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Clean formation and dynamic exchange reactions of a supramolecular equilateral triangle that is both heterometallic and heteroleptic†

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The self-assembly of an equilateral triangle that is both heterobimetallic and heteroleptic, its metal exchange to a homometallic triangle and further ligand exchange (= edge of the triangle) were elaborated.

Due to the auspicious opportunities for supramolecular devices in various applications, the fabrication of more and more refined, multi-faceted and multifunctional supramolecular architectures remains a pivotal cornerstone for future developments.[1] In recent years, coordination driven self-assembly has been utilised in the construction of a large assortment of metallosupramolecular entities with unique functionalities. Various groups have established the potential of supramolecular self-assembly techniques by fabricating not only two-dimensional architectures,[1] such as squares, grids, ladders,[2] pentagons, and hexagons, but also state-of-the-art three-dimensional objects like truncated tetrahedra, adamantanoids, cuboctahedra, dodecahedra, and a variety of other cages.[3] Surprisingly, very few attempts have been made to design and fabricate the simplest and smallest member of the two-dimensional family: the supramolecular triangle.[4,5] The constraint geometry and acute angles required render the supramolecular triangle a rather difficult topology. Typically, triangles show up in equilibrium with higher order entities, such as squares or other polygons,[6] so that only in a very few cases was their exclusive formation ascertained.[4,5]

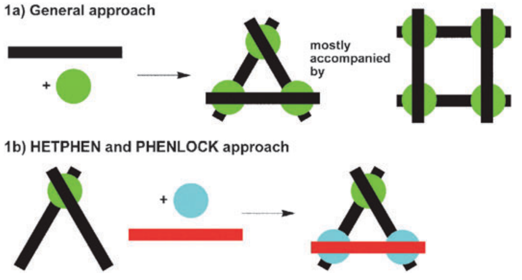
In general, fabrication of metallosupramolecular triangles has been accomplished by mixing two components: a ditopic ligand with a metal ion (Scheme 1a; mostly, the metal ion is located on the corner, but it may also be centred on the lateral side) using a homoleptic binding motif. Based on the coordination angle of the metal and the nature of the ligand, the outcome is either a mixture of triangle and square or a triangle only (rare).[4–6] Consequently, all reported triangles are homometallic and homoleptic in nature.[4,5] Even in the case of a so-called heterometallic triangle described by Mukherjee *et al.*,[5] the self-assembled triangular framework encloses homometallic vertices with the second metal being incorporated as a ferrocene residue in a bystander phosphane ligand. As a first step towards the "holy grail" of dynamic supramolecular triangles, the heterotrimetallic scalene triangle, we present herein an equilateral triangle that is both heterobimetallic and heteroleptic.

We have recently demonstrated the utility and power of the HETPHEN concept[7] through the preparation of a series of challenging heteroleptic structures, such as nanobaskets,[8] ring-in-ring structures,[9] racks,[10] *etc.* The HETPHEN concept makes it possible to assemble quantitatively dynamic heteroleptic bisphenanthroline metal complexes.[7] It is based on the use of bulky 2,9-diaryl-substituted phenanthroline subunits, as in **2a,b**,[11] whose steric shielding prohibits the assembly of two of those ligands about a single tetrahedral metal centre (Chart 1). As a result, the HETPHEN ligand combines with an unshielded, second phenanthroline at the metal centre forming a heteroleptic complex.

Another concept, the PHENLOCK protocol, that is based on the use of 3,5-di-*tert*-butyl-4-methoxyphenyl substituents in the 2,9-positions of phenanthrolines has led to the formation of kinetically stable[12] bishomoleptic copper(I) complexes.[13] An amalgamation of this concept with the HETPHEN approach along route 1b (Scheme 1) has now made it possible to realise a supramolecular triangle that is both heterobimetallic and heteroleptic.

