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Synthesis of Small Tetranuclear Cu(I) Metallacycles Based on Bridging Pseudohalogenide Ions

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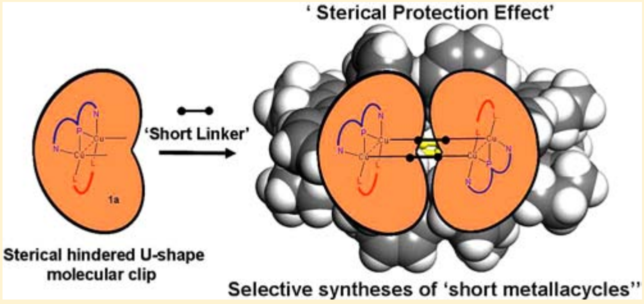
Ⓢ *Supporting Information*

ABSTRACT: Three new 'short' metallacycles are selectively obtained from the reaction of a bimetallic Cu^I 'U-shape' molecular clip with, respectively, the cyano CN^-, tricyanomethanide $C(CN)_3^-$, and azido N_3^- pseudohalogenide ions. These supramolecular assemblies have been characterized by spectroscopic methods, single-crystal X-ray diffraction, and elemental analysis. The single-crystal X-ray structures of these complexes reveal no short contact interaction between the pseudohalogenide ions within these self-assembled structures despite the short $Cu^I\cdots Cu^I$ distances within the molecular clips. The formation of these discrete metallacycles is rationalized by analyzing the structural features of the Cu^I 'U-shape' molecular clip.



■ INTRODUCTION

During the last two decades, a great interest has been devoted to the synthesis of discrete metallacycles[1] due to their potential to act as nanosized molecular flasks for the stabilization of reactive species or for the creation of unusual intermolecular contacts leading to original or enhanced reactivities or physical properties. The coordination driven synthetic approach[2a] toward these supramolecular objects relies on the design of individual building blocks having linking sites with symmetry in agreement with the overall shape of the targeted assembly. Most particularly, preorganized mono- or polymetallic coordination complexes acting as molecular clips having a well-defined symmetry and highly directional multibranched organic linkers have been synthesized for this purpose.[2] Among these molecular clips, the Cu^I-derivatives **1a,b**[3] (Scheme 1) based on assembling bis(2-pyridyl)phosphole N,P,N-pincer **2**[4] have recently emerged as a powerful bimetallic molecular clip for the coordination-driven synthesis of 2D metallacycles due to their peculiar structure. These bimetallic complexes present a rare constrained U-shape rigid geometry and short metal—metal distances (d(Cu···Cu); 2.551(1) Å revealing cuprophilic interaction) due to the original bridging phosphane coordination mode[5] for the N,P,N-pincer **2**. Two coordination sites on the Cu^I_2 fragments are occupied by chelating ligands which can be either ligand **2** acting as a P,N-donor or bis(1,2-diphenylphosphino)ethane (Scheme 1). The presence of both the N,P,N-pincer **2** and these blocking ligands affords clips **1a,b** with a large steric hindrance around the remaining coordination site of metal centers. The coordination sphere of the metal centers is completed by two labile acetonitrile ligands that can be displaced by a variety of cyano-capped linear ditopic π-conjugated systems affording very selectively supramolecular π-stacked metallocyclophanes **A** (Scheme 1). The powerfulness of this coordination driven synthetic approach toward stacked metallacyclophanes has been demonstrated with the use of π-linkers having different cores (*para*-phenylenevinylene, *para*-phenylene, *para*-phenylethynylene), nanosized length (up to 22.6 Å), and various topologies (linear, bent).[6a−d] Metal-based linear linker $[Au(CN)_2]^-$ which is able to display stabilizing metallophilic interactions also reacts with the molecular clips **1a** giving metal-rich assemblies **B** (Scheme 1).[6e] In contrast, using $Hg(CN)_2$ which displays putative very weak mercurophilic interactions, no selective supramolecular assembly process was observed and supramolecular rectangles of type **B** were formed together with linear oligomers and 1D coordination polymers.[6e] These results suggest that stabilizing noncovalent interlinker interactions (π−π interaction, aurophilic interactions) play a key role in the coordination driven synthetic process for driving the selective formation of metallacycles **A**, **B**.

In order to probe the scope and limits of the ability of U-shape molecular clips **1a** to assembly linkers within metallacycles having two short sides (the Cu^I_2 fragments and 'short' dipotic homoditopic linkers), we have been interested in reacting the molecular clips **1a** with pseudohalide ions (cyano CN^-, tricyanomethanide $C(CN)_3^-$, and azido N_3^- anions) for the following reasons. First, these ions display a versatile coordination chemistry, and they have been widely used for the synthesis of a variety of supramolecular derivatives with a broad range of dimensionalities, properties, and potential applications (molecular magnetism, gas sorption, emissive materials for optoelectronic applications, ...).[7] Second, these pseudohalide ions present shorter dimensions (N---N or C---N distances < 4.5 Å) than the organic and inorganic linkers (N---N distances

