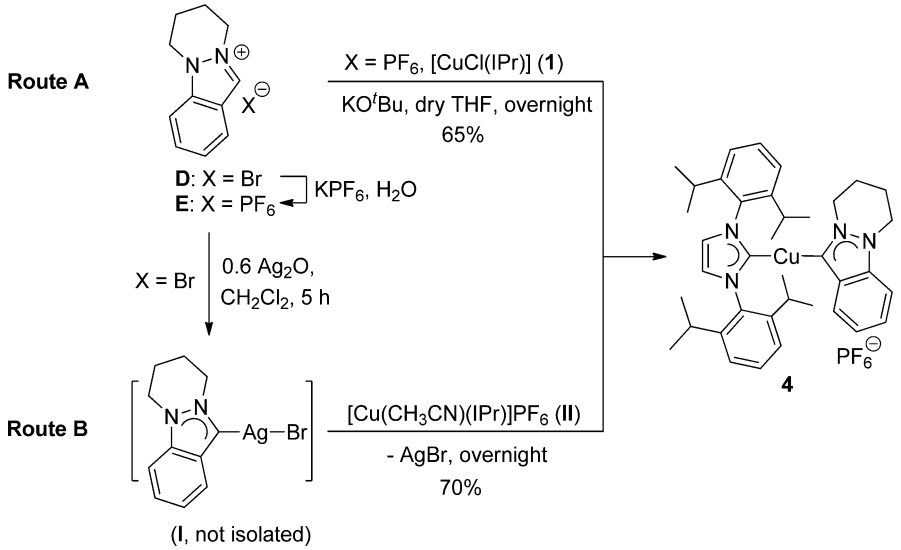
Scheme 1. Syntheses of Cu(I) Heteroleptic Bis(NHC) Complexes 2 and 3



Scheme 2. Synthesis of Cu(I) Heteroleptic Bis(NHC) Complex 4



(**B**) and $^{i}Pr_2$-bimy·$H^+PF_6^-$ (**C**) in the presence of K_2CO_3 in acetone, heteroleptic bis(NHC) complexes [Cu(IPr)(Bn_2-imy)]PF_6 (**2**) and [Cu(IPr)($^{i}Pr_2$-bimy)]PF_6 (**3**) can be cleanly obtained in high yields of 90% and 85%, respectively (Bn_2-imy = 1,3-dibenzylimidazolin-2-ylidene, $^{i}Pr_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene). Gratifyingly, no homo-bis(NHC) side products were observed (vide supra). A potential ligand redistribution process leading to the latter is likely to be hampered by the presence of the bulky IPr ligand.[7b] Finally, it should be noted that this synthetic protocol is well applicable to classical NHCs and can be carried out under aerobic conditions in wet acetone with little decomposition.

However, the same protocol failed in the attempt to incorporate the nonclassical carbene ligand Indy (Indy = 6,7,8,9-tetrahydropyridazino[1,2-a]indazolin-3-ylidene). The failure of this cupration reaction should result from the relatively weak acidity of the indazolium salt Indy·$H^+PF_6^-$ (**E**), which renders K_2CO_3 insufficiently basic for its deprotonation.[7a,b] In view of this, a stronger base, KO^{t}Bu, was examined (Scheme 2, Route A), and this reaction successfully afforded the hetero-bis(NHC) complex [Cu(IPr)(Indy)]PF_6 (**4**) in a moderate yield.

Nevertheless, it should be also noted that inert conditions are required for the reaction employing KO^{t}Bu as the base. Thus, to seek for a more "user-friendly" protocol, we opted for the silver−carbene transfer route, which was previously used to synthesize indazolin-3-ylidene complexes of Pd(II), Au(I), and Rh(I).[7a,b,10] The Ag−carbene intermediate **I**, formed by the reaction of azolium salt Indy·H^+Br^- (**D**) and Ag_2O, was treated with the known acetonitrile adduct [Cu(CH_3CN)(IPr)]PF_6 (**II**)[11] (Scheme 2, Route B), which also yielded hetero-bis(NHC) complex **4** in a decent yield. To the best of our knowledge, this is the first example employing the silver−

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Table 1. Selected NMR Data of Cu(I) Hetero-NHC Complexes 1−4

complex	δ_{H1}[a] (ppm)	δ_{H2}[a] (ppm)	δ_{C1}[b] (ppm)	δ_{C2}[b] (ppm)
[CuCl(IPr)] (**1**)[9]	2.55		180.5	
[Cu(IPr)(Bn_2-imy)]PF_6 (**2**)[c]	2.56	4.53	180.3	176.2
[Cu(IPr)($^i Pr_2$-bimy)]PF_6 (**3**)	2.59	3.95	179.3	178.7
[Cu(IPr)(Indy)]PF_6 (**4**)	2.58	4.09, 3.56, 2.19, 1.89	180.8	176.6

[a] δ_{H1} refers to the signals due to isopropyl C−H protons in the IPr ligand, and δ_{H2} refers to the signals due to benzylic (**2**), NCH (**3**), and methylene (**4**) protons in the second carbene ligand. [b] δ_{C1} refers to the carbene signal of the IPr ligand, and δ_{C2} refers to the carbene signal of the second NHC ligand. ^{13}C NMR spectra were measured in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm relative to TMS. [c] In CD_3CN.

