Alkynyl Complexes

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From Cluster to Polymer: Ligand Cone Angle Controlled Syntheses and Structures of Copper(I) Alkynyl Complexes

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Abstract: *Copper(I) alkynyl complexes have attracted tremendous attention in structural studies, as luminescent materials, and in catalysis, and homoleptic complexes have been reported to form polymers or large clusters. Herein, six unprecedented structures of* Cu^I *alkynyl complexes and a procedure to measure the cone angles of alkynyl ligands based on the crystal structures of these complexes are reported. An increase of the alkynyl cone angle in the complexes leads to a modulation of the structures from polymeric* $[((PhC{\equiv}CC{\equiv}C)Cu)_2(NH_3)]_\infty$, *to a large cluster* $[(TripC{\equiv}CC{\equiv}C)Cu]_{20}(MeCN)_4$, *to a relatively small cluster* $[(TripC{\equiv}C)Cu]_8$ *(Trip = 2,4,6-iPr*$_3$*-*C_6H_2*). The complexes exhibit yellow-to-red phosphorescence at ambient temperature in the solid state and the luminescence behavior of the* Cu_{20} *cluster is sensitive to acetonitrile.*

Over the past decades, Cu^I alkynyl complexes have been extensively studied for their structural diversity,[1] intriguing photoluminescent properties,[2] and as key active species in copper-catalyzed transformations of alkynes as well as in click chemistry.[3] The widely utilized copper-catalyzed azide–alkyne cycloaddition involves generation of Cu^I alkynyl species of varying nuclearities,[3c,4] the formation of which is driven by intermolecular Cu^I–Cu^I and Cu^I–ligand interactions.[1] Apart from these intermolecular interactions, the steric effect of ligand(s) plays an important role in the assembly process of polynuclear Cu^I alkynyl complexes since this can affect the metal–metal (M–M) contacts, M–L coordination modes (L = ligand), and thus the stability and crystal structures of the complexes. Introduction of sterically bulky phosphine,[2a–d] *s*-hydrindacenyl,[5] or alkynyl ligands can diminish intermolecular aggregation, consequently leading to the formation of small Cu^I alkynyl clusters. As a result of the difficulty in obtaining good quality crystals suitable for X-ray analysis, examples of structurally characterized homoleptic Cu^I alkynyl complexes are few. Reported examples include neutral Cu_{24}[6] and Cu_{20}[7] clusters, and cationic Cu_{18} and Cu_{17}[1d] clusters obtained by using the alkynyl ligand $tBuC{\equiv}C^-$ bearing a bulky *tert*-butyl group. The rarity of structural information poses challenges in probing the steric effect of alkynyl ligands. Herein we introduce 2,4,6-triisopropylphenyl (Trip) and 2-*tert*-butylphenyl (*t*BuPh) for the preparation of Cu^I alkynyl complexes with various nuclearities (Figure 1). Crystal structures ranging from relatively small Cu_8 (**1**) and Cu_{12} (**2**) clusters, to large Cu_{16} (**3a**) and Cu_{20} (**3b**) clusters, as well as to the Cu_∞ (**4b**) polymer, were obtained by varying the steric hindrance of the ligand employed. The steric hindrance is quantified herein by the "cone angle" of the alkynyl ligand (see below), with bulky or chelating ancillary ligands not being used in this work. These Cu^I alkynyl complexes adopt metal core structures which, to our knowledge, are unique among other reported metal alkynyl complexes. Based on the structural information obtained, a procedure to assess the cone angles of alkynyl ligands is proposed.