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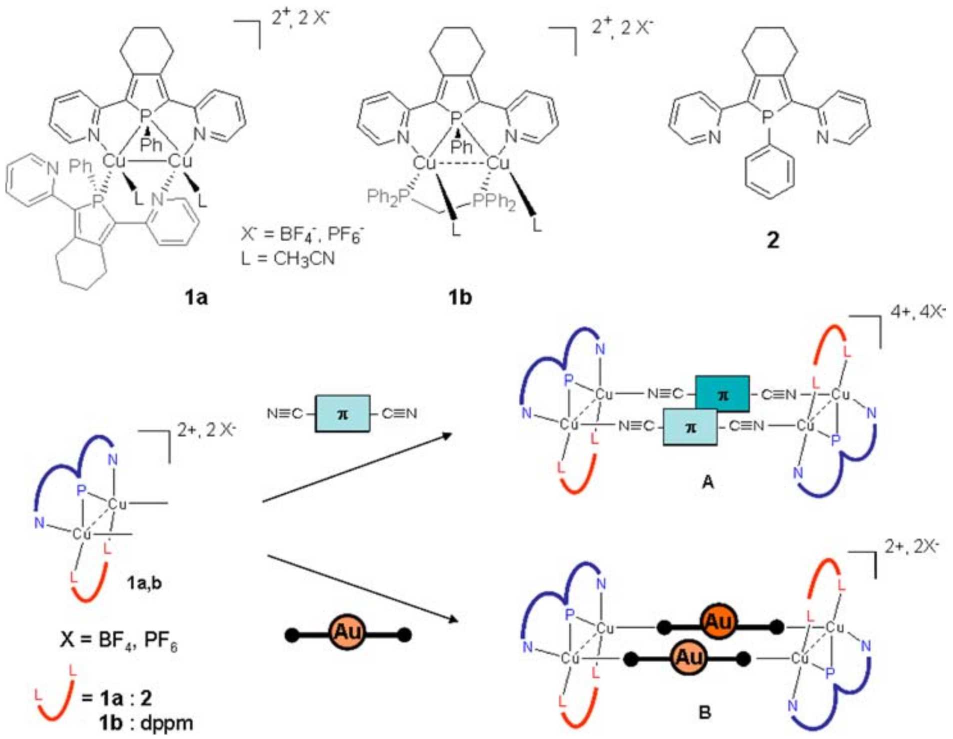
Scheme 1. Chemical Structure of Derivative 1a,b and 2 and Synthetic Approaches Towards π-Stacked Supramolecular Metallacycles A and Metallacycles B Displaying Intramolecular Aurophilic Interactions



> 6.2 Å)[6b,e] that have been used to prepare rectangles **A**,**B** from clips **1a**,**b** (Scheme 1). Therefore, the use of these short ions, and especially CN^- (C---N distance, 1.1 Å), will probe the lower limit of the linker length to obtain a metallacycle due to the close proximity induced for the two assembling bulky $(Cu^I)_2$ molecular clips. Third, tricyanomethanide (TCM) and azido pseudohalide ions are not known to exhibit stabilizing intermolecular interactions due to (i) their symmetric structure, which exclude favorable antiparallel dipole−dipole interactions that may be potentially observed with CN^-, (ii) their rather low polarizability compared to organic π-systems, due to the high electronegativity of the N-atoms, and (iii) their overall negative charge inducing electrostatic repulsion. This set of properties, which is clearly in disfavor of the use of these pseudohalide ions to prepare supramolecular rectangles with short lengths, can explain why up to now they have not been used for the coordination driven supramolecular syntheses of rectangles upon reaction with U-shape bimetallic molecular clips having short side metal−metal distances.[8]

In this paper, we describe the reaction of molecular clip **1a** with this series of pseudohalide ions. The fate of the reactions is analyzed following X-ray diffraction studies of the products and a discussion on the parameters controlling the formation of the supramolecular metallacycles with short sides instead of oligomeric or polymeric species is provided.

■ EXPERIMENTAL SECTION

Caution! Azide containing materials have been previously reported in several cases to be extremely hazardous and explosive materials and should be handled in a very small scale (a few mmoles) with appropriate safety precautions.

Chemicals and Instrumentation. All experiments were performed under an atmosphere of dry argon using standard Schlenk technique. Commercially available reagents $[Cu(CH_3CN)_4]PF_6$, KCN **3**, NaN_3 **4** (Aldrich), and $KC(CN)_3$ **5** (Alfa Aesar) were used as received without further purification. Solvents were freshly distilled under argon from an appropriate drying agent: dichloromethane (CaH_2), pentane (Na). ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at room temperature on a Bruker AV400 spectrometer. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign in ppm, relative to external 85% H_3PO_4. Elemental analyses were performed by the CRMPO, University of Rennes 1 on a Flash EA 1112 microanalysor CHSNS/O Thermo Electron. IR spectrometry measurements were recorded at room temperature on a Bruker ISS 28 spectrophotometer 4000−400 cm^{-1}. 1-Phenyl-2,5-bis(2-pyridyl)phosphole **2** was synthesized according to a previously reported procedure.[4a]

General Procedure for the Synthesis of Tetranuclear Complexes 6−8. To a solution of 40.0 mg of **2** (0.109 mmol) and 40.5 mg of $[Cu(CH_3CN)_4]PF_6$ (0.109 mmol) in 20 mL of CH_2Cl_2 was added 0.5 equiv of potassium/sodium pseudohalogenide salt dissolved in 2 mL of $H_2O{-}CH_3CN$ mixture (1:1 v/v). The resulting heterogeneous mixtures were vigorously stirred for 12 h, leading to color change from orange to deep red (**6**), red (**7**), deep orange (**8**). Organic layer was separated and was filtered off. Solutions were evaporated to dryness, washed with 20 mL of water and 3 × 20 mL of diethyl ether, and dried under a vacuum for 12 h affording derivatives **6**−**8** as reddish powders. Crystals suitable for X-ray analysis were grown by slow diffusion of pentene vapors into dichloromethane solution of derivatives **6**−**8** in approximately one week.

Synthesis of 6. Synthesis was done according to a general procedure starting from 40.0 mg of **2** (0.109 mmol), 40.5 mg of $[Cu(CH_3CN)_4]PF_6$ (0.109 mmol), and 3.6 mg of KCN (0.055 mmol). As a result 48.1 mg of derivative **6** (yield, 79%) was collected. ^1H NMR (CD_2Cl_2, 400 MHz, ppm): δ 1.59 (m, 2H, $C{=}CCH_2C\underline{H_2}$), 1.79 (m, 2H, $C{=}CCH_2C\underline{H_2}$), 2.40 (m, 2H, $C{=}CCH_2$), 2.97 (m, 2H, $C{=}CCH_2$), 7.11 (bs, 2H, m-Ph), 7.26 (bs, 2H, o-Ph), 7.35 (bs, 2H, H^5 Py), 7.45 (m, 1H, p-Ph), 7.62 (bs, 2H, H^3 Py), 7.88 (bs, 2H, H^4 Py), 8.29 (m, 2H, H^6 Py). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, ppm): δ 23.0 (s, $C{=}CH_2\underline{C}H_2$), 29.0 (s, $C{=}C\underline{C}H_2$), 123.7 (s, C^5 Py), 129.9 (s, m-Ph), 131.7 (s, p-Ph), 134.1 (s, o-Ph), 139.1 (s, C^4 Py), 150.0 (m, C^α), 150.6 (s, C^6 Py), 153.1 (s, br, C^2, Py), C^β, ipso-Ph, C^3 Py and CN