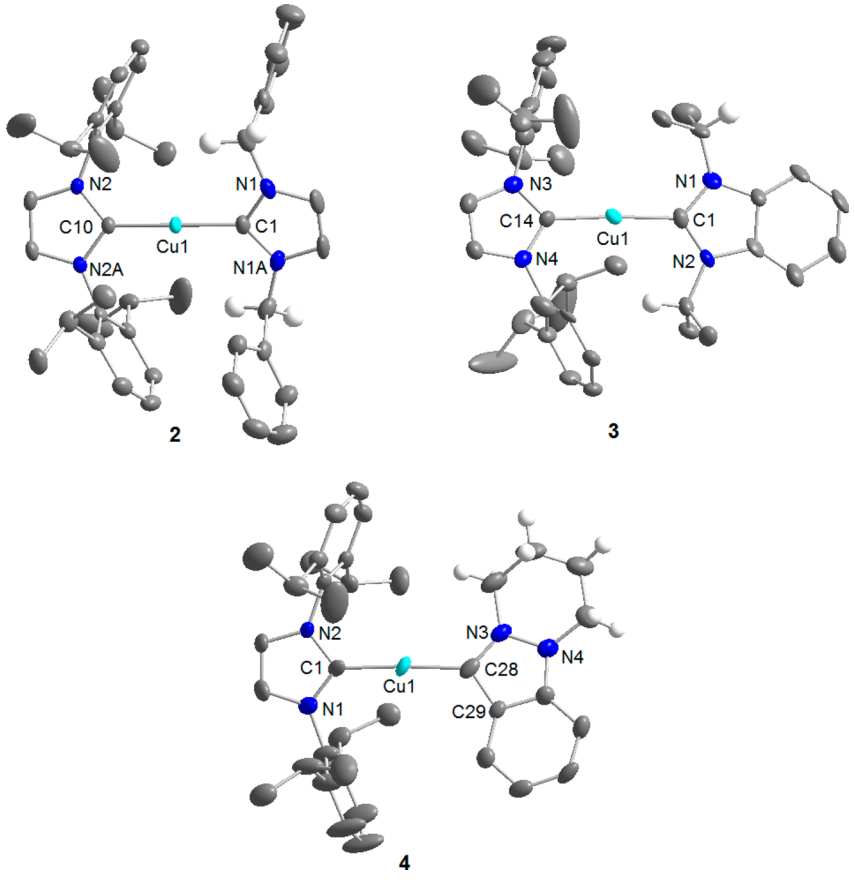

Figure 1. Molecular structures of **2**−**4** showing 50% probability ellipsoids. All the hydrogen atoms, PF_6^- anions, and solvent molecules have been omitted for clarity, except the hydrogen atoms of Bn_2-imy NCH_2 (**2**), ^{i}Pr2-bimy NCH (**3**) and Indy CH_2 (**4**) moieties. Selected bond lengths (Å) and bond angles (deg) for **2**: Cu1−C1 1.887(4), Cu1−C10 1.887(3); C10−Cu1−C1 180.00(10), N1−C1−N1A 104.0(3), N2−C10−N2A 103.9(3). For **3**: Cu1−C14 1.899(8), Cu1−C1 1.910(8); C14−Cu1−C1 175.7(4), N1−C1−N2 106.3(6), N3−C14−N4 104.2(7). For **4**: Cu1−C28 1.895(5), Cu1−C1 1.907(5); C28−Cu1−C1 176.5(2), N2−C1−N1 103.9(4), N3−C28−C29 103.9(4).

carbene transmetalation protocol for the synthesis of Cu(I) hetero-bis(NHC) complexes.

Complexes **2**−**4** were isolated as white solids, which are readily soluble in CH_2Cl_2, acetone, and DMSO, but sparingly soluble in ethyl acetate and insoluble in nonpolar solvents, such as diethyl ether and *n*-hexane. Their formation is supported by ESI mass spectrometry, where dominant peaks are observed at *m*/*z* 699 (**2**), 653 (**3**), and 623 (**4**) for the respective cationic $[M - PF_6]^+$ species.

In general, the ^{1}H NMR signals of the IPr ligand in all new hetero-bis(NHC) complexes resemble those observed for precursor **1** (Table 1). The benzylic protons of the Bn_2-imy ligand in **2** give rise to a singlet at 4.53 ppm, which shows a significant upfield shift in contrast to that in its precursor salt **B** (cf. 5.31 ppm). Similar upfield shifts were also observed for the $^i Pr_2$-bimy NCH protons in **3** and the Indy methylene protons in **4**, which are likely to result from the shielding effect exerted by IPr phenyl rings on the respective protons of the second carbene ligand.[12]

In the ^{13}C NMR spectra of hetero-bis(NHC) complexes **2**−**4**, two carbene carbon signals are observed as expected. These downfield resonances fall in a narrow region (176.2−180.8 ppm), and all of them can be unequivocally assigned by HMBC-NMR spectroscopic analyses. A closer inspection of the IPr $^{13}C_{carbene}$ signals among **2**−**4** revealed that these resonances do not correlate with the donating ability of the second NHC ligand, again possibly due to the shielding effect of the N-aryl substituents. This is in contrast to previously reported Pd(II) and Au(I) systems, i.e., *trans*-[$PdBr_2$($^i Pr_2$-bimy)(**NHC**)][13] or [Au($^i Pr_2$-bimy)(**NHC**)]BF_4/PF_6,[7b] where a very good "donor strength/$^{13}C_{carbene}$ signal" correlation was observed when the $^i Pr_2$-bimy ligand was employed as the diagnostic probe.

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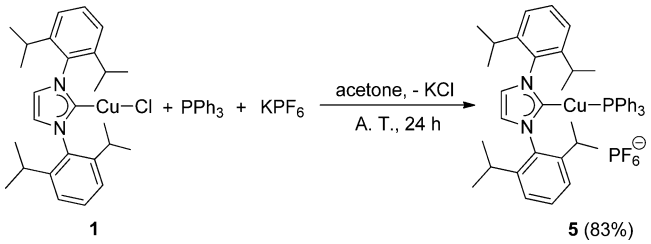
Single crystals of **2**–**4** suitable for X-ray diffraction studies were obtained by either slow evaporation of the solvent from a concentrated CH_2Cl_2/hexane solution (**2**) or vapor diffusion of Et_2O into a concentrated $CHCl_3$ solution (**3** and **4**). The molecular structures are shown in Figure 1, and the selected crystallographic data are listed in Table SI-1 (see the Supporting Information).

The complexes **2**–**4** contain essentially linear Cu(I) centers, each of which is coordinated by one IPr ligand and a second carbene ligand. The Cu–$C_{carbene}$ bond lengths of **2**–**4** are essentially equal within 3σ and comparable with values reported for other Cu(I) bis(NHC) analogues.[4a] The N–isopropyl substituents of complex **3** adopt an *anti* arrangement, which suggests a certain degree of rotational freedom around the N–^{i}Pr bond. This orientation has also been observed for ^{i}Pr$_2$-bimy complexes of Au(I).[7b,14] The two carbene planes in each complex are twisted out of coplanarity with dihedral angles of 18.62° (**2**), 10.37° (**3**), and 17.50° (**4**). Finally, it should be noted that the Bn$_2$-imy benzylic protons in **2**, ^{i}Pr$_2$-bimy NCH protons in **3**, and Indy methylene protons in **4** are all located in the shielding zone of the IPr phenyl rings, which leads to the aforementioned upfield shift of their ^{1}H NMR resonances (vide supra).

