Bi- and trinuclear copper(I) complexes of 1,2,3-triazole-tethered NHC ligands: synthesis, structure, and catalytic properties

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Abstract

A series of copper complexes (3–6) stabilized by 1,2,3-triazole-tethered N-heterocyclic carbene ligands have been prepared via simple reaction of imidazolium salts with copper powder in good yields. The structures of bi- and trinuclear copper complexes were fully characterized by NMR, elemental analysis (EA), and X-ray crystallography. In particular, [Cu2(L2)2](PF6)2 (3) and [Cu3(L3)2](PF6)2 (4) were dinuclear copper complexes. Complexes [Cu3(L4)2](PF6)3 (5) and [Cu3(L5)2](PF6)3 (6) consist of a triangular Cu3 core. These structures vary depending on the imidazolium backbone and N substituents. The copper–NHC complexes tested are highly active for the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction in an air atmosphere at room temperature. Complex 4 is the most efficient catalyst among these polynuclear complexes in an air atmosphere at room temperature.

Introduction

N-Heterocyclic carbene (NHC) have interesting electronic and structural properties. This resulted in their use as versatile ligands in organometallic chemistry and homogeneous catalysis [1-12]. A number of transition metal complexes of NHCs containing pyridine [13], pyrimidine [14], pyrazole [15,16], naphthyridine [17], pyridazine [18], and phenanthroline [19,20] donating groups have been studied in metal-catalyzed organic transformations. Recently, the easy synthesis and versatile coordination ability of 1,2,3-triazoles have led to an explosion of interest in coordination chemistry [21] and homogeneous catalysis [22-26]. Although a number of metal complexes containing 1,4-disubstituted-1,2,3-triazole ligands were well studied, reports concerning their preparation and use of 1,4-disubstituted-1,2,3-triazoles bearing NHC ligands are rare [22,23].
Elsevier et al. [23] reported several of palladium(II) complexes containing a heterobidentate N-heterocyclic carbene-triazolyl ligand. These palladium(II) complexes are active precatalysts in the transfer semihydrogenation of alkynes to Z-alkenes. Messerle et al. [26] synthesized a series of new cationic Rh(I), Rh(III) and Ir(III) complexes containing hybrid bidentate N-heterocyclic carbene-1,2,3-triazolyl donors. We [27] have synthesized a series of nonsymmetrical pincer palladium and platinum complexes containing 1,2,3-triazole-tethered NHC ligands. The obtained palladium complexes displayed high activity in aqueous Suzuki–Miyaura cross-coupling reactions.

We are interested in the synthesis and use of functionalized NHC ligands [20,28-31]. Herein, the synthesis, structural characterization, and catalytic properties of a few copper-1,2,3-triazole-tethered NHC complexes is reported.

Results and Discussion
Synthesis and spectroscopic characterization
The imidazolium salts (1a–e) were prepared according to the reported procedure in 61–90% yields [27]. These imidazolium salts have been characterized by NMR spectroscopy. The $^1$H NMR spectra of these imidazolium salts show singlet peaks between 10.04 and 10.89 ppm in DMSO-$d_6$. As seen in Scheme 1, copper–NHC complexes 3–6 can be obtained in 52–90% yields via directly reacting the corresponding imidazolium salts with an excess of copper powder in CH$_3$CN at 50 °C for 5 h.

As shown in Scheme 1, reactions of the pyrimidine imidazolium salt 1a with copper powder in acetonitrile afforded a light yellow Cu(II) complex. In complex 2, the carbenic carbon atom was oxidized into carbonyl, which is similar with the reported pyrimidyl-imidazole complex [32]. However, a red binuclear Cu(I) complex 3 was obtained in 57% yield when we reacted pyrimidyl benzimidazolium salt 1b with copper powder. Furtherly, we got a yellow Cu(I)–NHC complex 4 in about 70% yield from pyridine imidazolium salt 1c and copper powder (Scheme 1). In addition, a triangular Cu(I) complex 6 can be obtained when a flexible ligand was used. Complex 6 consists of a triangular Cu$_3$ core bridged by three NHCs, which is similar with the published Cu$_3$ complexes containing flexible
ligands [33]. Interestingly, we can also obtain a similar triangular Cu$_3$ complex 5 rather than a binuclear copper complex using a rigid pyridine benzimidazolium salt 1d. These results demonstrated that the structures vary depending on the N substituents and on the imidazolium backbone. Fine adjustment of the structure of the ligand can lead to different structures.