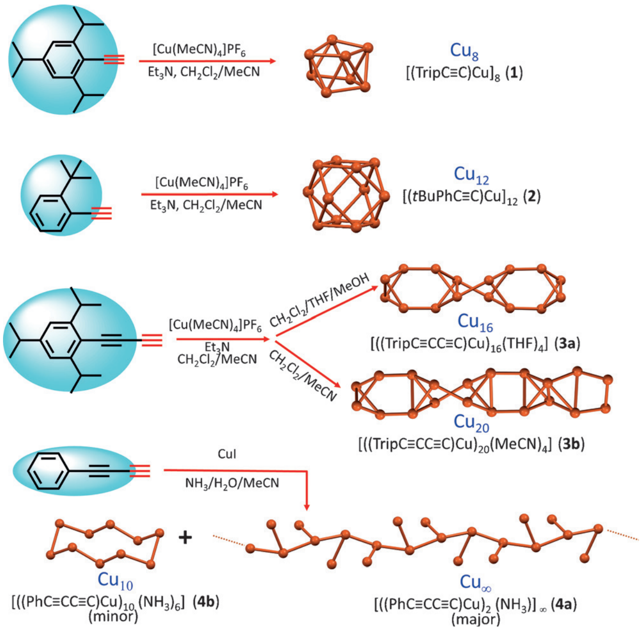

Figure 1. The synthesis of **1**, **2**, **3a**, **3b**, **4a**, and **4b**. The structures of their Cu_8, Cu_{10}, Cu_{12}, Cu_{16}, Cu_{20}, and Cu_∞ cores are shown.

Although alkynyl ligands usually have little steric effect around the donor carbon atom, remote bulky aromatic substituent(s) could impose sizeable steric influence. In this work, the bulky aryl group Trip was first chosen, which is rarely employed in the alkynyl ligands of known metal alkynyl complexes[8] and has not been incorporated in the alkynyl ligands of reported homoleptic alkynyl complexes of coinage metals.[1c,9] The reaction of $TripC{\equiv}CH$ with

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$[Cu(MeCN)_4]PF_6$ in CH_2Cl_2/MeCN in the presence of triethylamine led to the formation of **1** (Figure 1), which crystallized from CH_2Cl_2/MeCN in the monoclinic space group $P2_1/n$.[19] As shown in Figure 2, eight copper atoms form a square antiprism with Cu–Cu distances in the range of 2.5000(7)–2.8724(6) Å. The eight TripC≡C$^-$ ligands bound to the Cu_8 core adopt four types of coordination mode: μ_2, $\eta^{1,1}$; μ_2, $\eta^{1,2}$; μ_3, $\eta^{1,1,1}$; and μ_3, $\eta^{1,1,2}$, with Cu–C distances ranging from 1.890(2) Å to 2.538(2) Å. The Cu_8 cluster can be viewed as an assembly of two [(TripC≡C)Cu]$_4$ units with Cu_4 in a nearly square arrangement.

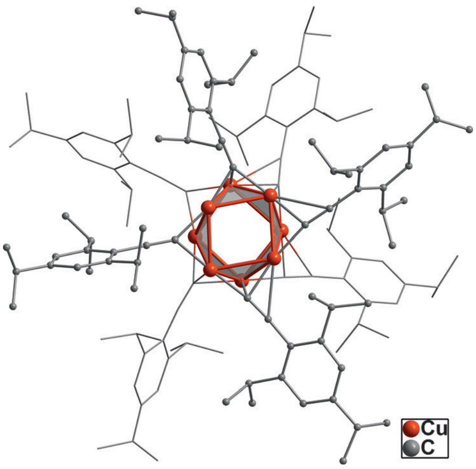

Figure 2. Crystal structure of **1**.[19] Hydrogen atoms are omitted; alkynyl ligands at the back of the molecule are represented as wireframe.

As a less bulky alkyne, *t*BuPhC≡CH reacted with $[Cu(MeCN)_4]PF_6$ in the presence of triethylamine to afford **2** as a red solid. Recrystallization of **2** in CH_2Cl_2/MeCN gave red crystals from which diffraction data sets at low resolution (2.0 Å) were collected. The space group was determined to be cubic $Fm\bar{3}m$.[19] Attempts to obtain higher quality crystals of **2** were unsuccessful. Complex **2** has a cuboctahedral Cu_{12} core similar to that in $[Cu_{12}S_8]^{4-}$,[10a] $[Cu_{12}S_6(dpppt)_4]$,[10b] $[Cu_{12}(NPh)_8]^{4-}$,[11] $[Cu_{12}(NPEt_3)_8]^{4+}$,[12] and $[Cu_{12}(tBu_3SiP)_6]$.[13]

As the steric bulkiness of alkynyl ligands could be decreased by coupling a second C≡C unit to the terminal sp carbon atom, we prepared a Trip-capped diynyl ligand TripC≡CC≡CH. Reaction of this ligand with $[Cu(MeCN)_4]PF_6$ in the presence of triethylamine afforded an orange solid which gave yellow bipyramidal crystals **3a** and orange crystals **3b** upon recrystallization in CH_2Cl_2/THF/MeOH and CH_2Cl_2/MeCN, respectively.