Syntheses and Characterization of Cu(I) Mixed NHC/Phosphine Complexes. In further extending the scope of cationic heteroleptic Cu(I) complexes, phosphines and diphosphines were explored as neutral and strongly donating coligands. A one-pot reaction involving chlorido precursor **1**, PPh_3, and excessive KPF_6 in acetone afforded the heteroleptic mixed NHC/phosphine complex [Cu(IPr)(PPh_3)]PF_6 (**5**) in a good yield of 83% (Scheme 3).

Scheme 3. Synthesis of Heteroleptic Complex 5



Complex **5** was isolated as a white solid, which is readily soluble in common organic solvents with the exception of less polar ones, such as ethyl acetate, diethyl ether, and *n*-hexane. The first evidence for its formation was provided by ESI mass spectrometry, which shows a base peak at *m*/*z* 713 assignable to the cationic species [M – PF_6]$^+$. The ^{1}H NMR spectrum of **5** in $CDCl_3$ shows additional aromatic signals due to the newly introduced PPh_3 ligand in addition to those for the IPr ligand. Coordination of the phosphine ligand is further supported by a singlet observed at 8.8 ppm in the ^{31}P NMR spectrum of the complex. On the other hand, the $^{13}C_{carbene}$ resonance could not even be resolved after overnight data acquisition. However, the identity of **5** as a mixed NHC/phosphine complex could finally be corroborated by subjecting single crystals grown by slow vapor diffusion of Et_2O into a concentrated $CHCl_3$ solution to X-ray diffraction analysis. The molecular structure depicted in Figure 2 shows the expected geometry, which slightly deviates from linearity with a C1–Cu1–P1 angle of 176.0(3)°. The Cu–$C_{carbene}$ bond length of 1.912(9) Å is found to be essentially the same with those observed in the hetero-

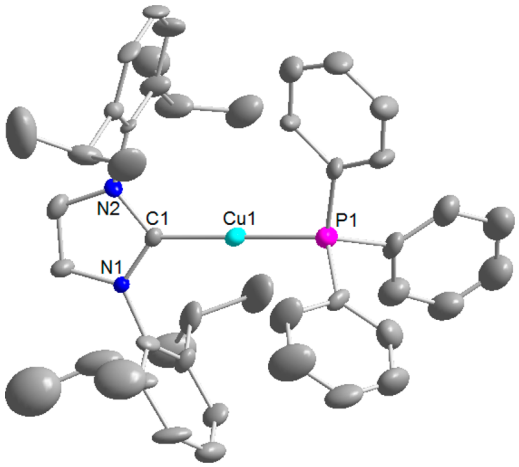


Figure 2. Molecular structure of **5** showing 50% probability ellipsoids. Hydrogen atoms and PF_6^- anions have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Cu1–C1 1.912(9), Cu1–P1 2.187(3); C1–Cu1–P1 176.0(3), N1–C1–N2 105.3(7).

bis(NHC) counterparts **2**–**4**. In addition, a comparison of the Cu–P distances in **5** with its reported trialkylphosphine analogue [Cu(IPr)(P^{t}Bu$_3$)]BF_4[4a] revealed a pronounced elongation in the latter. This can be primarily attributed to the larger steric hindrance of P^{t}Bu$_3$ compared to the PPh_3 ligand, which is clearly indicated by the percent buried volume (%V_{Bur}) value of 41.9 for P^{t}Bu$_3$ vs 33.4 for PPh_3,[15] although the stronger σ-donating and weaker π-accepting properties of the P^{t}Bu$_3$ ligand do play an important role in this bond elongation as well.

Although a wide range of multicoordinate Cu(I)–NHCs have been reported,[16] 3-coordinated 16-electron complexes of the general formula [Cu(NHC)(L_2)]$^+$ supported by a simple bidentate ligand L_2 are surprisingly rare.[17] Moreover, the reported examples exclusively employed rigid planar *N*,*N*-chelators as supporting ligands.

Hence, the reactivity of precursor **1** toward diphosphine ligands was explored with the objective to gain access to novel 3-coordinate mixed NHC/diphosphine Cu(I) complexes. The reactions of complex **1** with 1,2-bis(diphenylphosphino)ethane (DPPE) or 1,1′-bis(diphenylphosphino)ferrocene (DPPF) in the presence of KPF_6 indeed afforded 3-coordinate complexes [Cu(IPr)(DPPE)]PF_6 (**6**) and [Cu(IPr)(DPPF)]PF_6 (**7**), respectively (Scheme 4). Due to the increased difficulty of coordinating two additional donors to a d^{10} Cu(I) center, the reaction time was extended to 48 h.

Complexes **6** and **7** were isolated as white and yellow solids, respectively, which have very similar solubilities compared to that of the monophosphine counterpart **5**. Base peaks centered at *m*/*z* 849 (**6**) and 1005 (**7**) in their ESI mass spectra with the correct isotopic patterns for the respective [M – PF_6]$^+$ fragments lend support for the formation of mixed NHC/diphosphine complexes. The presence of diphosphine ligands was also confirmed by ^{1}H NMR spectra of **6** and **7**. While the ethylene bridge in DPPE of **6** gives rise to one multiplet at 2.02 ppm, two broad singlets are found at 4.32 and 4.14 ppm, characteristic for the Cp protons of the DPPF ligand in **7**. These spectroscopic features suggest a 2-fold symmetry of the molecules in solution. In addition, the resonance due to IPr isopropyl C–H protons shows a pronounced downfield (**6**) or upfield (**7**) shift upon the coordination of diphosphine ligands. The $^{13}C_{carbene}$ signal of complex **6** could not be detected, but is

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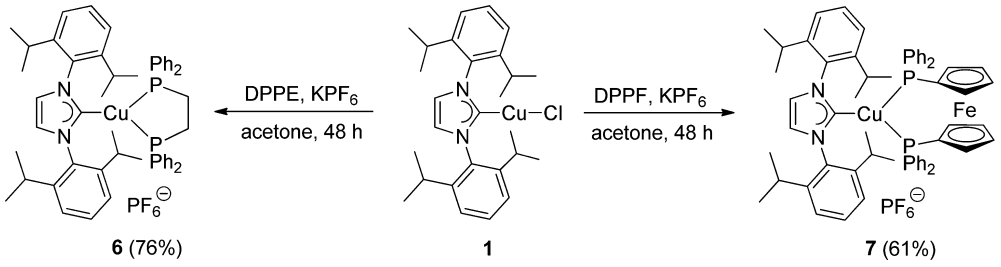
Scheme 4. Synthesis of Complexes 6 and 7