Table 1. Crystallographic Data[a]

	6	7	8
formula	$C_{98}H_{84}Cu_4F_{12}N_{10}P_6$ {$C_{99}H_{86}Cu_4Cl_2F_{12}N_{10}P_6$}	$C_{104}H_{84}Cu_4F_6N_{14}P_5$ {$C_{105}H_{86}Cu_4Cl_2F_{12}N_{14}P_6$}	$C_{96}H_{84}Cu_4F_{12}N_{14}P_6$ {$C_{97}H_{86}Cu_4Cl_2F_{12}N_{14}P_6$}
fw/g mol^{-1}	2069.73 {2154.72}	2052.86 {2170.84}	2101.75 {2182.19}
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*21/*c*	*C*2/*c*	*C*2/*c*
a/Å	13.3250(6)	25.039(2)	28.698(2)
b/Å	20.6150(11)	15.5308(12)	24.479(2)
c/Å	18.4860(9)	30.655(3)	22.7420(18)
α/°	90	90	90
β/°	100.491(2)	100.474(3)	133.955(3)
γ/°	90	90	90
V/Å^3	4993.1(4)	11722.3(17)	11501.0(16)
T/K	150	150	100
Z	2	4	4
data/restraints/ parameters	10063/63/622	11605/29/618	13173/130/695
GOF on F^2	1.063 {1.222}	0.639 {1.75}	1.093 {2.04}
R_1 ($I > 2\sigma(I)$)	0.0599 {0.0871}	0.0519 {0.1394}	0.0775 {0.1422}
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1745 {0.2635}	0.1551 {0.4080}	0.2435 {0.4392}
CCDC number	905108	905109	905110

[a] Crystallographic data before squeeze treatment[12] are given in curly brackets.

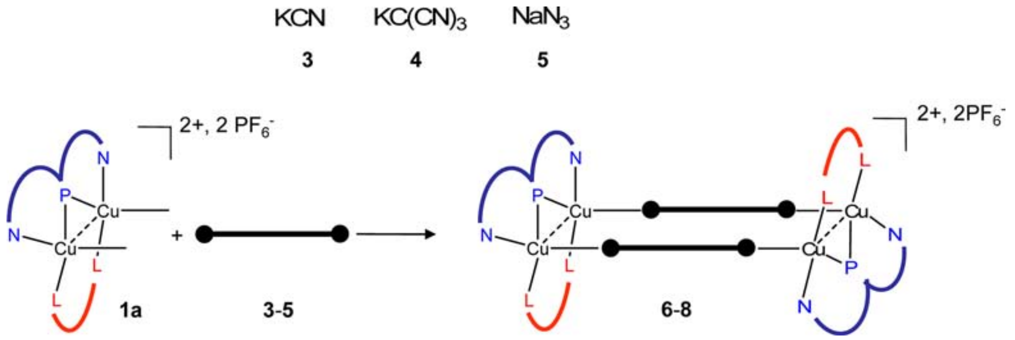
were not observed due to the very low solubility in the solvent used for the measurement). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz, ppm): δ −144.6 (sept, ^{1}J (P,F) = 706 Hz, PF_6^-), 5.8 (bs, $\nu_{1/2}$ = 28 Hz, $P_{phosphole}$). ^{19}F{^{1}H} NMR (CD_2Cl_2, 376.5 MHz, ppm): δ −73.0 (d, ^{1}J (P,F) = 706 Hz, PF_6^-). IR (KBr, cm^{-1}): 445(w), 556 (s), 694(m), 746(s), 778(s), 848(s),1055(w), 1093(w), 1159(m), 1278(w), 1309(m), 1432(s), 1463(s), 1463(s), 1514(w), 1563(m), 1590(s), 2124 (m), 2867(m), 2938(m), 3055(w), 3446 (w). Elemental analysis for **6** calcd (%) $C_{98}H_{84}Cu_4F_{12}N_{10}P_6$ (2066.23 g/mol): C 56.87, H 4.09, N 6.77; Found: C 56.54; H 3.92; N 6.57.

Synthesis of 7. Synthesis was done according to general procedure starting from 40.0 mg of **2** (0.109 mmol), 40.5 mg of $[Cu(CH_3CN)_4]$-PF_6 (0.109 mmol), and 7.0 mg of $KC(CN)_3$ (0.055 mmol). As a result 45.8 mg of derivative **7** (yield, 71%) were collected. ^{1}H NMR (CD_2Cl_2, 400 MHz, ppm): δ 1.49 (m 2H, C═CCH$_2$C$\underline{H_2}$), 1.80 (m 2H, C═CCH$_2$C$\underline{H_2}$), 2.18 (m, 2H, C═CCH$_2$), 2.90 (m, 2H, C═CCH$_2$), 7.10−7.30 (m 5H, m-Ph, p-Ph, o-Ph), 7.35 (bs, 2H, H^3 Py), 7.77 (m, 4H, H^5 Py, H^4 Py), 8.39 (bs, 2H, H^6 Py). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz, ppm): δ 22.6 (s, C═CH$_2\underline{C}$H$_2$), 28.7 (s, C═$\underline{C}$CH$_2$), 123.4 (s, C^5 Py), 124.6 (s, C^3, Py), 127.5 (bs, ipso-Ph), 129.3 (s, m-Ph), 130.6 (s, p-Ph), 132.8 (s, o-Ph), 138.4 (s, C^4 Py), 141.4 (bs, C$^\beta$), 149.9 (s, C^6, Py), 150.2 (bs, C$^\alpha$), 152.4(s, C^2 Py), carbon atoms of the TCM ion were not observed due to the very low solubility in the solvent used for the measurement). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz, ppm): δ −144.5 (sept, ^{1}J (P,F) = 712 Hz, PF_6^-), 6.8 (bs, $\nu_{1/2}$ = 90 Hz, $P_{phosphole}$). ^{19}F{^{1}H} NMR (CD_2Cl_2, 376.5 MHz, ppm): δ −73.4 (d, ^{1}J (P,F) = 712 Hz, PF_6^-). IR (KBr, cm^{-1}): 477(w), 554(m), 692(w), 742(m), 778(m), 841(s), 961(w),1008(w), 1059(w), 1154(m), 1257(m), 1308(m), 1433(m), 1459(s), 1563(m), 1589(s), 2183 (s)), 2866(w), 2936(s), 3058(w), 3440(m), 3658(w). Elemental analysis for **7** calcd (%) $C_{104}H_{86}Cu_4F_{12}N_{14}P_6$ (2196.25g/mol): C 56.78, H 3.94, N 8.91; Found: C 56.59; H 3.59; N 9.02.

