

Ag^I Bimetallic Molecular Clips with Adaptive Coordination Behavior for Supramolecular ChemistryStefan Welsch,^{†,‡} Christophe Lescop,[‡] Manfred Scheer,^{*,†} and Régis Réau^{*,†}*Sciences Chimiques, UMR 6226, CNRS, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France, and Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany*

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An Ag^I dimer featuring a bridging phosphane ligand acts as an adaptive molecular clip for the coordination-driven synthesis of π -stacked metallocylophanes.

The “directional-bonding approach” is a general and rational methodology for the synthesis of supramolecular self-assemblies via coordination of multibranching monodentate linkers to metal centers.¹ This approach is based on the design of metal clips having free sites available arranged at the desired angles for coordination of the incoming linkers to form the target shape. Consequently, it is essential that the value of the directing angle of the metal clips must not change significantly upon their incorporation into the self-assembled structures.¹ Therefore, the Ag^I ion is a priori not an attractive metal center to design molecular clips according to the directional-bonding approach because (i) it has no strong geometrical preferences and (ii) its coordination sphere is very flexible.² Indeed, using Ag^I, subtle changes of the multibranching monodentate linkers afford very different structures during coordination-driven self-assembly processes.^{2f,g} Herein, we report the synthesis and structural characterization of the first Ag^I dimer featuring a bridging σ^3 -P donor, which is a rare coordination mode for phosphane ligands.^{3,4} This compound is an appealing bimetallic clip for supramolecular synthesis because it can form target assemblies as a result of a predictable reorganization of the two Ag ions' coordination sphere. This “adaptive” coordination behavior is, to the best of our knowledge, unprecedented for metal dimer molecular clips.

Bis(2-pyridyl)phosphole **A** (Scheme 1) is a versatile heteroditopic N,P,N-pincer for the stabilization of metal

dimers.³ In these complexes, the P moiety of **A** bridges the two metal centers. This coordination mode for phosphane ligands was discovered in 2000 only^{4b} and is still limited to few examples.^{3,4} Derivative **A** reacted with 1 equiv of AgPF₆ in CH₂Cl₂, affording bimetallic complex **1** in 81% yield (Scheme 1). Its ³¹P{¹H} NMR spectrum in CD₂Cl₂ displays a broad triplet at +13.9 ppm with a large ¹J_{Ag,P} coupling constant (218 Hz), indicating the coordination of the phosphole moiety to the Ag^I centers. The proposed structure was confirmed by an X-ray diffraction study. Complex **1** is a bimetallic Ag^I complex [metal–metal distance = 2.7040(6) Å] featuring two ligands **A**, one acting as a μ -1 κ N:1,2 κ P:2 κ N donor and one acting as a 1 κ N:2 κ P-bridging ligand (Scheme 1). The distance between the Ag^I center and the N4 atom of the pendant pyridine is 3.591(5) Å, ruling out any Ag–N interaction. The coordination spheres of the two Ag^I ions are almost coplanar (maximum deviation from the Ag₂P₂N₃ mean plane = 0.14 Å). The ability of the Ag^I ion to readily adopt different coordination geometries is nicely illustrated by the fact that the two tricoordinated Ag^I centers of dimer **1** present different coordination-sphere geometries. Ag1 is a distorted trigonal-planar center with an acute P1–Ag1–N1 angle [79.09(12)°], with the two other angles

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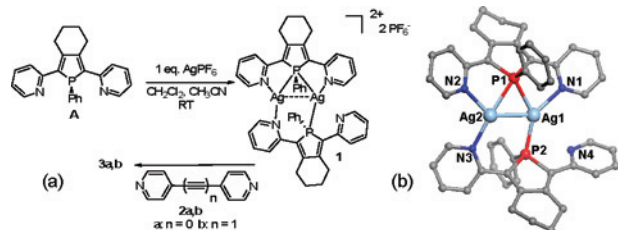
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Scheme 1. (a) Synthesis of Ag^I Clip **1** and Assemblies **3a** and **3b** and (b) Molecular Structure of the Dicationic Complex **1**^a



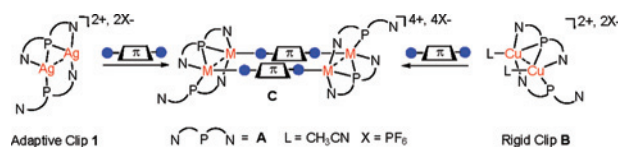
^a Hydrogen atoms and counteranions have been omitted for clarity.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Dimer **1** and Supramolecular Assemblies **3a** and **3b**