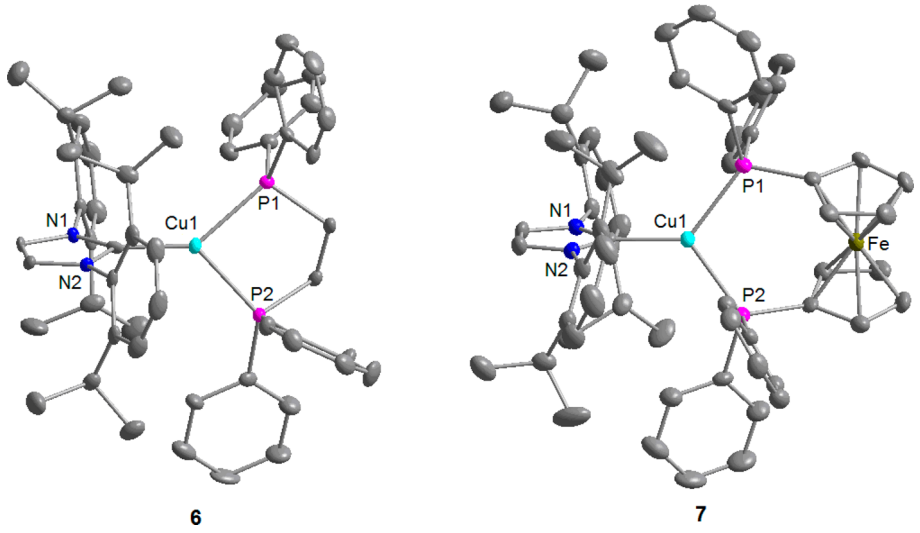


Figure 3. Molecular structures of **6** and **7** showing 50% probability ellipsoids. Hydrogen atoms, PF_6^- anions, and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **6**: Cu1−C1 1.940(4), Cu1−P1 2.3138 (11), Cu1−P2 2.2855(11); C1−Cu1−P1 139.68(11), C1−Cu1−P2 132.29(11), P2−Cu1−P1 87.97(4), N1−C1−N2 102.8(3). For **7**: Cu1−C1 1.964(3), Cu1−P1 2.3025(10), Cu1−P2 2.3151(10); C1−Cu1−P1 126.87(10), C1−Cu1−P2 125.99(10), P1−Cu1−P2 107.14(4), N1−C1−N2 102.9(3).

observed at 178.1 ppm for complex **7**. The coordination of the diphosphine ligands was further verified by ^{31}P NMR spectra of **6** and **7**, which display a singlet at −6.0 and −15.2 ppm, respectively, falling in the range typically observed for Cu(I) diphosphine complexes.[18] Notably, these ^{31}P NMR signals show marked upfield shifts compared to that in monophosphine counterpart **5**.

X-ray diffraction analyses were conducted on single crystals of **6** and **7** obtained by slow vapor diffusion of Et_2O into their concentrated solutions in $CHCl_3$. These reveal a distorted trigonal-planar geometry for both complexes (Figure 3). The chelating diphosphine ligands are oriented almost perpendicularly to the IPr imidazole backbones with dihedral angles of ∼73° (**6**) and ∼77° (**7**) between the NHC planes and those defined by the Cu center and the two P donor atoms. The bite angles of 87.97(4)° (**6**) and 107.14(4)° (**7**) fall in the range typically observed in Cu(I) diphosphine complexes.[18] The Cu−P bond lengths in complexes **6** and **7** ranging from 2.2855(11) to 2.3151(10) Å are essentially equal, but significantly longer than that observed in monophosphine counterpart **5** (cf. 2.187(3) Å). This can be attributed to the increased steric bulk around the Cu(I) center and its lower Lewis acidity as a consequence of diphosphine coordination compared to that of a complex with one monodentate phosphine ligand.

Sequential One-Pot Catalytic CuAAC Reactions. A few Cu(I) systems are known to be active in one-pot sequential CuAAC reactions, which exploit in situ generated aryl azides from aromatic amines via diazotization and subsequent azidation (vide supra).[6a−c] To the best of our knowledge, however, the catalytic activities of Cu(I)−NHCs in such one-pot sequential CuAAC reactions remain unexplored. In a preliminary study, all Cu(I) NHC complexes (**1**−**7**) described herein, and as comparators, monocarbene complex $[Cu(IPr)(CH_3CN)]PF_6$ (**II**) and homo-bis(NHC) complex $[Cu(IPr)_2]PF_6$ (**III**), were, therefore, subjected to a test reaction employing aniline (**8a**) and phenylacetylene (**9a**) as substrates and isopentyl nitrite as diazotization and sodium azide as azidation reagents at a 1 mol % catalyst loading in pure H_2O as an environmentally benign medium. In initial attempts, all components were mixed prior to heating for 16 h. However, this approach gave a nonnegligible amount (ca. 20% yield) of 1,4-diphenyl-1,3-butadiyne, generated by the oxidative homocoupling of **9a**. The formation of this undesired side product can be largely suppressed, when a one-pot, two-step protocol was applied, according to which a mixture of **8a**, isopentyl nitrite, and sodium azide was allowed to stir in H_2O for 2 h before the addition of phenylacetylene and the Cu(I) precatalyst (Table 2).

All Cu(I) complexes proved to be active for this one-pot sequential CuAAC reaction, whereas, in the absence of precatalyst, no formation of triazoles was observed (Table 2, entry 1). Hetero-bis(NHC) complexes were generally superior to mixed NHC−phosphine complexes (entries 3−5 vs entries 6−8). Notably, homo-bis(NHC) complex $[Cu(IPr)_2]PF_6$ (**III**), although inferior compared to most of the hetero-bis(NHC) counterparts, also gives a moderate yield (entry 10).