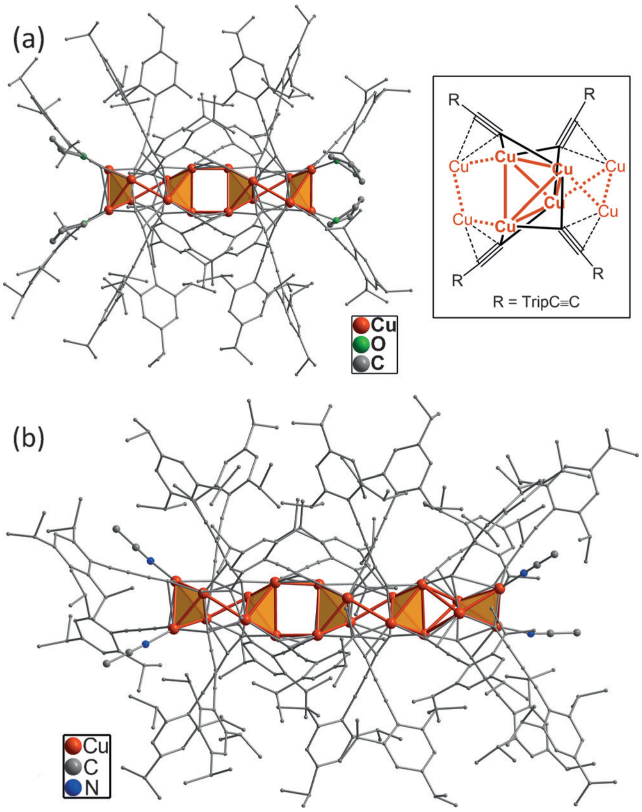

Figure 3. Crystal structures of a) **3a** and b) **3b**.[19] Inset: chemical structure of the repeat unit in **3a** and **3b**. Hydrogen atoms are omitted for clarity. Cu–Cu distances (Å) in the Cu_4 units: 2.462(2)–2.880(1) (**3a**), 2.413(1)–2.890(1) (**3b**); Cu–Cu distances (Å) between Cu_4 units: 2.563(2)–2.614(1) (**3a**), 2.473(1)–2.596(1) (**3b**).

X-ray crystal analysis of **3a** reveals a cluster structure bearing a rod-like Cu_{16} core.[19] As shown in Figure 3a, the structure can be considered as packing of four Cu_4 tetrahedrons supported by Cu–Cu (2.462(2)–2.880(1) Å) and π C≡C–Cu (Cu–C: 1.920(8)–2.452(9) Å) interactions. The Cu_4R_4 unit has a pseudo D_2 symmetry (Figure 3, inset). Each diynyl ligand σ-coordinates to two Cu atoms of the Cu_4 tetrahedron and π-coordinates to another copper atom of a nearby Cu_4 unit. Upon viewing the structure along the chain direction, the ligands are approximately oriented in eight different directions because of the staggered packing of Cu_4 units (see Figure S1a in the Supporting Information). There are four THF molecules coordinating to terminal copper atoms with Cu–O distances of 2.04(2)–2.15(4) Å.

For **3b**, the X-ray crystal analysis showed that it has a structure similar to that of **3a** except for the presence of a fifth Cu_4 unit and four MeCN (instead of THF) molecules (Figure 3b).[19] Presumably, the replacement of THF by MeCN results in the extension of the structure from Cu_{16} to Cu_{20}. Recrystallization of **3b** in CH_2Cl_2/THF was found to give **3a** as confirmed by X-ray crystal analysis, indicative of cluster core transformation in solution. The similarity of the metal alkynyl frameworks observed in **3a** and **3b** indicates that both THF and MeCN function as ancillary ligands to stabilize the cluster but have minor effects on the assembly mode of the clusters. Also, the MeCN coordinated at the end of **3b** is away from the steric repulsion between adjacent Trip units, therefore it is conceivable that the homoleptic [TripC≡CC≡CCu] complex has a similar nuclearity and configuration to **3b**.