	1	3a	3b
Ag–μ-P1	2.4890(14)	2.5282(9)	2.5243(10)
	2.6373(14)	2.8084(9)	2.8645(11)
Ag–N ^a	2.222(5)	2.287(3)	2.217(6)
	2.296(5)	2.449(3)	2.493(3)
Ag···Ag	2.7040(6)	2.8584(4)	2.8807(8)
N1–Ag1–P2	137.43(13)	127.21(8)	127.1(3)
N1–Ag1–P1	79.09(12)	75.22(8)	72.3(3)
P1–Ag1–P2	143.20(5)	124.08(3)	118.01(3)
P1–Ag1–N100		97.38(7)	105.21(7)
P2–Ag1–N100		119.09(7)	118.39(8)
N1–Ag1–N100		103.41(10)	109.9(3)
N2–Ag2–N3	111.95(17)	104.41(11)	105.00(9)
P1–Ag2–N3	164.77(13)	122.08(8)	127.02(7)
P1–Ag2–N2	77.79(12)	74.47(7)	75.69(7)
P1–Ag2–N200		127.43(8)	117.66(8)
N2–Ag2–N200		98.53(10)	91.32(9)
N3–Ag2–N200		110.23(11)	115.29(10)

^a For the μ-ligand **A**.

Scheme 2. Synthesis of π-Stacked Metallocyclophanes **C** Using Adaptative Ag^I or Rigid Cu^I Clips



being around 140° (Table 1). In contrast, the Ag₂ coordination sphere can be described as T-shaped (Scheme 1) because of the large P1–Ag2–N3 angle [164.77(13)°, Table 1]. Not surprisingly in this nonsymmetric environment, the μ-P center displays a semibridging coordination mode [Ag–μP distances = 2.6373(14) and 2.4890(14) Å]. This makes complex **1** the first example of a Ag^I dimer featuring a binucleating ligand based on a σ³-P bridging phosphane, demonstrating that this rare coordination mode for phosphanes can be encountered for tricoordinate metal centers⁵ and confirming that phosphanes should now be included among the list of classical bridging ligands.

It is interesting to note that the (Ag₂A₂) dimer **1** (Scheme 2) has a structure that is very different from that of its (Cu₂A₂) analogue **B**.^{3c} Complex **B** also features two ligands **A**, one acting as a six-electron μ-1κN:1,2κP:2κN donor with a semibridging P center and one acting as a 1κN:2κP chelate, but the two Cu^I ions have a tetrahedral geometry due to the

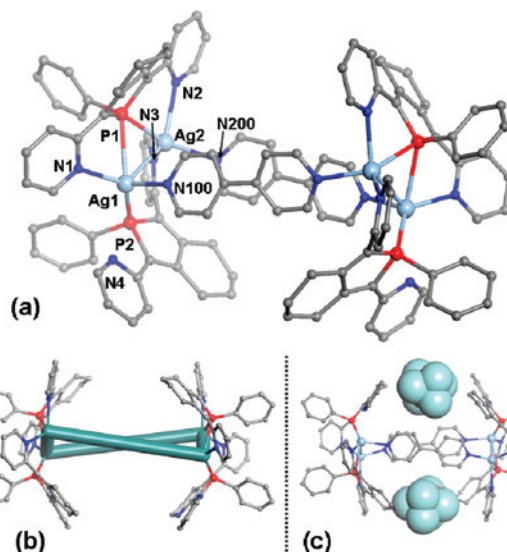


Figure 1. (a) Molecular structure of the tetracationic derivative **3a**. (b) Schematic view showing the topology of the metallacycle. (c) View with the PF₆⁻ counterion. Solvent molecules and hydrogen atoms have been omitted for clarity.

presence of additional acetonitrile ligands (Scheme 2).⁶ Therefore, dimer **B** has a “U-shaped” topology (i.e., two closely aligned cis coordinatively labile acetonitrile ligands) and can be used as a molecular clip for the coordination-driven supramolecular synthesis of π-stacked metallocyclophanes **C** (Scheme 2).⁷ It is noteworthy that this (Cu₂A₂) clip fulfills the rigidity criteria required by the directional-bonding approach because the geometry of the coordination sphere of the Cu^I ions does not change significantly upon their incorporation into the self-assembled structures **C**.⁷