All of the prepared copper–NHC complexes are stable in air. They were fully characterized by NMR, elemental analysis (EA), and X-ray crystallography. The generation of these copper–NHC complexes were confirmed by the absence of the $^1$H NMR resonance signal of the acidic imidazolium protons between 10.04 and 10.89 ppm. The $^1$H NMR spectra of all the complexes display only one set of resonance signals assignable to the corresponding ligands, indicating two or three magnetically equivalent ligands. $^{13}$C NMR spectra of the copper(I) complexes showed their carbenic carbon resonances at 177.6–191.2 ppm, which are in the normal range of 157.6–216 ppm [34,35].

Single crystal X-ray diffraction studies

To obtain additional insight into the coordination and supramolecular properties, suitable single crystals of all the copper complexes were obtained for single-crystal X-ray diffraction analysis. Crystals were grown by slow diffusion of diethyl ether into an acetonitrile solution of the copper complex at room temperature.

Green-yellow single crystals of complex 2 suitable for an X-ray diffraction study were grown from acetonitrile solution and diethyl ether. The molecular structure of complex 2 in the solid state is depicted in Figure 1 along with the principal bond lengths and angles. Complex 2 crystallizes in the orthorhombic space group \textit{Pnna}. The remaining atoms of the cation are related by a crystallographic 2-fold symmetry. In complex 2, the copper ion is four-coordinate in a distorted square planar ligand environment of two nitrogen atoms and two oxygen atoms. The Cu–O bonds are in \textit{trans} configuration and Cu–O distances are shorter than Cu–N distances. The two ligands are arranged in head-to-tail manner. And the N$_{triazole}$ did not participate in the coordination.

Single crystals of complex 3 suitable for an X-ray diffraction study were grown from acetonitrile solution and diethyl ether. The molecular structure of complex 3 is depicted in Figure 2.
Complex 3 crystallizes in the monoclinic space group C2/c. The Cu(I) complex contains two crystallographically equivalent Cu centers, which are doubly bridged by two \( L_2 \) ligands. The two ligands are arranged in head-to-tail manner. The copper ions are each tri-coordinated by one carbene carbon atom, one nitrogen from pyrimidine, and one nitrogen atom of the triazole rings from two different \( L_2 \) ligands. The Cu–carbene bond distances are 1.896(6) and 1.899(5) Å, which are comparable to the known Cu(I)–NHC complexes [36-39]. The Cu1–Cu2 separation is 2.7867(7) Å, showing a weak metal–metal interaction.

The molecular structure of complex 4 is depicted in Figure 3. Complex 4 consists of the cation unit \([Cu_2(L_3)_2]^2+\) and two hexafluorophosphate anions. Complex 4 crystallizes in the triclinic space group P-1. The two ligands are also arranged in head-to-tail manner. Each copper ion is three-coordinate in a trigonal planar ligand environment of two nitrogen atoms and one NHC carbon center. The Cu–carbene bond distances are 1.888(6) and 1.899(5) Å which are similar with reported copper-carbene complexes (1.85–2.18 Å) [40]. The Cu1–Cu2 separation is 2.6413(12) Å is shorter than in complex 3, and slightly higher than reported Cu–Cu separations (2.4907 to 2.5150 Å) of the triangular Cu(I)–NHC clusters [33], showing a weak metal–metal interaction.