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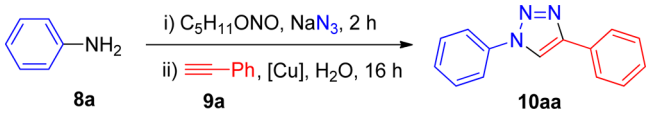
Table 2. One-Pot Sequential CuAAC Catalyzed by Complexes 1−7, II, and III[a]



entry	precatalyst	yield [%][b]
1		0
2	[CuCl(IPr)] (**1**)	46
3	[Cu(IPr)(Bn_2-imy)]PF_6 (**2**)	71
4	[Cu(IPr)($^i Pr_2$-bimy)]PF_6 (**3**)	40
5	[Cu(IPr)(Indy)]PF_6 (**4**)	58
6	[Cu(IPr)(PPh_3)]PF_6 (**5**)	27
7	[Cu(IPr)(DPPE)]PF_6 (**6**)	29
8	[Cu(IPr)(DPPF)]PF_6 (**7**)	32
9	[Cu(IPr)(CH_3CN)]PF_6 (**II**)	24
10	[Cu(IPr_2)]PF_6 (**III**)	51

[a]Reaction conditions: (i) 0.5 mmol of aniline, 0.525 mmol of sodium azide, 0.8 mmol of isopentyl nitrite, 1 mL of H_2O, ambient temperature, 2 h; (ii) 0.525 mmol of phenylacetylene, 1 mol % of [Cu], 1 mL of H_2O, 60 °C, 16 h. [b]Yields were determined by GC-MS with naphthalene as internal standard for an average of two runs.

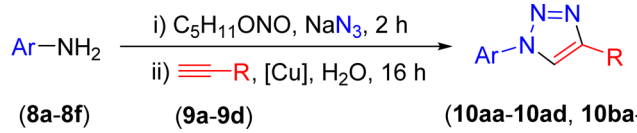
Monocarbene complex [Cu(IPr)(CH_3CN)]PF_6 (**II**) proved to be the poorest performer (entry 9), whereas, interestingly, the chlorido precursor complex **1** showed moderate activity (entry 2). Among all the complexes surveyed, complex **2**, bearing the dibenzylimidazolin-2-ylidene ligand, exhibited the highest catalytic activity. In a previous "CuAAC" study employing neat azides and alkynes, Cazin et al. have postulated that the catalytic activity of Cu(I) hetero-bis(NHC) complexes is enhanced by stronger donating abilities and improved flexibilities of the supporting NHC ligands. The results obtained here support this concept only in part. It seems that ligand flexibility does play a crucial role, since the dibenzylimidazolin-2-ylidene ligand in the best performer **2** is the most flexible. However, it is also the weakest donating NHC among all the cocarbene ligands in **2**−**4**, which partly contrasts the above postulation.

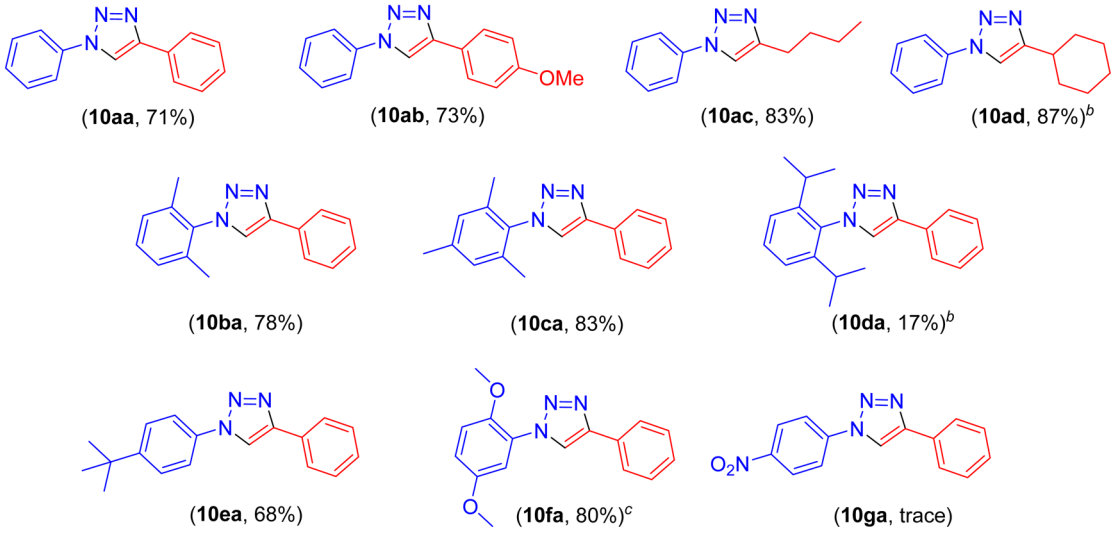
Using complex **2** as the best performer, a selection of electronically and sterically varied alkynes and aromatic amines were exploited in a small substrate scope study, and the results are summarized in Scheme 5.

The reactions employing either aliphatic or aromatic terminal alkynes all proceeded smoothly, and a series of 1,2,3-triazoles (**10aa**−**10ad**) were afforded in good yields of up to 87%. Notably, aliphatic alkynes showed better reactivity, suggesting a slight preference for electron-rich alkynes in this one-pot sequential CuAAC reaction (**10aa**, **10ab** vs **10ac**, **10ad**).

However, no simple trend depending on the electronic nature of aromatic amines emerged. It appears that electron-rich aromatic amines are more suitable substrates, giving decent yields of generally >70%, whereas the reactions employing electron-deficient amines are rather sluggish (**10ba**−**10fa** vs **10ga**). More importantly, steric factors play a more crucial role, which is best evidenced by the sharp drop of yield in the case of **10da** where highly bulky isopropyl groups in the ortho-positions were introduced. Nevertheless, it should be noted here that the low yields in the cases of **10da** and **10ga** are largely affected by the difficult in situ formation of the corresponding aryl azides prior to the CuAAC process. To confirm this, tests reactions were carried out without the Cu(I) complexes ceteris paribus in order to isolate the free azide. Indeed, only trace amounts of aryl azides were observed. Further optimization of the reaction conditions, in order to

Scheme 5. One-Pot Sequential CuAAC Reactions Catalyzed by Complex 2[a,b,c]





[a]Reaction conditions: (i) 0.5 mmol of aromatic amine, 0.525 mmol of sodium azide, 0.8 mmol of isopentyl nitrite, 1 mL of H_2O, ambient temperature, 2 h; (ii) 0.525 mmol of alkyne, 1 mol % of **2**, 1 mL of H_2O, 60 °C, 16 h. Isolated yield from an average of two runs. [b]The reaction mixture was heated at 60 °C for 2 h before the addition of phenylacetylene and catalyst. [c]THF was used as the solvent.

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broaden the scope of the aromatic amines, remains to be explored in the future.