The formation of Cu_{16}/Cu_{20} clusters **3a**/**3b**, Cu_{12} cluster **2**, and Cu_8 cluster **1** from reactions of $[Cu(MeCN)_4]PF_6$ with TripC≡CC≡CH, *t*BuPhC≡CH, and TripC≡CH, respectively, revealed that enhanced steric effect of the alkynyl ligand allows formation of homoleptic Cu^I alkynyl complexes with decreased nuclearity of down to Cu_8, in contrast to the Cu_{24},[6] Cu_{20},[7] and Cu_{18}/Cu_{17}[1d] analogues reported in literature.

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We further explored the structures of Cu^I alkynyl complexes using a ligand having minimal steric hindrance. PhC≡CC≡CH was employed because of its compact configuration and ease of preparation. To obtain diffraction-quality crystals for structure determination, the following method was developed. A mixture of acetonitrile and ammonium hydroxide (1:1 v/v; ammonium hydroxide concentration 28 % NH_3 in H_2O), as a buffer layer, was carefully dropped onto a solution of CuI in ammonium hydroxide prior to adding a dilute solution of PhC≡CC≡CH in acetonitrile. All solutions were degassed and the reaction was protected from oxygen. One week later, yellow needle-shaped crystals of **4a** were obtained as the major product with orange needle-shaped crystals **4b** obtained as the minor product.

As shown in Figure 4, the structure of **4a** reveals two crystallographically non-equivalent copper atoms, Cu1 and Cu2, two PhC≡CC≡C$^-$ ligands, and one ammonia ligand in each polymer repeat unit.[19] The polymeric structure could be viewed as a spiral staircase: the central column was formed by bonding of Cu1 atoms (Cu1−Cu1 2.4441(8) Å) and the stairs were composed of Cu1−Cu2 bonds (2.5350(8) Å). The diynyl ligands are coordinated to copper atoms in μ_2, $\eta^{1,1}$ and μ_4, $\eta^{1,1,1,2}$ coordination modes, with Cu−C distances of 1.986(5)–2.632(4) Å. No intermolecular interaction is observed between the polymeric chains. Thermogravimetric analysis (TGA) measurements (Figure S3) revealed that **4a** underwent explosive decomposition with a recoil effect.

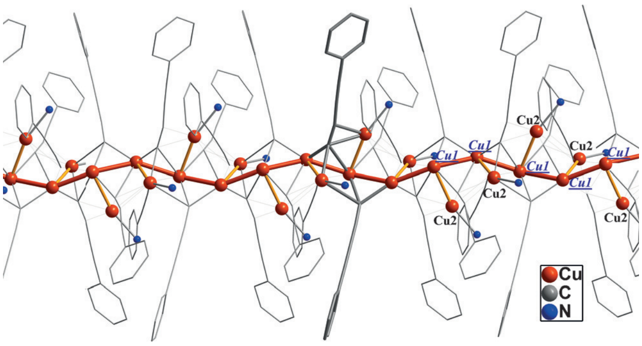

Figure 4. Polymeric chain structure of **4a**.[19] Hydrogen atoms are omitted.

Complex **4b** crystallized in the monoclinic space group $P2_1/n$ and was characterized as a decanuclear cluster.[19] As shown in Figure 5, the structure of **4b** consists of ten PhC≡CC≡C$^-$ ligands, six ammonia ligands, and a unique cyclic "wrinkled" Cu_{10} cluster core consisting of two zigzag Cu_5 units. The two Cu_5 units in **4b** (Cu–Cu 2.4258(6)–2.5518(7) Å) are connected in head-to-tail manner by two Cu–Cu bonds (2.5518(7) Å), unlike the discrete zigzag Cu_4 unit (Cu–Cu 2.450–2.693 Å) in $[(\mathrm{PhC{\equiv}CCu})_4(\mathrm{PMe_3})_4]$ containing phosphine ligands.[14]

The Cu−Cu distances observed in complexes supported by Trip-capped alkynyl ligands, such as **1**, **3a**, and **3b**, are significantly longer than those of **4a** and **4b** having less bulky alkynyl ligands, probably due to larger steric interactions between the Trip-capped alkynyl ligands. Some of the Cu−Cu distances (2.4258(6)–2.7692(9)) are less than the sum of metallic radii (2.56 Å) and/or the van der Waals radii of two copper atoms (2.80 Å). In addition, π C≡C–Cu interactions between secondary C≡C units (the one far away from the metal core) of the diynyl ligands and copper atoms have not been detected in the crystal structures of **3a**, **3b**, **4a** and **4b**.