Synthesis of 8. Synthesis was done according to general procedure starting from 40.0 mg of **2** (0.109 mmol), 40.5 mg of $[Cu(CH_3CN)_4]$-PF_6 (0.109 mmol) and 3.6 mg of NaN_3 (0.055 mmol). As a result 46.3 mg of derivative **8** (yield, 69%) were collected. ^{1}H NMR (CD_2Cl_2, 400 MHz, ppm): δ 1.57 (m, 2H, C═CCH$_2$C$\underline{H_2}$), 1.80 (m, 2H, C═CCH$_2$C$\underline{H_2}$), 2.30 (m, 2H, C═CCH$_2$), 2.91 (m, 2H, C═CCH$_2$), 7.04 (dd, $^3J_{HH,}$ = 6.2 Hz, $^3J_{HH}$ = 6.2 Hz, 2H, m-Ph), 7.19 (d, $^3J_{HH}$ = 7.1 Hz, 2H, o-Ph), 7.28 (t, $^3J_{HH}$ = 6.2 Hz, 1H, p-Ph), 7.35 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H^3 Py), 7.62 (dd, $^3J_{HH}$ = 4.2, $^3J_{HH}$ =7 Hz, 2H, H^5 Py), 7.65 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7, Hz, 2H, H^4 Py), 8.37 (d, $^3J_{HH}$ =4.2, 2H, H^6 Py). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz, ppm): δ 22.7 (s, C═CH$_2\underline{C}$H$_2$), 28.7 (s, C═$\underline{C}$CH$_2$), 122.8 (s, C^5 Py), 124.1 (s, C^3, Py), 128.5 (bs, ipso-Ph), 129.3 (s, m-Ph), 130.8 (s, p-Ph), 132.8 (s, o-Ph), 137.9 (s, C^4 Py), 141.4 (bs, C$^\beta$), 149.9 (C^6, Py), 152.6 (s, C^2 Py), C$_\alpha$ was not observed due to the very low solubility in the solvent used for the measurement. ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz, ppm): δ −144.5 (sept, $^1J_{P,F}$ = 711 Hz, PF_6^-), 6.7 (bs, $\nu_{1/2}$ = 90 Hz, $P_{phosphole}$). ^{19}F{^{1}H} NMR (CD_2Cl_2, 376.5 MHz, ppm): δ −73.4 (d, $^1J_{P,F}$ = 711 Hz, PF_6^-). IR (KBr, cm^{-1}): 479(w), 556(m), 694(w), 745(m), 778(m), 841(s), 1095(w), 1307(w), 1433(m), 1462(s), 1563(m), 1590(s), 2092(s), 2037(m), 2864(w), 2934(w), 3051(w). Elemental analysis for **8** calcd (%) $C_{96}H_{84}Cu_4F_{12}N_{14}P_6$ (2098.24 g/mol): C 54.86, H 4.03, N 9.33; Found: C 55.08; H 3.87; N 9.12.

Crystal Structure Determination. Single crystals suitable for X-ray crystal analysis were obtained by slow diffusion of vapors of pentane into a dichloromethane solution of the derivatives **6**, **7**, and **8** at room temperature. Single crystal data collection were performed at 100 or 150 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-*Kα* radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.[9] Structure determinations were performed by direct methods with the solving program SIR97,[10] that revealed all the non-hydrogen atoms. SHELXL program[11] was used to refine the structures by full-matrix least-squares based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. In the crystal lattices of the coordination complexes studied, dichloromethane solvent molecules were found in addition to the cationic coordination complexes and to their counteranions. These solvent molecules in most cases have a strong tendency to leave the bulk crystal via evaporation once the crystals are removed from their mother solution, a process that induced a rapid degradation of the single-crystal integrity of the crystals investigated. In order to slow down this process, single crystals of all these derivatives were always coated in paratone oil once removed from the mother solution, mounted at low temperature (100 or 150 K) as quickly as possible on the diffractometer gionometer and X-ray data collection was performed at low temperature. In all cases, X-ray crystal structure resolution revealed these solvent molecules highly disordered. A correct modeling of the disorders of all these CH_2Cl_2 solvent molecules was not possible, as well as one PF_6^- counteranion for the

Scheme 2. Derivatives 3−5 and Synthesis of the Metallacycles 6−8



derivative 7, and we have proceeded to a 'squeeze' treatment[12] in order to remove the scattering contribution of these molecules which cannot be satisfactory modeled. In these cases, anisotropic displacement parameters associated with the atoms of the cationic coordination complexes and the counteranions molecules are always satisfactory. Table 1 gives the crystallographic data for the derivatives **6**, **7**, and **8**. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[13] CCDC reference numbers 905108, 905109, and 905110 contain the supplementary crystallographic data for derivatives **6**, **7**, and **8** respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44−1223−336−033; e-mail: deposit@ccdc.cam.ac.uk].

■ RESULTS AND DISCUSSION

The reaction of 2 equiv of phosphole **2** with 2 equiv of $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2 at room temperature afforded the bimetallic complex **1a** that was subsequently treated with 1 equiv of KCN **3** dissolved in a 1:1 H_2O-CH_3CN mixture (Scheme 2).