CONCLUSION

We have reported the syntheses of 2- and 3-coordinate Cu(I) heteroleptic bis(NHC) and mixed NHC/phosphine complexes, all bearing the bulky IPr spectator ligand. Hetero-bis(NHC) complexes [Cu(IPr)(NHC)]PF_6 (**2**–**4**), incorporating additional imidazole- (**2**), benzimidazole- (**3**), and indazole- (**4**) derived NHC ligands, were prepared via "in situ" deprotonation using K_2CO_3/KO^{t}Bu or by the Ag–carbene transmetalation protocol. 2- and 3-coordinate mixed NHC/phosphine complexes [Cu(IPr)(PPh_3)]PF_6 (**5**), [Cu(IPr)(DPPE)]PF_6 (**6**), and [Cu(IPr)(DPPF)]PF_6 (**7**) were straightforwardly accessed by treating precursor complex [CuCl(IPr)] (**1**) with the respective phosphine or diphosphine ligands. In addition, the catalytic activities of all complexes in one-pot sequential CuAAC reactions, where aromatic amines served as precursors to aryl azides, were evaluated. Generally, hetero-bis(NHC) complexes proved to be superior to their mixed NHC/phosphine counterparts, with complex [Cu(Bn_2-imy)(IPr)]PF_6 (**2**) bearing the flexible dibenzylimidazolin-2-ylidene ligand, performing the best. The straightforward synthetic methods to heteroleptic Cu(I) NHC complexes reported here will facilitate the search for further catalytic applications of such complexes. Current work in our laboratory is focused on broadening the scope of heteroleptic Cu(I) complexes to other types of NHCs.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on 300 and 500 MHz spectrometers, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^{1}H and ^{13}C) or externally to 85% H_3PO_4 (^{31}P) and CF_3CO_2H (^{19}F). ESI mass spectra were measured using an LCQ spectrometer. Elemental analyses were performed on a Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore. Salts **A**,[19a] **C**,[7a] and **D**[19b] were synthesized following previously reported procedures. Salts **B** and **E** were obtained from the bromide salts Bn_2-imy·H$^+$Br$^-$[13a] and **D** by anion exchange with excess KPF_6 in H_2O, respectively.

Synthesis of [CuCl(IPr)] (1). This complex was synthesized via a modified procedure.[9] Salt **A** (213 mg, 0.50 mmol) and Cu_2O (93 mg, 0.65 mmol) were mixed and heated in dry toluene (10 mL) at 120 °C for 48 h. All the volatiles were removed in vacuo, and the residue was dissolved (partially) in CH_2Cl_2 and subsequently filtered through Celite. The filtrate was dried in vacuo, affording the product as a white solid (212 mg, 0.44 mmol, 87%). NMR spectroscopic data agree well with the reported ones.[9]

Synthesis of [Cu(IPr)(Bn_2-imy)]PF_6 (2). Complex **1** (98 mg, 0.20 mmol), salt **B** (79 mg, 0.20 mmol), and K_2CO_3 (36 mg, 0.26 mmol) were mixed and stirred in acetone (20 mL) at ambient temperature for 48 h. All the volatiles were removed in vacuo, and the residue was taken up in CH_2Cl_2 and subsequently filtered through Celite. The filtrate was dried in vacuo and washed with ethyl acetate (2 × 1 mL), affording the product as a white solid (152 mg, 0.18 mmol, 90%); mp 242–244 °C. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a concentrated CH_2Cl_2/hexane solution of **2**. ^{1}H NMR (300 MHz, CD_3CN): δ 7.54 (s, 2 H, Ar–H), 7.42–7.27 (m, 12 H, Ar–H), 6.90 (s, 2H, Ar–H), 6.76–6.73 (m, 4 H, Ar–H), 4.53 (s, 4 H, NCH_2), 2.56 (m, 4 H, CH(CH_3)$_2$, ^3J(H,H) = 7 Hz), 1.20 (d, 12 H, CH(CH_3)$_2$, ^3J(H,H) = 7 Hz), 1.12 (d, 12 H, CH(CH_3)$_2$, ^3J(H,H) = 7 Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD_3CN): δ 180.4 (NCN–IPr), 176.2 (NCN–Bn_2-imy), 146.9, 137.0, 135.3, 131.8, 129.8, 129.1, 125.3, 125.2, 123.2 (Ar–C), 54.8 (CH_2Ph), 29.6 (CH(CH_3)$_2$), 25.0, 24.0 (CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_3CN): δ −143.2 (m, PF_6). ^{19}F{^{1}H} NMR (282.4 MHz, CD_3CN): δ 3.41 (d, PF_6). Anal. Calcd for $C_{44}H_{52}CuF_6N_4P$: C, 62.51; H, 6.20; N, 6.63%. Found: C, 62.69; H, 6.38; N, 6.74%. MS (ESI): m/z 699 [M − PF_6]$^+$.

Synthesis of [Cu(IPr)(^{i}Pr_2-bimy)]PF_6 (3). Complex **1** (98 mg, 0.20 mmol), salt **C** (70 mg, 0.20 mmol), and K_2CO_3 (36 mg, 0.26 mmol) were mixed and stirred in acetone (20 mL) at ambient temperature for 48 h. All the volatiles were removed in vacuo, and the residue was partially dissolved in CH_2Cl_2 and filtered via Celite. The filtrate was dried in vacuo and washed with ethyl acetate (2 × 1 mL), affording the product as a white solid (136 mg, 0.17 mmol, 85%); mp 253–255 °C. Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a concentrated solution of **3** in chloroform. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65–7.60 (m, 2 H, Ar–H), 7.48–7.39 (m, 8 H, Ar–H), 7.28–7.25 (m, 2 H, Ar–H), 3.95 (m, 2 H, CH(CH_3)$_2$–^{i}Pr_2-bimy, ^3J(H,H) = 7 Hz), 2.59 (m, 4 H, CH(CH_3)$_2$–IPr, ^3J(H,H) = 7 Hz), 1.27, 1.22, 1.19 (d, 36 H, CH(CH_3)$_2$, ^3J(H,H) = 7 Hz). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 179.3 (NCN–IPr), 178.7 (NCN–^{i}Pr_2-bimy), 146.4, 134.9, 133.2, 131.6, 125.1, 125.0, 124.7, 113.4 (Ar–C), 53.7 (NCH), 29.4 (CH(CH_3)$_2$–IPr), 25.6, 24.5, 23.0 (CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −143.6 (m, PF_6). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ 2.52 (d, PF_6). Anal. Calcd for $C_{40}H_{54}CuF_6N_4P$: C, 60.10; H, 6.81; N, 7.01%. Found: C, 60.52; H, 6.98; N, 6.91%. MS (ESI): m/z 653 [M − PF_6]$^+$.