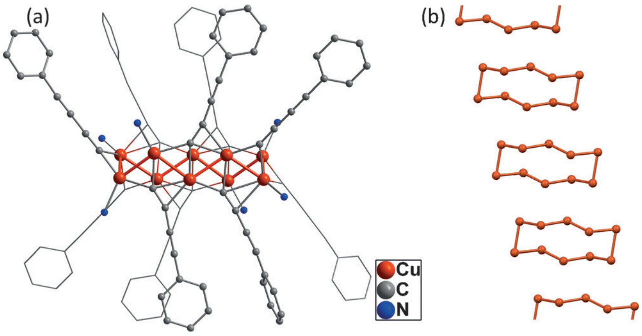

Figure 5. Crystal structure of **4b**.[19] a) Side view with hydrogen atoms omitted for clarity; b) packing diagram of Cu_{10} cores in the crystal lattice.

The self-assembly of homoleptic Cu^I alkynyl complexes involves competitive intermolecular metal–metal and metal–ligand interactions as well as steric interactions of alkynyl ligands. Bulky ligand substituents facilitate the generation of clusters, whereas relatively small groups have a tendency towards the formation of polymeric structures. In this work, we introduce the use of the term ligand cone angle θ to describe the steric bulkiness of alkynyl ligands. Ligand cone angle is commonly used to reflect the size of phosphine ligands.[15] Based on the Tolman's cone angle concept, Mingos developed a method to assess the cluster cone angle.[16] The cone angles of other ligands including isocyanides have also been reported.[17]

In view of the multinuclear nature of Cu^I alkynyl clusters, the bridging mode of alkynyl ligands, and the difference in geometries between phosphine and alkynyl ligands, there is no universally applicable method for the cone angle determination of Cu^I alkynyl systems. Analogous to Mingos' cluster cone angle definition, we estimated the cone angles by setting the apex of the cone in the center of the metal core polyhedron. For complexes without a regular polyhedron metal arrangement (**3a**/**3b** and **4a**), the metal core can be treated as a combination of small polyhedra and the center of the sub-polyhedron is set as the apex. Based on the crystal structural data, a general model with a distance of 2.68 Å from the apex to the terminal sp carbon atom is proposed. To better cover the phenyl- and alkyl-substituted alkynyl ligands, a trapezoid–circle equivalent cone angle method is used. The geometrical definition of θ is shown in Figure 6a, using TripC≡C$^-$ as an example. Firstly a trapezoid (green area in Figure 6a) perpendicular to the C≡C unit is employed to reflect the bulkiest part of the ligand, and the bases (a and b) and height (h) of the trapezoid are determined by using the thickness and width of ligand (space-filling model), respectively. A circle (red area in Figure 6a) with the same area as the trapezoid is defined for obtaining the radius (r) of the

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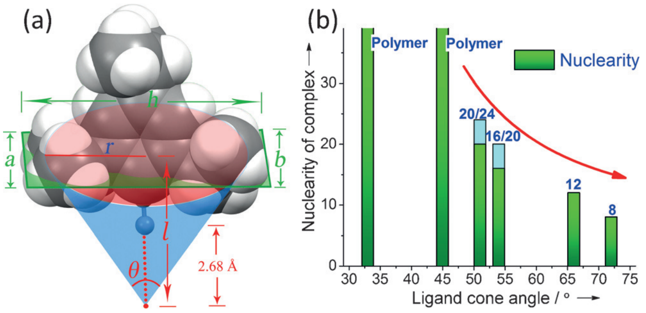

Figure 6. a) Schematic diagram showing the cone angle θ in $\mathrm{Cu^I}$ alkynyl complexes (the $\mathrm{TripC{\equiv}C^-}$ ligand is used as an example, in this case $a = b$). b) Chart showing the change of nuclearity of $\mathrm{Cu^I}$ alkynyl complexes with changes in the cone angle of the alkynyl ligands.