As the key building block for the heterometallic triangle we devised the angular unit **1** on the basis of the PHENLOCK concept. It contains a kinetically locked copper(I) complex as a hinge and two free unshielded phenanthroline terminals. The latter are conceived to bind to bisphenanthroline **2a** through silver(I) ions along the HETPHEN protocol.[7]

Synthesis of the angular unit **1** proved to be challenging. Because **4** contains two different phenanthroline binding sites, **1** = $[\mathrm{Cu}(\mathbf{4})_2]^+$ cannot be obtained from **4** simply by addition of 0.5 equiv. of $[\mathrm{Cu(MeCN)_4}]\mathrm{PF_6}$. Indeed, a test reaction of **3** and **5**, mimicking the two binding sites in **4**, with Cu^+ in $\mathrm{CH_2Cl_2}$ led to a mixture of the heteroleptic $[\mathrm{Cu}(\mathbf{3})(\mathbf{5})]^+$ and homoleptic complex $[\mathrm{Cu}(\mathbf{5})_2]^+$, as monitored by ESI-MS. To circumvent this problem, the angular unit **1** was prepared by a



Scheme 1 Two approaches to supramolecular triangles.

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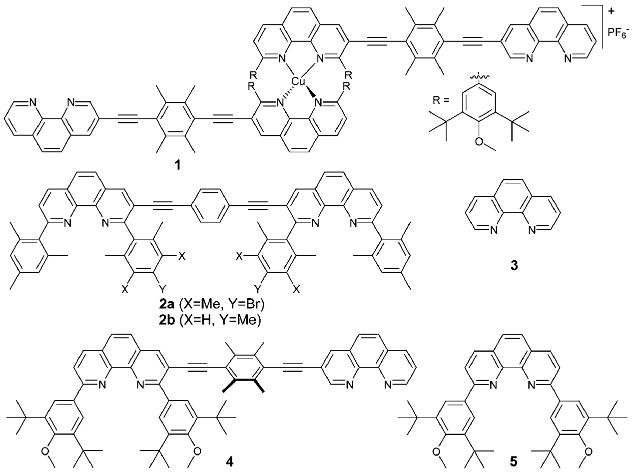


Chart 1 Ligands used in this study.

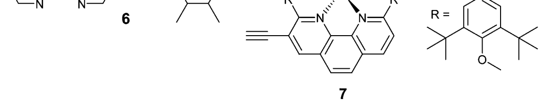
different route (Scheme 2). Accordingly, we first constructed **7** containing the kinetically locked copper(I) complex as hinge and only thereafter attached the free phenanthroline units. While we were unsuccessful with normal cross-coupling conditions, the Shonogashira reaction between **6** and **7** was readily effected in the solid state in presence of TBAF·3H_2O and $PdCl_2(PPh_3)_2$ at 80 °C for 12 h under N_2 atmosphere (60%, see ESI†).[14]

As reported for a structurally similar copper(I) complex,[13] complexes **1** and **7** are kinetically stable and soluble in common organic solvents. Their structures were confirmed by ^{1}H NMR, ^{13}C NMR, ESI-MS and elemental analysis. In **7**, the *ortho*-protons and *tert*-butyl protons of the aromatic substituent R are equivalent by ^{1}H NMR. On the other hand, in complex **1** those protons are not equivalent and split into two different sets (see ESI†).