Complex 5 was also characterized via X-ray diffraction. It's structure is shown in Figure 4. Complex 5 consists of two independent molecules in the unit cell. Here, only one molecule was given in Figure 4. The molecule structure consists of a triangular Cu3 core bridged by three NHCs ligands. Each NHC forms the 3c-2e bond with two Cu(I) ions with almost equal bond distances (average 2.085 Å), longer than normal Cu–NHC bonds and reported triangular Cu3 complexes [33,41]. The Cu3 cores of complex 5 possess nearly equilateral angles close to 60°, whereas in complex 6, the core is crystallographically restrained to an equilateral triangle. The Cu–Cu distances are around 2.4887 Å and are shorter than that of complexe 6, which may be attributed to more rigid ligand.
space group $R3c$, which is different to the reported trinuclear copper(I) complex containing the symmetric 1,3-bis(2-pyridinylmethyl)benzimidazolylidene ligand (monoclinic, $P21/c$) [33] and to the trinuclear copper(I) complex containing a symmetric 1,3-bis(triazole)benzimidazolylidene ligand (monoclinic, $C2/c$) [38]. Three copper atoms are bridged by three N$_{\text{pyridine}}$CN$_{\text{triazole}}$NHC ligands forming a Cu$_3$ ring with three Cu–Cu–Cu angles of 60.0. The geometry of the copper center can be described as distorted trigon planar. Each copper ion is coordinated by one pyridine, one triazole, and two benzimidazolylidene ligands displaying a distorted tetrahedral geometry. The Cu–Cu distance is around 2.5145(12) Å showing a weak metal–metal interaction, which is similar with the reported triangle Cu(I) complexes and is shorter than in complexes 3 and 4. The Cu–N and Cu–C bond distances fall in the range of 2.092(5)–2.152(5) Å and 2.024(6)–2.092(6) Å, respectively, which are slightly longer than in dinuclear complexes 3 and 4. Benzimidazolylidene acts as a bridging ligand in a u2 mode and bonded equally to two Cu(I) ions, which is only observed in a few silver(I) and copper(I) complexes.

**Catalytic application in CuAAC reactions**

Inspired by the catalytic activity of Cu(I) species supported by NHC ligand in Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction under mild conditions, copper complexes 2–6 were investigated in the CuAAC reaction of azide and phenylacetylene. Firstly, we compared the catalytic activity of different complexes with a complex loading of 0.5 mol %. The reactions were monitored by $^1$H NMR analysis at different time points within 4 h (Figure 6). As seen in Figure 6, the yield increased with the extension of reaction time. The results showed that complex 4 displays the best activities for the CuAAC reaction of benzyl azide and phenylacetylene giving a conversion of...
95%. To further examine the catalytic efficiency of complex 4, a variation of the catalyst loading from 0.1 to 0.25 to 0.5 mol % within 5 h was performed to give the expected product in yields of 17%, 48%, and 100%. As expected, the coupling reaction with low catalyst loading results in incomplete conversion.

Subsequently the catalytic activity of different solvents was tested at a Cu loading of 0.5 mol % (Table 1). Moderate catalytic activities were obtained for DMSO or without solvent. When CH$_3$CN was used, the reaction gave an excellent yield (Table 1, entry 4). However, only a moderate yield was obtained when a CH$_3$CN/H$_2$O solvent mixture was used (Table 1, entry 6). Thus, CH$_3$CN was selected as the optimal solvent.

Having optimized the reaction conditions, we extended the CuAAC reaction to other azides and alkynes at room temperature in CH$_3$CN. As shown in Table 2 (entries 1–5), (azidomethyl)benzene, azidobenzene, (2-azidoethyl)benzene, and 2-(azidomethyl)pyridine could react with phenylacetylene in more than 83% yield (Table 2, entries 1–4). What is more, methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate could be afforded in 85% yield via reacting methyl propiolate with (azidomethyl)benzene. This promising catalytic behavior of complex 4 prompted us to extend our studies toward a one-pot synthesis of 1,2,3-triazoles from alkyl halides, sodium azide, and alkynes. The three-component version has already been successfully performed and described in previous work [20]. As displayed in Table 2, the reactions proceeded smoothly to completion, and the products were isolated in good to excellent yields (83–95%).

**Conclusion**

In summary, a series of di-, and trinuclear copper(I) complexes (3–6) stabilized by 1,2,3-triazole-tethered N-heterocyclic carbene ligands have been prepared via simple reactions of imidazolium salts with copper powder in good yields. These complexes have been fully characterized by NMR, elemental analysis (EA) and X-ray crystallography. Fine adjustment of the structure of the ligand can lead to different structures. All the Cu–NHC complexes showed high catalyst activity in CuAAC reactions at room temperature. Among these complexes, complex 4 is the most efficient catalyst in an air atmosphere at room temperature.