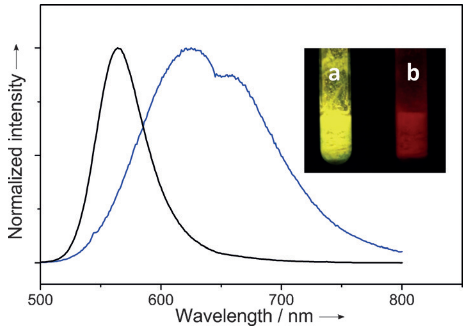

Figure 7. Emission spectra of **3b** in the solid state before (black line) and after (blue line) vacuum drying. Inset: photo of solid **3b** (a) and vacuum-dried **3b** (b) under irradiation with UV light ($\lambda = 365$ nm).

circular cone [Eq. (1)], and subsequently the equivalent cone angle for the alkynyl ligand is estimated by using Equation (2):

$$r = \sqrt{\frac{(a+b)h}{2\pi}} \tag{1}$$

$$\theta = 2\tan^{-1}\frac{r}{l} \tag{2}$$

where l denotes the distance between the apex and trapezoid. As this is a semiquantitative method, crystal packing effects and ligand meshing are not taken into account in the model. The steric bulkiness of the alkynyl ligands are found to fall in the order: $\mathrm{TripC{\equiv}C^-} > t\mathrm{BuPhC{\equiv}C^-} > \mathrm{TripC{\equiv}CC{\equiv}C^-} > t\mathrm{BuC{\equiv}C^-} > \mathrm{PhC{\equiv}C^-} > \mathrm{PhC{\equiv}CC{\equiv}C^-}$. This order is based on their θ values, which were estimated to be 72°, 66°, 54°, 51°, 45°, and 33°, respectively. Correspondingly, clusters with nuclearities of 8, 12, 16(20), 20(24), and polymers ($[\mathrm{PhC{\equiv}CCu}]_\infty$ and **4a**) have been observed (Figure 6b). In view of the similarities in the repeating units, metal core arrangement, and ligand orientations between **3b** and polymer **4a** (Figure S1), **3b** (an interesting intermediate structure between a small cluster and a one-dimensional polymer) can be viewed as a depolymerized fragment resulting from ligand repulsion in a polymeric chain. It is reasonable to use the cone angle of $\mathrm{TripC{\equiv}CC{\equiv}C^-}$ (54°, ligand in **3b**) as an approximate lower limit value of aryl alkynyl ligands for the formation of $\mathrm{Cu^I}$ alkynyl cluster structures: upon increasing the cone angle of the alkynyl ligand, a cluster with smaller nuclearity can be prepared. Similarly, by decreasing the cone angle of the alkynyl ligand, a polymerized product can be anticipated.

The luminescence behavior of the $\mathrm{Cu^I}$ alkynyl complexes was investigated (except for **4a** and **4b** owing to their instability in air); the photophysical and spectroscopic data are summarized in Table S2. Homoleptic complex **1** exhibited an orange emission in the solid state ($\lambda_{\mathrm{em}} = 599$ nm, quantum yield $\Phi = 0.21$) and in solution ($\lambda_{\mathrm{em}} = 582$ nm, $\Phi = 0.18$ in $\mathrm{CH_2Cl_2}$), while **2** of higher nuclearity showed a weak red emission in the solid state. Excitation of **3a** and **3b** in the solid state at $\lambda_{\mathrm{exc}} = 450$ nm gave rise to yellow emission bands ($\lambda_{\mathrm{em}} = 571$ and 564 nm for **3a** and **3b**, respectively). Notably, a bathochromic shift of the yellow emission to weak red emission was observed upon drying the sample of **3b** under vacuum (Figure 7). This effect is probably as a result of the loss of coordinated MeCN molecules,[18] as supported by fact that nitrogen was not detected in the elemental analysis of a vacuum-dried sample. Additionally, the yellow emission was restored after the vacuum-dried **3b** was treated with MeCN or exposed to MeCN vapor. All of the emission lifetimes of the $\mathrm{Cu^I}$ alkynyl complexes are in the microsecond range revealing that the emissive excited states are triplet in origin.

In summary, six $\mathrm{Cu^I}$ alkynyl complexes with various nuclearities have been prepared and structurally characterized by single-crystal X-ray analysis. The steric effect of the alkynyl ligands plays a major role in the formation of the complexes. The use of the term cone angle is introduced to evaluate the steric hindrance of alkynyl ligands and the cone angles correlate reasonably well with the nuclearities of the complexes formed.

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[19] CCDC 1473525 (**1**), 1474744 (**2**), 1473526 (**3a**$\cdot$4 THF), 1473527 (**3b**$\cdot$10 MeCN$\cdot$2 CH_2Cl_2), 1473528 (**4a**), and 1473529 (**4b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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