The resulting heterogeneous mixture was vigorously stirred for 12 h at room temperature leading to a change of the color of the organic phase from red-orange to dark red together with the appearance of a light colorless precipitate of KPF_6. The organic phase was collected, filtered, evaporated, washed with water and diethyl ether, and finally dried under a vacuum affording derivative **6** as a red powder (yield, 79%). This novel derivative **6** is sparingly soluble in CH_2Cl_2 and insoluble in *n*-alkanes, $CHCl_3$, MeOH, or THF. Its $^{31}P\{^1H\}$ NMR spectrum, besides the resonances due to the PF_6^- ion ($\delta = -144.6$ ppm, $J_{P,F} = 706$ Hz), displays a broad singlet at +5.8 ppm, a chemical shift similar to that of the molecular clip **1a** ($\delta = 8.9$ ppm).[3a] This observation suggests that the $Cu^I_2(\mathbf{2})_2$ moiety featuring a bridging P-center is maintained in compound **6**. This assumption is supported by the room temperature ^1H NMR spectrum of **6** which displays one set of broad signals assignable to the coordinated 1-phenyl-2,5-bis(2-pyridyl)phosphole ligands **2**. As previously demonstrated, this simple ^1H NMR spectrum is in agreement with a fluxional behavior of the ligands **2** at room temperature due to the hemilability of the N,P,N-pincer (intramolecular exchange between the pendant and coordinated pyridyl groups resulting in interconversion of the P-atoms).[3b] Notably, no signals due to coordinated CH_3CN ligands are observed, while the infrared spectrum of derivative **6** reveals the presence of cyanide groups ($\nu(C{\equiv}N)$, 2124 cm^{-1}). Altogether these spectroscopic data suggest a substitution of the labile acetonitrile ligands of the derivative **1a** by the pseudohalide ion CN^-. The exact structure of compound **6** was established by a single-crystal X-ray diffraction study (Table 1). A CH_2Cl_2 solution of derivative **6** was exposed to pentane vapors for 7 days affording a homogeneous batch of dark red singles crystals suitable for X-ray diffraction studies. The red prisms of **6** crystallize in the $P2_1/c$ space group of the monoclinic system. The asymmetric unit contains one-half of a metallacycle, one PF_6^- anion, and one CH_2Cl_2 solvent molecule, the entire supramolecular assemblies being generated via symmetry operation associated with the $P2_1/c$ space group. Derivative **6** is a dicationic metallacycle (Figure 1) resulting from the coordination of two CN^- anions acting as ditopic linkers on two molecular clips **1a**. Note that (i) the cyano carbon and nitrogen atoms are disordered, and crystallography symmetry requires occupancies of 50% carbon and 50% nitrogen on both atomic sites, and (ii) counterions and cocrystallized solvent molecules are located outside and isolated from the self-assembled structure. No specific intermolecular interactions between the individual metallacycles are observed.

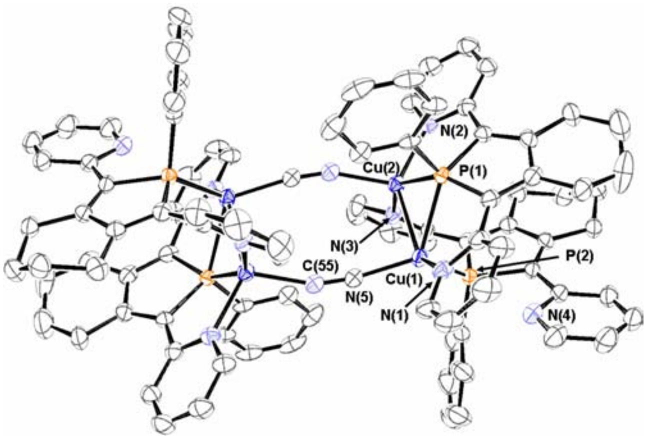


Figure 1. ORTEP[14] representation on the 50% probability level of the crystal structure of the dicationic metallacycle **6**. (H atoms, counteranions, and solvent molecules have been omitted for clarity; the location of the carbon and the nitrogen atoms of the cyano ligands are arbitrary.)

In this derivative, the four Cu^I centers lay in the same plane defining a rectangle (Figure 2a). As observed in the molecular clip **1a**, the $(Cu^I)_2$-fragments are coordinated to two bis(2-pyridyl)phosphole ligands **2**, one acting as a μ-1κN:1,2κP:2κN 6-electron donor with a bridging P-center, and one acting as μ-1κN:2κP chelate. Their μ-P atoms have a mutual *anti*-position with respect to the metallacycles with the P-phenyl substituents pointing toward the cyanide ligands (Figure 2a). This arrangement is usually observed also in stacked metal-

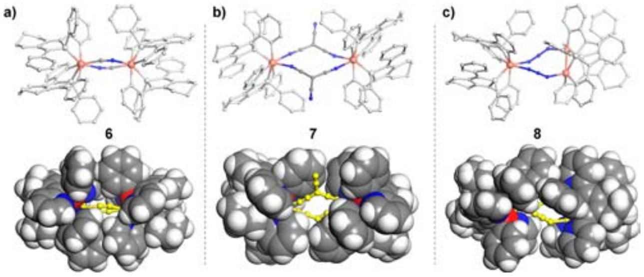


Figure 2. (a−c) 'Lateral' views (phosphole ligand atoms are shown in white) and CPK views (the Cu_2(linker)$_2$ metallacycles are highlighted in stick and ball style in yellow) of the metallacycles **6**−**8**.

locyclophanes **A**, **B** (Scheme 1, see Table S1 for a comparison of the geometric parameters for the derivative **6** and a selection of metallacycles **A**, **B**) based on organic cyano capped homoditopic linkers.[6]

The CuI···Cu^{I} distance within the dicationic Cu^I_2(**2**)$_2$ cores (2.6225(6) Å, Table 2) is longer than observed in the crystal structure of the free clip **1a**[3] (2.5552(8) Å) but compares well with the values observed in the π-stacked metallocyclophanes **A**.[6] Such a rather short Cu^I···Cu^I distance indicates that cuprophilic interactions[15] take place between the two metal centers of the Cu^I_2(**2**)$_2$ cores of **6** as observed in the molecular clip **1a**. All the other metric parameters, including the metal-μP distances or the directing (C≡N)−Cu−Cu−(C≡N) angles, are very similar to those of the corresponding free molecular clip **1a**[3] (Table 2) and related tetracationic rectangles based on neutral cyano-capped organic connectors,[6a−d] suggesting there is no steric strain associated with the formation of the metallacycle **6**. The C−Cu−Cu−N dihedral angles (21.99(3)°) and the bond lengths of the CN^- fragments are typical. The coordination angle of the CN^- ions deviates slightly from linearity (C−N−Cu; 161.1(3)°, 169.8(5)°, Figure 2a), as observed in the case of the coordination of cyano capped ditopic organic linkers within rectangles **A**.[6] The lateral interlinker shortest atomic distance (3.343(4) Å) is large, indicating that no interaction takes place between the assembled CN^- linkers.