### Experimental

All the chemicals were obtained from commercial suppliers and were used without further purification. Elemental analyses were performed on a Flash EA1112 instrument. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer or a Varian 600 MHz NMR spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at δ = 0 ppm and coupling constants (J) are expressed in Hz.

**Synthesis of 3-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-1-(pyrimidin-2-yl)-1H-benzo[d]imidazol-3-ium hexafluorophosphate [(HL)$_2$PF$_6$] (1b):** Analogously as described in a published work [27], (azidomethyl)benzene (160 mg, 1.2 mmol), copper sulfate pentahydrate (12.5 mg, 0.05 mmol), sodium ascorbate (20 mg, 0.1 mmol), and 3-(prop-2-yn-1-yl)-1H-benzo[d]imidazol-3-ium bromide (314 mg, 1 mmol) were added to a Schlenk tube containing 2 mL of water and tert-butyl alcohol (1:1). After the heterogeneous mixture was stirred vigorously for 24 h at 50 °C, the reaction mixture was diluted with water (20 mL). The obtained yellow solution was dropwise added to the aqueous solution of NH$_4$PF$_6$. A white precipitate was collected by filtration and dried. Yield: 315 mg, 61%. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 10.89 (s, 1H), 9.14 (d, J = 4.9 Hz, 2H), 8.83 (d, J = 8.1 Hz, 1H), 8.39 (s, 1H), 9.14 (d, J = 4.9 Hz, 2H), 8.83 (d, J = 8.1 Hz, 1H), 8.39 (s, 1H),

### Table 1: CuAAC reaction with different solvents$^a$.

| entry | solvent       | cat. | yield %$^b$ |
|-------|---------------|------|-------------|
| 1     | neat          | 4    | 50          |
| 2     | H$_2$O        | 4    | 22          |
| 3     | DMSO          | 4    | 53          |
| 4     | CH$_3$CN      | 4    | 95          |
| 5     | t-BuOH/H$_2$O (1:1) | 4 | trace       |
| 6     | CH$_3$CN/H$_2$O (1:1) | 4 | 59          |

$^a$Reaction carried out using 0.5 mol % of complex 4 with different solvents. $^b$Yields were determined by $^1$H NMR spectra and are reported after 4 h, hexamethyldibenzene was used as internal standard.
Table 2: CuAAC Reaction using complex 4 as catalyst.

| entry | substrate | substrate | product | isolated yield % |
|-------|-----------|-----------|---------|-----------------|
| 1<sup>a</sup> | ![substrate image] | ![substrate image] | ![product image] | 94 [42] |
| 2<sup>a</sup> | ![substrate image] | ![substrate image] | ![product image] | 95 [43] |
| 3<sup>a</sup> | ![substrate image] | ![substrate image] | ![product image] | 95 [44] |
| 4<sup>a</sup> | ![substrate image] | ![substrate image] | ![product image] | 83 [42] |
| 5<sup>a</sup> | ![substrate image] | ![substrate image] | ![product image] | 85 [44] |
| 6<sup>b</sup> | ![substrate image] | ![substrate image] | ![product image] | 90 [42] |
| 7<sup>b</sup> | ![substrate image] | ![substrate image] | ![product image] | 84 [45] |
| 8<sup>b</sup> | ![substrate image] | ![substrate image] | ![product image] | 85 [44] |

<sup>a</sup>Reaction conditions: azide 0.5 mmol, ethynylbenzene 0.6 mmol, catalyst 0.5 mol%, CH<sub>3</sub>CN 3 mL, rt, 6 h.  
<sup>b</sup>Reaction conditions: alkyl halide 0.5 mmol, NaN<sub>3</sub> 0.6 mmol, ethynylbenzene 0.6 mmol, catalyst 0.5 mol%, CH<sub>3</sub>CN/H<sub>2</sub>O 1:1 (3 mL), rt, 16 h.