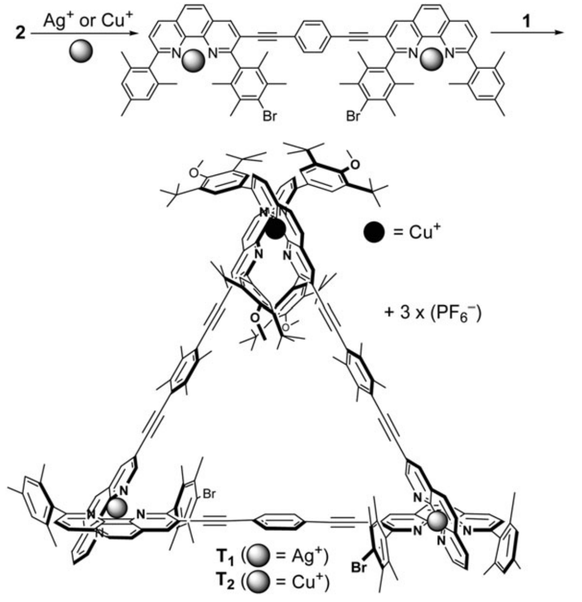
The heterometallic triangle $\mathbf{T_1}$ (= $[CuAg_2(\mathbf{4})_2(\mathbf{2a})](PF_6)_3$) was prepared in a clean manner from the angular unit **1**, bisphenanthroline **2a** and $AgPF_6$ in CH_2Cl_2–MeCN = 1 : 3 (Scheme 3). Formation of $\mathbf{T_1}$ was ascertained by ESI-MS, ^{1}H NMR and UV–Vis spectroscopy. Rewardingly, the ESI-MS spectrum of $\mathbf{T_1}$ (Fig. 1) showed only two peaks, both being diagnostic of the triangle. The two peaks at *m*/*z* = 1123.4 and 1757.5 correspond to $\mathbf{T_1}$ after loss of three or two hexafluorophosphate counter ions, *i.e.* $[CuAg_2(\mathbf{4})_2(\mathbf{2a})]^{3+}$ and $[CuAg_2(\mathbf{4})_2(\mathbf{2a})](PF_6)^{2+}$.

^{1}H NMR data further supported the formation of the triangle. The chemical shifts of the mesityl protons ($\delta \approx 7.0$ ppm in ligand **2a**, $\delta \approx 6.2$–6.5 ppm in complex $\mathbf{T_1}$) are most diagnostic for heteroleptic complex formation as demonstrated earlier.[7] To secure further insight we studied the UV–Vis properties of triangle $\mathbf{T_1}$. The assembly absorbs in a broad region of the UV and visible spectrum (see ESI†). It shows very intense ligand-centred (LC) absorption bands in the UV region and very weak bands in the visible region. The latter are ascribed to an envelope of MLCT electronic transitions[15] attesting the formation of the HETPHEN complex. Finally, the elemental analysis of $\mathbf{T_1}$ also agreed well with the calculated value, confirming again the exclusive formation of the heterometallic and heteroleptic triangle.

Due to the HETPHEN design, the supramolecular assembly contains two dynamic silver(I)–phenanthroline complex units. Their dynamic nature was verified by a metal exchange study. Upon addition of $[Cu(MeCN)_4]PF_6$ (2 equiv.) to a solution of $\mathbf{T_1}$ in CH_2Cl_2, we observed by ESI-MS complete replacement of Ag^+ in $\mathbf{T_1}$ by Cu^+ to generate $\mathbf{T_2}$ (= $[Cu_3(\mathbf{4})_2(\mathbf{2a})](PF_6)_3$). As the ESI-MS was recorded within 5 min after addition of the copper(I) solution, this points to a fast replacement process. Conversion of the heterometallic triangle $\mathbf{T_1}$ to the



Scheme 2 Retrosynthesis of the angular building block **1**.



Scheme 3 Preparation of heterometallic triangles $\mathbf{T_1}$ and $\mathbf{T_2}$.

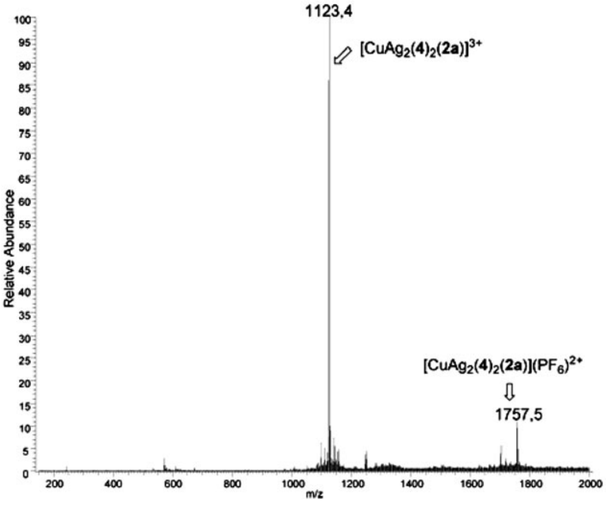


Fig. 1 ESI-MS of heterometallic triangle $\mathbf{T_1}$.