Therefore, the reaction of the pseudohalide CN^- anions acting as ditopic linear linkers with clip **1a** affords selectively a small metallacycle (Cu···Cu distances, 2.62 and 5.0 Å) (Scheme 1). Note that despite the very short CN^- anion length (C−N distance, 1.1 Å) neither steric constraints nor short contact interactions are observed between the two bulky molecular clips **1a** presents in this metallacycle (Figure 2a). This result confirms that the Cu^I dimer **1a** is a powerful and unique U-shaped molecular clip for the coordination-driven supramolecular syntheses of metallacycles upon reaction with ditopic donors. In addition, the synthesis of **6** clearly demonstrates the robustness of the bridging phosphane coordination mode observed in the Cu^I_2(**2**) moiety since the CN^- ligand, which is known to have a very strong affinity for Cu^I ions, substitutes only the labile acetonitrile ligands of **1a**, leaving the Cu^I_2(**2**)$_2$ units intact.

Since no intermolecular interactions take place between the metallacycles **6**, the source of the driving force leading to the selective formation of this assembly can be intramolecular only. It is very likely that in metallacycle **6**, the two CN^- linkers display an antiparallel arrangement, although the solid state structure cannot establish this fact, resulting in antiparallel favorable close interaction of their dipolar moment.

The synthesis of metallacycle **6** prompted us to investigate the reaction of **1a** with the other pseudohalide ions $C(CN)_3^-$ (TCM) and N_3^- for the following reasons. First, these pseudohalide ions present coordination geometry and/or connectivity differently than those of the linear CN^- linker allowing studying the impact of the variation of these parameters in the geometry of the resulting supramolecular assemblies. For example, the N_3^- anion is known to exhibit several coordination behaviors including terminal, angular end-to-end, or angular end-on modes.[16] Second, besides a terminal ligand behavior toward single metal ion, the TCM ion can act also as a ditopic or tritopic linker to bridge respectively two or three metal centers.[17] It was thus of interest to react molecular clip **1a** with TCM to see whether this ligand will act as a ditopic or tritopic short linker in order to further probe the synthetic limits imposed by the steric hindrance of **1a**. Lastly, since dipole−dipole interactions can rationalize the stabilization of the 'small' supramolecular metallacycle **6**, the use of pseudohalide N_3^- anion as linkers was interesting since it is also a short species (N---N distance, ca. 2.3 Å) but without a dipolar moment.

The reaction of the molecular clip **1a** with $KC(CN)_3$ **4** and NaN_3 **5** (Scheme 2), following the procedure applied for the synthesis of metallacycle **6**, afforded the derivative **7** as a red powder (71% yield) and the derivative **8** as an orange powder (69% yield), respectively. These compounds are soluble in CH_2Cl_2 and CH_3CN but insoluble in MeOH, THF, and nonpolar solvents such as *n*-alkanes and toluene. Their spectroscopic data show that these species do not bear the acetonitrile ligands present in the clip **1a**, while their infrared spectra suggest the presence of the TCM or N_3^-, respectively. The exact geometry of these new supramolecular derivatives **7**

Table 2. Selected Bond Lengths [Å], Angles and Torsion Angles [°] of the Cu_2(Nμ-PN) Moieties of Molecular Clips 1a[3] and Supramolecular Assemblies 6−8

	Cu−μP	Cu−N^a	Cu···Cu	N^a−Cu−μP	Cu−μP−Cu	μP−Cu−Cu	Cu−X (X = NC^- (**6**), $C(CN)_3^-$ **7**), N_3^- (**8**))	X−Cu−Cu−X (X = NC^- (**6**), $C(CN)_3^-$ (**7**), N_3^- (**8**))
1a[3]	2.293(1)	2.048(4)	2.5552(8)	82.85(1)	66.15(4)	55.17(3)	1.980(4)	34.1
	2.386(1)	2.043(4)		86.14(1)		58.68(3)	2.042(4)	
6	2.2993(10)	2.097(3)	2.6225(6)	82.18(9)	66.28(3)	53.39(2)	1.981(4)	21.9
	2.4888(10)	2.117(3)		84.76(9)		60.33(3)	2.006(3)	
7	2.2959(10)	2.039(3)	2.5653(6)	84.08(10)	67.29(3)	55.65(3)	1.951(3)	37.2
	2.3338(10)	2.052(3)		84.73(10)		57.06(3)	2.034(3)	
8	2.2749(11)	2.061(4)	2.5508(7)	83.96(10)	66.54(3)	54.89(3)	1.982(4)	22.6
	2.3726(11)	2.062(3)		84.79(12)		58.57(3)	2.051(4)	

[a] Nitrogen atoms of the Cu_2(Nμ-PN) moieties.

and **8** was elucidated by single X-ray diffraction studies (Table 1). Homogeneous batches of single crystals of derivatives **7** and **8** were obtained at room temperature from pentane diffusion into a CH_2Cl_2 solution of derivative **7** and **8** respectively. Both compounds **7** and **8** crystallize in the *C*2/*c* space group of the monoclinic system with one-half of a metallacycle ligand, one PF_6^- counteranion, and one CH_2Cl_2 solvent molecule.