Synthesis of [Cu(IPr)(Indy)]PF_6 (4). Route A: Complex **1** (98 mg, 0.20 mmol), salt **E** (64 mg, 0.20 mmol), and KO^{t}Bu (29 mg, 0.26 mmol) were mixed and stirred in dry THF (5 mL) under inert conditions at ambient temperature for overnight. All the volatiles were removed in vacuo, and the residue was partially dissolved in CH_2Cl_2 and filtered via Celite. The filtrate was dried in vacuo and washed with ethyl acetate (2 × 3 mL), affording the product as an off-white solid (99 mg, 0.13 mmol, 65%); mp > 185 °C, dec. Route B: Salt **D** (126 mg, 0.5 mmol) and Ag_2O (68 mg, 0.29 mmol) were mixed in CH_2Cl_2 (10 mL), and the reaction mixture was stirred at ambient temperature in the dark for 6 h. The resulting suspension was filtered into a solution of [Cu(IPr)(CH_3CN)]PF_6, which was prepared by stirring the mixture of complex **1** (245 mg, 0.5 mmol) and $AgPF_6$ (127 mg, 0.5 mmol) in CH_3CN (3 mL) in the dark for 5 min, followed by filtration. The reaction mixture was stirred at ambient temperature shielded from light overnight and filtered through Celite. The filtrate was dried in vacuo, and the residue was washed with ethyl acetate (2 × 3 mL), affording the product as an off-white solid (268 mg, 0.35 mmol, 70%). Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a concentrated solution of **4** in chloroform. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63–7.50 (m, 3 H, Ar–H), 7.39–7.36 (m, 7 H, Ar–H), 7.07–7.04 (m, 1 H, Ar–H), 6.86–6.84 (m, 1 H, Ar–H), 4.09 (t, 2 H, NCH_2, ^3J(H,H) = 6 Hz), 3.56 (t, 2 H, NCH_2, ^3J(H,H) = 6 Hz), 2.58 (m, 4 H, CH(CH_3)$_2$, ^3J(H,H) = 7 Hz), 2.19 (br s, 2 H, NCH_2CH_2), 1.89 (br s, 2 H, NCH_2CH_2), 1.27, 1.21 (d, 24 H, CH(CH_3)$_2$, ^3J(H,H) = 7 Hz). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 180.7 (NCN–IPr), 176.6 (NCN–Indy), 146.6, 141.7, 134.8, 132.4, 131.3, 127.1, 124.8, 124.5, 123.6, 110.2 (Ar–C), 53.1, 47.4 (NCH_2), 29.3 (CH(CH_3)$_2$), 25.8, 24.3 (CH(CH_3)$_2$), 22.7, 21.2 (NCH_2CH_2). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −143.7 (m, PF_6). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ 2.44 (d, PF_6). Anal. Calcd for $C_{38}H_{48}CuF_6N_4P$·0.25$CHCl_3$: C, 57.49; H, 6.09; N, 7.01%. Found: C, 57.47; H, 5.88; N, 7.41%. MS (ESI): m/z 623 [M − PF_6]$^+$.

Synthesis of [Cu(IPr)(PPh_3)]PF_6 (5). Complex **1** (98 mg, 0.20 mmol), PPh_3 (53 mg, 0.20 mmol), and KPF_6 (110 mg, 0.60 mmol) were mixed and stirred in acetone (10 mL) at ambient temperature for 24 h. All the volatiles were removed in vacuo, and the residue was partially dissolved in CH_2Cl_2 and subsequently filtered through Celite. The filtrate was dried in vacuo, and the residue was washed with ethyl acetate (3 × 10 mL) and dried in vacuo, affording the product as a white solid (142 mg, 0.166 mmol, 83%); mp 244–245 °C. Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a concentrated solution of **5** in

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chloroform. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64−7.28 (m, 21 H, Ar−H), 7.14 (s, 2 H, Imd−H), 2.56 (m, 4 H, C*H*(CH_3)$_2$, ^3J(H,H) = 7 Hz), 1.29, 1.23 (d, 24 H, CH(C*H*$_3$)$_2$, ^3J(H,H) = 7 Hz). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 146.5, 134.4 (Ar−C), 133.9 (d, Ar−C (PPh_3), ^1J(P,C) = 15 Hz), 132.7, 132.6, 131.8 (Ar−C), 130.2 (d, Ar−C (PPh_3), ^2J(P,C) = 10 Hz), 125.5, 125.1 (Ar−C), 29.4 (CH(CH_3)$_2$), 25.9, 24.3 (CH(*C*H$_3$)$_2$). The carbene signal could not be resolved despite prolonged acquisition time. ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ 8.8 (s, PPh_3), −143.7 (m, PF_6). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ 2.31 (d, PF_6). Anal. Calcd for $C_{45}H_{51}CuF_6N_2P_2$: C, 62.89; H, 5.98; N, 3.26%. Found: C, 62.66; H, 5.78; N, 3.33%. MS (ESI): m/z 713 [M − PF_6]$^+$.

Synthesis of [Cu(IPr)(DPPE)]PF_6 (6). Complex **1** (98 mg, 0.20 mmol), 1,2-bis(diphenylphosphino)ethane (104 mg, 0.26 mmol), and KPF_6 (110 mg, 0.60 mmol) were mixed and stirred in acetone (20 mL) at ambient temperature for 48 h. All the volatiles were removed in vacuo, and the residue was suspended in CH_2Cl_2 and subsequently filtered through Celite. The filtrate was dried in vacuo, and the residue was washed with ethyl acetate (3 × 10 mL) and dried in vacuo, affording the product as a white solid (151 mg, 0.15 mmol, 76%); mp > 310 °C, dec. Single crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether into a concentrated solution of **6** in $CHCl_3$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52−7.49 (m, 3 H, Ar−H), 7.42−7.39 (m, 4 H, Ar−H), 7.26−7.21 (m, 14 H, Ar−H), 6.88−6.87 (m, 7 H, Ar−H), 2.75 (m, 4 H, C*H*(CH_3)$_2$, ^3J(H,H) = 7 Hz), 2.02 (m, 4 H, PCH_2), 1.11 (d, 12 H, CH(C*H*$_3$)$_2$, ^3J(H,H) = 7 Hz), 0.76 (d, 12 H, CH(C*H*$_3$)$_2$, ^3J(H,H) = 7 Hz). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 146.3, 135.9, 133.2, 133.1, 133.0, 131.6, 131.1, 130.1, 125.7, 125.2, 124.2 (Ar−C, coupling to phosphorus is not considered), 29.3 (*C*H(CH_3)$_2$), 25.4, 24.2 (CH(*C*H$_3$)$_2$). The carbene signal could not be resolved despite prolonged acquisition time. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −6.0 (s, PPh_2), −143.7 (m, PF_6). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ 2.37 (d, PF_6). Anal. Calcd. for $C_{53}H_{60}CuF_6N_2P_3$·0.5$C_4H_{10}O$: C, 63.97; H, 6.34; N, 2.71%. Found: C, 63.74; H, 6.70; N, 3.02%. MS (ESI): m/z 849 [M − PF_6]$^+$.