8.17 (d, J = 8.0 Hz, 1H), 7.79 (br, 3H), 7.34–7.30 (m, 5H), 6.06 (s, 2H), 5.63 (s, 2H); 13C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 160.34, 159.78, 143.41, 140.45, 136.12, 132.14, 129.62, 129.26, 128.69, 128.49, 127.79, 125.52, 53.47, 42.95.

Synthesis of 3-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-1-(pyridin-2-yl)-1H-imidazol-3-ium hexafluorophosphate [(HL<sub>3</sub>)PF<sub>6</sub>] (1c): Similarly as described in a previous procedure [27], a mixture of (azidomethyl)benzene (160 mg, 1.2 mmol), copper sulfate pentahydrate (12.5 mg, 0.05 mmol), and sodium ascorbate (20 mg, 0.1 mmol), 3-(prop-2-ynyl)-1-(pyridin-2-yl)-1H-imidazol-3-ium bromide (265 mg, 1 mmol) was added to 2 mL of water and tert-butyl alcohol (1:1). The heterogeneous mixture was stirred vigorously for 24 h at 50 °C. The reaction mixture was diluted with water (20 mL), and the yellow solution was dropwise added to the aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. A white precipitate was collected by filtration and dried. Yield: 415 mg, 90%. 1H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.19 (s, 1H), 8.69–8.63 (m, 1H), 8.54 (t, J = 1.9 Hz, 1H), 8.35 (d, J = 2.4 Hz, 1H), 8.31–8.17 (m, 1H), 8.03 (q, J = 4.3, 3.5 Hz, 2H), 7.70–7.61 (m, 1H), 7.36 (qd, J = 7.0, 6.5, 2.5 Hz, 5H), 5.65 (dd, J = 5.1, 2.4 Hz, 4H), 3.39 (s, 1H); 13C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 149.69, 146.78, 141.06, 141.02, 135.68, 129.29, 128.76, 128.55, 125.77, 125.23, 124.14, 120.07, 114.75, 53.49, 44.85.

Synthesis of 3-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-1-(pyridin-2-yl)-1H-benzo[d]imidazol-3-ium hexafluorophosphate [(HL<sub>4</sub>)PF<sub>6</sub>] (1d): Similarly as described in a previous procedure [27], the imidazolium salt was prepared similarly as for [(HL<sub>3</sub>)PF<sub>6</sub>] from (azidomethyl)benzene (160 mg, 1.2 mmol), copper sulfate pentahydrate (12.5 mg, 0.05 mmol), sodium ascorbate (20 mg, 0.1 mmol), and 3-(prop-2-ynyl)-1-(pyridin-2-yl)-1H-benzo[d]imidazol-3-ium bromide (314 mg, 1 mmol). Yield: 317 mg, 62%. 1H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.60 (s, 1H), 8.75 (d, J = 4.7 Hz, 1H), 8.46–8.31 (m, 2H), 8.25 (t, J = 8.0 Hz, 1H), 8.19–8.10 (m, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.79–7.65 (m, 3H), 7.31 (dt, J = 21.5, 7.4 Hz, 7H), 5.95 (s,
Synthesis of 3-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-1-(pyridin-2-ylmethyl)-1H-benzimidazole-3-ium hexafluorophosphate \([\text{HL}_2\text{PF}_6]\): This complex was synthesized by the reaction of \([\text{HL}](\text{L})_2\) (106 mg, 0.20 mmol) with copper powder (64 mg, 1.0 mmol) at 50 °C for 10 h, orange yellow solid. Yield: 71 mg, 68%. \(^{1}\)H NMR (600 MHz, acetone-\(d_2\)) \(\delta\) 7.96 (s, 1H, triazole), 7.90 (br, 1H, 1H, 2-py), 7.83 (br, 1H, imidazole), 7.76 (s, 1H, 4-py), 7.57 (br, 1H, imidazole), 7.41 (s, 1H, 5-py), 7.37 (d, \(J = 7.8\) Hz, 3H, phenyl), 7.30–7.22 (m, 3H, phenyl + 3-py), 5.47 (s, 2H), 5.38 (s, 2H); \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) \(\delta\) 181.20 (C=C), 149.68, 147.26, 140.72, 138.41, 134.71, 129.02, 128.89, 128.80, 128.28, 128.04, 123.96, 123.48, 112.13, 54.36, 45.69; Anal. calcd for C_{36}H_{33}Cu_{2}F_{2}N_{12}P_{2}C_{2}: C, 41.19; H, 3.31; N, 15.46.