In the crystal packing, all molecules **7** are isolated, and no intermolecular interactions are observed between these assemblies neither with the counteranions and included solvent molecules. Derivative **7** is a centrosymmetric metallacycle (Figure 3) resulting from the coordination of two TCM ligands on two $Cu^I_2(\mathbf{2})_2$ moieties. Within the metallacycle, the TCM ligands act as ditopic ligands bridging two $Cu^I_2(\mathbf{2})_2$ moieties and possess one noncoordinated moiety. The conformation of ligand **2** within the Cu^I-clips is similar to that found in the assembly **6** (all the P-phenyl substituents pointing toward the center of the metallacycle), and the geometrical parameters within the $Cu^I_2(\mathbf{2})_2$ cores (Cu−P, Cu−N, Cu···Cu distances and valence angles, Table 2) are comparable to those of other metallacycles based on the molecular clip **1a** (see Table S1 for a comparison of the geometric data for the derivative **7** and a selection of metallacycles **A**,**B**). The four Cu^I centers define a rectangle (Figure 2b) with the two *μ*-P center having an *anti*-arrangement. The C−N−Cu angles (164.7(3)−170.1(3)°) do not deviate significantly from linearity, and these coordination valence angles compare with those observed in the cyanide bridged rectangle **6**. The TCM ligands are planar (sum of the C−C−C angles, 359.99°) and significantly bent toward the plane of the Cu_4 rectangle (53.2°) most probably to fit with the steric hindrance of the P-phenyl substituents pointing toward the center of the metallacycle (Figure 2b). Within the TCM ligands, the N−C−C angles are close to 180° (177.7(4)−179.3(4)°) and the N−C and C−C bond length ranges from 1.120(5) Å to 1.159(5) Å and 1.387(5) Å to 1.427(6) Å respectively, showing a typical triple and single-double bonding character, respectively. Finally, the two TCM ligands are located on both sides of the Cu_4 rectangle with the two uncoordinated cyano groups pointing in opposite directions preventing therefore short contacts between the atoms of these ligands. Note that, upon coordination, TCM ligands acquire a dipole moment, and their antiparallel arrangement (Figure 2b) can rationalize the fact that the free cyano groups point in opposite directions. It is noteworthy that using an excess of clip **1a**, only the metallacycle **7** is formed showing that the molecular clip **1a** cannot coordinate the pendant cyano groups, probably due to its steric hindrance, to form molecular boxes.

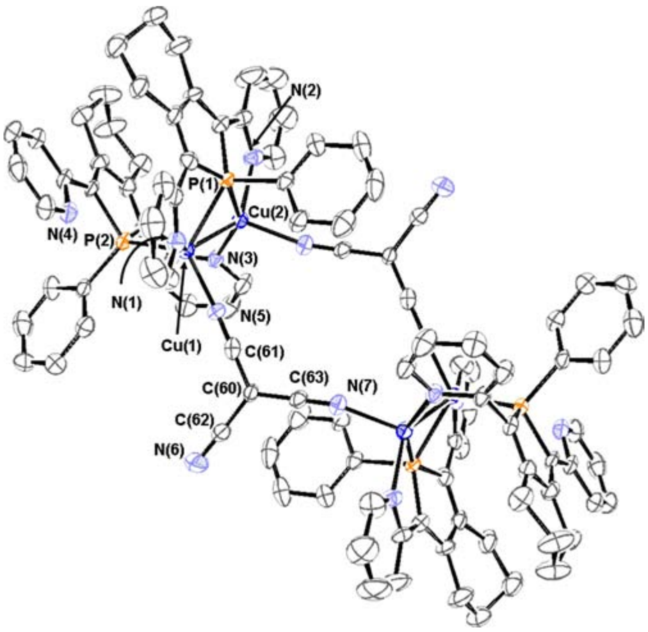


Figure 3. ORTEP[14] representation on the 50% probability level of the crystal structure of the dicationic metallacycle **7**. (H atoms, counteranions, and solvent molecules have been omitted for clarity.)

Compound **8** is a supramolecular metallacycle resulting from the coordination of two azide linkers in an angular end-to-end coordination mode on two binuclear units $Cu^I_2(\mathbf{2})_2$ (Figure 4). In the crystal packing, all metallocyclophanes **8** are isolated, and no intermolecular interactions are observed between these

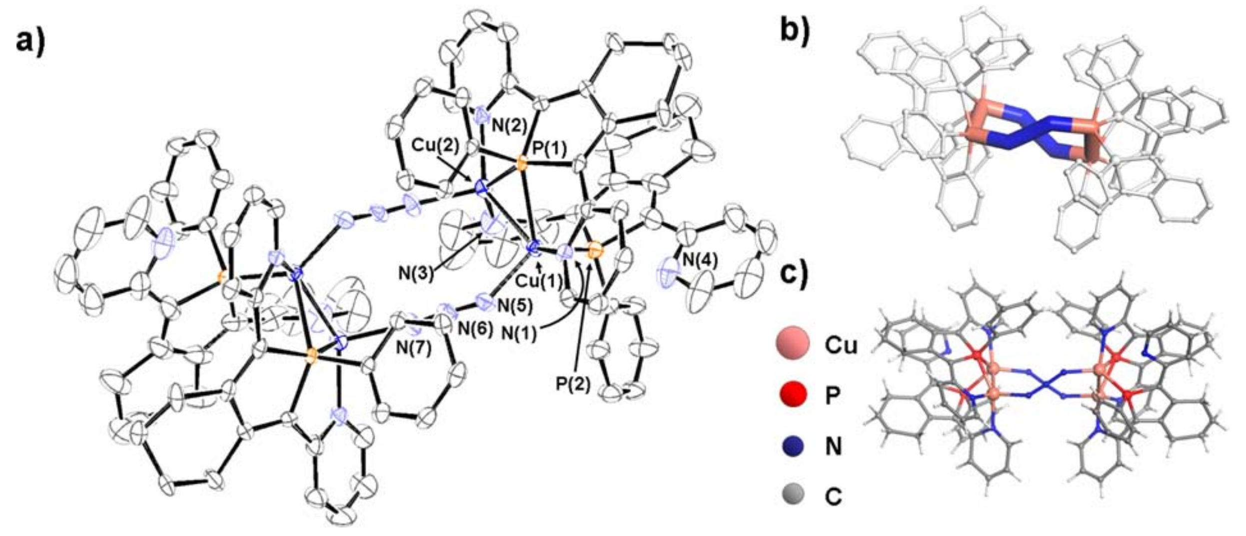


Figure 4. (a) ORTEP[14] representation on the 50% probability level of the dicationic metallacycle **8**. (H atoms, counter-anions and solvent molecules have been omitted for clarity), (b) view highlighting the 'twisted-ribbon' geometry of the metallacycle, (c) view highlighting the pseudosymmetry of the derivative **8**.