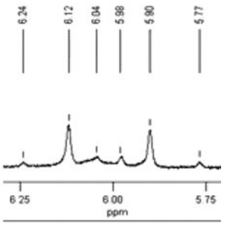
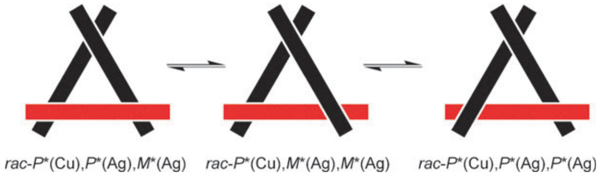


Fig. 2 Part of the ^{1}H NMR spectrum of triangle $\mathbf{T_2}$.



Scheme 4 Cartoon representation of the three different stereoisomers of triangles (the metal ions are omitted).

homometallic $\mathbf{T_2}$ is not unexpected as copper(I)–diimine complexes are stronger than those with silver(I) ions.[16] $\mathbf{T_2}$ was prepared independently by the synthetic route depicted in Scheme 3 and characterised by ESI-MS, ^{1}H NMR, UV–Vis spectroscopy and also by differential pulse voltammetry (DPV). Notably, DPV of the homometallic triangle $\mathbf{T_2}$ in MeCN confirmed the presence of two different copper(I) centres in a 2 : 1 ratio (see ESI†). Exclusive formation of the supramolecular triangle $\mathbf{T_2}$ in solution was supported by a DOSY experiment.

The dynamic nature of the assembly $\mathbf{T_2}$ was furthermore attested by a ligand exchange study. Addition of 1.0 equiv. of **2b** to a solution of $\mathbf{T_2}$ resulted in a mixture of the equilateral triangles $\mathbf{T_2}$ and $\mathbf{T_2}'$ (= $[Cu_3(\mathbf{4})_2(\mathbf{2b})](PF_6)_3$), both being homometallic and heteroleptic, as evidenced by ESI-MS through the detection of the ions $[Cu_3(\mathbf{4})_2(\mathbf{2a})]^{3+}$ and $[Cu_3(\mathbf{4})_2(\mathbf{2b})]^{3+}$ (see ESI†).

Upon closer inspection, the ^{1}H NMR of $\mathbf{T_2}$ at 5.7–6.2 ppm revealed six different singlets for the mesityl protons (Fig. 2), appearing as three sets of two singlets each. Also this finding is in agreement with the suggested structure as triangle $\mathbf{T_2}$ should be present as three diastereomers (Scheme 4). Since in each diastereomeric triangle the mesityl protons of ligand **2a** are diastereotopic, six different singlets are expected.

In conclusion, we have illustrated the exclusive formation of supramolecular heteroleptic triangles, either heterometallic ($\mathbf{T_1}$) or homometallic ($\mathbf{T_2}$, $\mathbf{T_2}'$), that are potential precursors to adjustable metal-chelation driven tweezers.[17] Our strategy relies on the utilisation of two concepts: (a) the HETPHEN concept, which leads to the formation of heteroleptic aggregates, and (b) the PHENLOCK concept that provides the kinetically stable copper(I) complex serving as angular unit in **1**. Astoundingly, no other possible aggregate was detected in the assembly process, such as the square complex $[Ag_2(\mathbf{1})_2]^{4+}$ most likely due to (a) entropic reasons and (b) the high thermodynamic stability of the HETPHEN complex. $\mathbf{T_1}$ is not only a heterometallic and heteroleptic triangle, but can easily undergo metal exchange processes due to its dynamic nature.

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