Synthesis of \([\text{Cu}_3(\text{L})_3](\text{PF}_6)_3\) (6): The compound was prepared similarly as for complex 3 from \([\text{HL}_4](\text{PF}_6)_3\) (106 mg, 0.20 mmol) with copper powder (64 mg, 1.0 mmol) at 50 °C for 10 h, yellow light solid. Yield: 106 mg, 90%. \(^{1}\)H NMR (600 MHz, acetone-\(d_2\)) \(\delta\) 8.13 (s, 1H, triazole), 7.92 (td, \(J = 7.8\), 1.8 Hz, 1H, pyridine), 7.77 (d, \(J = 7.8\) Hz, 1H, pyridine), 7.59 (d, \(J = 7.8\) Hz, 1H, pyridine), 7.51–7.36 (m, 6H, phenyl + benzimidazole), 7.14–7.08 (m, 2H, benzimidazole), 6.94–6.92 (m, 2H, phenyl), 5.84 (d, \(J = 15.8\) Hz, 1H), 5.37 (d, \(J = 15.8\) Hz, 1H), 5.18 (s, 2H); \(^{13}\)C NMR (151 MHz, DMSO-\(d_6\)) \(\delta\) 178.99 (C=C), 149.61, 148.44, 142.25, 140.55, 136.19, 134.91, 133.34, 129.31, 128.93, 128.09, 126.05, 125.82, 124.48, 124.27, 119.09, 118.51 (CH_3CN), 112.74, 111.59, 54.13, 41.17. 1.56(CH_3CN); Anal. calcd for C_{123}H_{108}Cu_{4}F_{36}N_{36}P_{6}: 3CH_3CN: C, 46.39; H, 3.30; N, 15.29; found: C, 45.87; H, 3.40; N, 15.30.

Synthesis of \([\text{Cu}_3(\text{L})_3](\text{PF}_6)_3\) (6): This compound was prepared similarly as for complex 3 from \([\text{HL}_5](\text{PF}_6)_3\) (106 mg, 0.20 mmol) with copper powder (64 mg, 1.0 mmol) at 50 °C for 10 h, yellow light solid. Yield: 106 mg, 90%. \(^{1}\)H NMR (600 MHz, nitromethane-\(d_3\)) \(\delta\) 8.13 (s, 1H, triazole), 7.92 (td, \(J = 7.8\), 1.8 Hz, 1H, pyridine), 7.77 (d, \(J = 7.8\) Hz, 1H, pyridine), 7.59 (d, \(J = 7.8\) Hz, 1H, pyridine), 7.51–7.36 (m, 6H, phenyl + benzimidazole), 7.14–7.08 (m, 2H, benzimidazole), 6.95 (d(d, \(J = 7.5\), 5.2, 1.1 Hz, 1H, pyridine), 6.49–6.45 (d, \(J = 4.8\) Hz, 1H, benzimidazole), 5.40 (d, \(J = 15.0\) Hz, 1H, -CH_2-), 5.30 (d, \(J = 15.0\) Hz, 1H, -CH_2-), 5.27 (d, \(J = 15.0\) Hz, 1H, -CH_2-), 5.26 (d, \(J = 15.6\) Hz, 1H, -CH_2-), 5.21 (d, \(J = 15.0\) Hz, 1H, -CH_2-), 4.98 (d, \(J = 15.6\) Hz, 1H, -CH_2-); \(^{13}\)C NMR (150 MHz, nitromethane-\(d_3\)) 177.57 (C=C), 151.99, 148.85,
141.78, 139.93, 135.15, 134.68, 133.85, 129.16, 128.98, 128.81, 128.12, 125.04, 124.62, 124.35, 123.79, 110.58, 110.26, 54.49, 51.29, 40.72; Anal. calc’d for C_{60}H_{56}Cu_{2}F_{18}N_{13}P_{3}: C, 46.90; H, 3.42; Cu, 10.79; N, 14.27; found: C, 46.35; H, 3.31; N, 13.95.