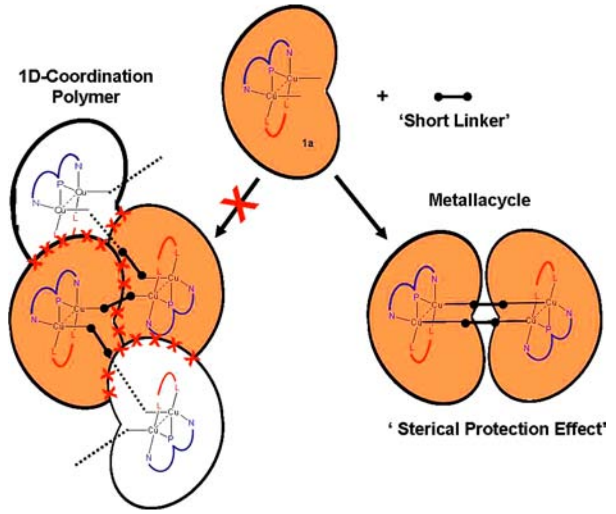
assemblies. The conformation of ligand **2** within the Cu^{I}-clips is similar to that found in the assembly **6** (all the P-phenyl substituents pointing toward the azide ligands), and the geometrical parameters within the Cu$^{I}_{2}$(**2**)$_2$ cores (Cu−P, Cu−N, Cu$\cdots$Cu distances, and valence angles) compare to those of the other metallacycles synthesized from the molecular clip **1a** (see Table S1 for a comparison of the geometric data for the derivative **8** and a selection of metallacycles **A**,**B**).

The intermetallic CuI$\cdots$Cu^{I} distance (2.5508(7) Å) is among the shortest recorded to date for a Cu$^{I}_{2}$(**2**)$_2$ core[3], and the four Cu^{I}-atoms are not in the same plane (Cu−Cu−Cu−Cu dihedral angle, 64.9°). Consequently this metallacycle presents a 'twisted ribbon' geometry (Figure 4b) with the two μ-P center having a *syn*-arrangement with respect to the surface of the metallacycle. This type of 'twisted ribbon' geometry was previously observed with supramolecular metallacycles **A** bearing biphenyl-based cyano capped π-conjugated organic linkers.[6b] The metric data of the N_3^- fragments are classical (N−N−N angle, 176.7(5)°; distances: N−N, 1.161(6) and 1.186(5) Å as well as the Cu−N distances (1.982(4) and 2.051(4) Å), but the N−N−Cu azide coordination angles (138.7(3)−140.9(3)°) are larger than those usually observed (<130°) in the case of the end-to-end coordination mode of the azide ion. Within metallacycle **8**, the shortest interlinker N−N distance (3.279(6) Å) is observed between the two central nitrogen atoms, but this rather large value indicates that no interaction takes place between these two N-atoms. This distance is similar to those observed in recently reported Ag_2N_6 'nitrogen-rich' small metallacycles (ca. 3.1−3.5 Å).[18a] Note that the N_3^- ligands do not acquire dipole moment upon coordination (Figure 4c).

These results illustrate the versatility of the supramolecular synthesis of metallacycles using U-shape molecular clip **1a**. The formation of the 'nitrogen-rich' Cu_4N_6 small metallacycle **8** is particularly interesting since 'nitrogen-rich' derivatives have a high potential as energetic materials.[18] However, the nature of the driving forces governing their formation is unclear. It was suggested that the selective syntheses of metallacycles **A** and **B** (Scheme 1) is due to the formation of lateral nonconvalent interlinker stabilizing π−π interactions or aurophilic interaction respectively within these stacked assemblies. This hypothesis cannot be taken into account in the case of derivatives **6**−**8** since no intramolecular short contact interactions are observed between the N-rich linkers in these self-assembled structures. In derivatives **6** and **7**, the coordinated ligands exhibit local dipolar moments which display antiparallel orientation that can contribute to metallacycle stabilization. However, this is not the case in derivative **8**, and therefore dipole−dipole interaction cannot be the only factor rationalizing the *selective* synthesis of the metallacycles **6**−**8** toward linear oligomers or coordination polymers.

One hypothesis to rationalize the selective formation metallacycles **6**−**8** instead of oligomeric or polymeric species can be proposed. The shape and steric hindrance allow the (Cu^{I})$_2$(**2**) molecular clips adopting a "face-to-face" arrangement within metallacycles **6**−**8** in spite of the short lengths of the pseudohalide linkers **3**−**5** ('sterical protection effect', Figure 2, Scheme 3). The formation of oligomers or polymers would require a "lateral-displaced" arrangement of these (Cu^{I})$_2$ molecular clips, an arrangement which is impossible to accommodate for the clips due to the short lengths of the pseudohalide linkers **3**−**5** (Figure 2, Scheme 3). Therefore, the selective formation of discrete metallacycles is due to the specific shape and steric hindrance of the (Cu^{I})$_2$ molecular clips.

Scheme 3. 'Sterical Protection Effect' Driving the Selective Syntheses of 'Small' Metallacycles from the Reaction of the Molecular Clip 1a with Pseudohalide Ions



■ CONCLUSION

The ability of molecular clips **1a** to assemble ditopic linkers selectively within supramolecular metallacycles can be extended to the anionic pseudohalide linkers CN^-, N_3^-, and $C(CN)_3^-$. In contrast to what was observed with homoditopic cyano-capped organic π-conjugated systems or $[Au(CN)_2]^-$ linear anionic linker, intramolecular interactions between the linkers do not take place in spite of the short Cu$^{I}\cdots$Cu^{I} distances. The selective formation of metallacycles using these 'short' pseudohalide linkers is assigned to a 'sterical protection effect' resulting from the large steric hindrance and specific shape of the (Cu^{I})$_2$ molecular clips. These results illustrate the versatility of bimetallic clip **1a** to drive the selective synthesis of supramolecular metallacycles upon reaction with diverse ditopic linkers and highlight the importance of the design of the molecular clips used to drive the fate of the self-assembling processes in coordination-driven supramolecular chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data of the derivatives **6**−**8** in CIF format. Labeling scheme of the Cu$^{I}_{2}$(**2**)$_2$ moieties in the derivatives **6**, **7**, and **8**. Table compiling selected spectroscopic and structural data of the derivatives **6**, **7**, and **8** and a selection of metallacycles **A**, **B**. NMR spectra recorded for the derivatives **6**, **7**, and **8**. 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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