Synthesis of [Cu(IPr)(DPPF)]PF_6 (7). Complex **1** (98 mg, 0.20 mmol), 1,1′-bis(diphenylphosphino)ferrocene (144 mg, 0.26 mmol), and KPF_6 (48 mg, 0.26 mmol) were mixed and stirred in acetone (20 mL) at ambient temperature for 48 h. All the volatiles were removed in vacuo, and the residue was dissolved (partially) in CH_2Cl_2 and subsequently filtered through Celite. The filtrate was dried in vacuo, and the residue was washed with diethyl ether (3 × 10 mL) and dried in vacuo. Crystallization from $CHCl_3$/Et_2O afforded the product as a yellow solid (140 mg, 0.12 mmol, 61%); mp > 280 °C, dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63−7.62 (m, 6 H, Ar−H), 7.47−7.10 (m, 20 H,, Ar−H), 6.98 (s, 2 H, Ar−H), 4.32 (br, s, 4 H, Cp−H), 4.14 (br, s, 4 H, Cp−H), 2.28 (m, 4 H, C*H*(CH_3)$_2$, ^3J(H,H) = 7 Hz), 1.01 (d, 12 H, CH(C*H*$_3$)$_2$, ^3J(H,H) = 7 Hz), 0.82 (d, 12 H, CH(C*H*$_3$)$_2$, ^3J(H,H) = 7 Hz). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 178.1 (NCN), 145.7, 135.3, 134.8, 134.6, 134.5, 131.3, 130.7, 129.3, 129.2, 125.9, 125.1 (Ar−C, coupling to the phosphorus is not considered), 74.5, 74.4, 72.6 (Cp−C, coupling to the phosphorus is not considered), 29.3 (CH(CH_3)$_2$), 25.0, 24.8 (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ −15.2 (s, PPh_2), −143.7 (m, PF_6). ^{19}F{^{1}H} NMR (282.4 MHz, $CDCl_3$): δ 2.8 (d, PF_6). Anal. Calcd for $C_{61}H_{64}CuF_6FeN_2P_3$·0.25$CH_3CN$: C, 63.58; H, 5.62; N, 2.71. Found: C, 63.74; H, 5.88; N, 3.05%. MS (ESI): m/z 1005 [M − PF_6]$^+$.

General Procedure for Azide−Alkyne Cycloaddition Catalysis. In a typical run, a Schlenk tube was charged with aromatic amine (0.5 mmol), sodium azide (0.525 mmol, 34.1 mg), isopentyl nitrite (0.80 mmol, 108 μL), and solvent (1 mL). The reaction mixture was stirred for 2 h at the temperature indicated in Scheme 5. Phenylacetylene (0.525 mmol, 58 μL) and Cu(I) precatalyst (0.005 mmol, 1 mol %), and 1 mL of solvent were then added. The reaction mixture was heated at 60 °C for another 16 h. The reaction mixture was cooled to ambient temperature, and H_2O (5 mL) was added, followed by extraction with ethyl acetate (3 × 10 mL). The organic phases were collected and dried over Na_2SO_4. All the volatiles were removed in vacuo, and the product was isolated by column chromatography and analyzed by ^{1}H NMR spectroscopy.

1-(4-*tert*-Butyl-phenyl)-4-phenyl-1,2,3-triazole (10ea). This compound was isolated as a pale yellow solid; mp 145−146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1 H, Ar−H), 7.94−7.91 (m, 2 H, Ar−H), 7.73−7.69 (m, 2 H, Ar−H), 7.57−7.54 (m, 2 H, Ar−H), 7.49−7.44 (m, 2 H, Ar−H), 7.39−7.34 (m, 1 H, Ar−H), 1.38 (s, 9 H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 152.8, 129.6, 129.0, 127.3, 126.5, 120.9 (Ar−C), 35.5 (*C*(CH_3)$_3$), 31.9 (C(*C*H$_3$)$_3$). ESI (MS): m/z 278 [M + H]$^+$.

1-(2,5-Dimethoxyl-phenyl)-4-phenyl-1,2,3-triazole (10fa). This compound was isolated as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 1 H, Ar−H), 7.93−7.90 (m, 2 H, Ar−H), 7.45−7.42 (m, 3 H, Ar−H), 7.37−7.32 (m, 1 H, Ar−H), 7.04−6.94 (m, 2 H, Ar−H), 3.85 (s, 3 H, *o*-OCH_3), 3.82 (s, 3 H, *m*-OCH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 154.5, 147.8, 145.5, 131.1, 129.5, 128.8, 127.1, 126.5, 122.4, 116.2, 114.3, 110.9 (Ar−C), 57.2 (*o*-OCH_3), 56.6 (*m*-OCH_3). ESI (MS): m/z 282 [M + H]$^+$.

X-ray Diffraction Studies. X-ray data for **2**, **3**, **4**·$CHCl_3$, **5**, **6**, and **7**·0.75$CHCl_3$·0.25$C_4H_{10}O$ were collected with a Bruker AXS SMART APEX diffractometer, using Mo−Kα radiation at 100(2) K with the SMART suite of programs.[20] Data were processed and corrected for Lorentz and polarization effects with SAINT,[21] and for the absorption effect with SADABS.[22] Structural solution and refinement were carried out with the SHELXTL suite of programs.[23] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table SI-1 in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for **2**, **3**, **4**·$CHCl_3$, **5**, **6**, and **7**·0.75$CHCl_3$·0.25$C_4H_{10}O$ in a table and as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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