**General procedure for the copper-catalyzed CuAAC reaction:** Analogously as described in [31], in a 10 mL Schlenk tube, azide (0.5 mmol), alkyne (0.6 mmol), and 0.5 mol % copper complex were dissolved in 3.0 mL of CH_{3}CN. After the mixture was stirred at rt under air for a desired time, the reaction was stopped by the addition of HCl (2 mL) to the resultant mixture. Then the mixture was extracted with CH_{2}Cl_{2}. The organic layer was separated from the aqueous phase. After the organic phase was dried over MgSO_{4}, the solution was filtered and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate, 3:1) to give the desired product.

**X-ray diffraction analysis**

Analogously as described in [27], single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart/CCD area-detector or Oxford Diffraction Gemini A Ultra diffractometer with a Mo Kα radiation (λ = 0.71073 Å) by using an ω-2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software [46]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTXL package [47]. Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with the C–H distances of 0.93–0.97 Å and U_{eq}(H) = 1.2 – 1.5U_{eq}(C). Disordered solvent molecules that could not be modeled successfully were removed with SQUEEZE [48]. Further details of the structural analysis are summarized in Table 3.

**Supporting Information**

**Supporting Information File 1**

X-ray crystallographic data in cif format CCDC 1424013–1424017. [http://www.beilstein-journals.org/bjoc/content/ supplementary/1860-5397-12-85-S1.cif]

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**Table 3: Crystallographic data for complexes 2–6.**

|  | 2   | 3   | 4   | 5   | 6   |
|---|-----|-----|-----|-----|-----|
| CCDC number | 1424013 | 1424014 | 1424015 | 1424016 | 1424017 |
| formula | C_{60}H_{56}Cu_{2}F_{18}N_{13}P_{3} | C_{60}H_{56}Cu_{2}F_{18}N_{13}P_{3} | C_{60}H_{56}Cu_{2}F_{18}N_{13}P_{3} | C_{60}H_{56}Cu_{2}F_{18}N_{13}P_{3} | C_{60}H_{56}Cu_{2}F_{18}N_{13}P_{3} |
| Fw. | 2081.47 | 1161.93 | 1049.76 | 7186.59 | 1766.88 |
| crystal system | orthorhombic | monoclinic | triclinic | hexagonal | hexagonal |
| space group | Pnna | C2/c | P-1 | R3c | R3c |
| a/Å | 14.0847(15) | 34.298(3) | 12.9626(10) | 28.178(3) | 21.4692(13) |
| b/Å | 14.5426(16) | 13.2602(12) | 13.0382(9) | 28.178(3) | 21.4692(13) |
| c/Å | 22.599(2) | 26.605(4) | 13.1663(10) | 16.3997(19) | 71.858(9) |
| β/deg | 90.00 | 92.8310(10) | 80.661(6) | 90.00 | 90.00 |
| V/Å^3 | 4629.0(9) | 9291.9(19) | 2111.7(3) | 45655(10) | 28684(4) |
| Z | 2 | 8 | 2 | 6 | 12 |
| D/ρ cm^{-3} | 1.493 | 1.661 | 1.651 | 1.568 | 1.228 |
| Reflns collected | 18121 | 10632 | 7571 | 21009 | 5624 |
| ind reflns, Rint | 12510.0, 0.0545 | 7828, 0.0250 | 4679, 0.0467 | 15722, 0.0869 | 3716, 0.0650 |
| goodness-of-fit on F2 | 1.063 | 1.018 | 1.023 | 1.031 | 1.157 |
| R1, wR2 (|I| > 2σ(|I|)) | 0.0869, 0.2496 | 0.0562, 0.1652 | 0.0696, 0.1774 | 0.0622, 0.1353 | 0.0688, 0.2044 |
| R1, wR2 (all data) | 0.1338, 0.3001 | 0.0779, 0.1858 | 0.1122, 0.2172 | 0.0917, 0.1543 | 0.1200, 0.2623 |
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