Unlike its Cu^I analogue molecular clip **B**, complex **1** clearly does not possess a programmed U shape with strongly directional available coordination sites. However, considering the ability of the Ag^I ions to access coordination modes higher than trigonal planar, it was tempting to investigate the use of **1** as a molecular clip for the coordination-driven supramolecular synthesis of π-stacked metallocyclophanes **C** (Scheme 2). The reaction of Ag^I dimer **1** with 4,4'-bipyridine **2a**, a widely used linear organic linker,^{1,8} affords the supramolecular assembly **3a** (Scheme 1), which was isolated in 58% yield. In addition to the PF₆⁻ signal, the room temperature ³¹P{¹H} NMR spectrum of **3a** in CD₂Cl₂ shows a broad triplet (δ 8.3 ppm, ¹J_{Ag,P} = 191 Hz). This resonance is only slightly low-frequency-shifted compared to that of clip **1**, suggesting that the (Ag₂A₂) fragment is retained in assembly **3a**. An X-ray diffraction study revealed that compound **3a** is a supramolecular metallacycle in which two (Ag₂A₂) dimers **1** are connected by two ligands **2a** via coordination of their pyridyl termini (Figure 1a). The tetracoordinated Ag^I metal centers of assembly **3a** now

(6) Complex **1** is unreactive toward acetonitrile and thus does not afford a Ag^I complex, which would be the exact analogue of clip **A**.

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(5) Bridging phosphanes have been encountered in dimers with tetracoordinated metals having square-planar (Pd^I, Pt^I),^{3a–c} tetrahedral (Rh^I,^{4c,d} Cu^I ^{3c,d}), or square-pyramidal coordination (Rh^I,^{4c,d}) spheres.

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exhibit a distorted tetrahedral coordination sphere (Table 1), something that has clearly necessitated a profound reorganization of the metal coordination sphere of dimer **1** during the self-assembly process. The metric data for the ($\text{Ag}^{\text{I}}_2\text{A}_2$) cores of **3a** are essentially comparable to those observed for the clip **1**, except for one $\mu\text{-P-Ag}$ distance that slightly elongated (Table 1). These data show that the change in the Ag^{I} coordination geometry on going from **1** to **3a** is not accompanied by a steric stress, and they nicely underline the high coordination flexibility of Ag^{I} ions. Because of a 30.3° twist angle of the two pyridine rings and as a result of the mutual hindered rotation, assembly **3a** presents a novel “twisted-ribbon” topology (torsion angle between the axes of the two Ag^{I} dimers = 66.9° ; Figure 1b). In this metallocyclophane, the pyridine moieties have a face-to-face arrangement with rather short centroid–centroid distances ($<3.7 \text{ \AA}$), suggesting $\pi\text{-}\pi$ interactions between the two connectors **2a**.⁹ Assembly **3a** can be thus regarded as a novel example of a π -stacked metallocyclophane of type **C**. Finally, it is noteworthy that each face of this metallacycle defines a “supramolecular basket” in which a PF_6^- counterion is included (Figure 1c; minimum PF_6^- –fluorine–CH distance = ca. 2.4 \AA).¹⁰

It is striking that the ($\text{Ag}^{\text{I}}_2\text{A}_2$) cores of **3a** have exactly the same structure as the ($\text{Cu}^{\text{I}}_2\text{A}_2$) fragments of π -stacked metallocyclophanes **C** (Scheme 2). Therefore, this rare supramolecular topology can be obtained either from the use of rigid Cu^{I} -based molecular clips **A** having a U shape or from adaptive bimetallic Ag^{I} complex **1** having no programmed shape (Scheme 2). It is noteworthy that the general mechanism leading to supramolecular assemblies **C** is quite different using the rigid clip **B** or the adaptive clip **1**. With **B**, the formation of **C** implies a ligand-exchange process, which is the classic building process used in the directional-bonding approach.¹ In contrast, the synthesis of **C** from **1** requires only simple coordination of the incoming linker, avoiding competitive coordination processes (Scheme 2).

In order to check the generality of this synthetic approach toward metallocyclophanes **C**, Ag^{I} dimer **1** was reacted with 1 equiv of bis(4-pyridyl)acetylene **2b** (Scheme 1). An X-ray diffraction study revealed that the resulting product **3b** (52% yield) is a metallocyclophane of type **C** having a “basket” topology with two PF_6^- anions located on each face (Figure 2). The ($\text{Ag}^{\text{I}}_2\text{A}_2$) moieties of **3b** have the same structure as those of **3a**, with two distorted tetrahedral Ag^{I} ions enclosed by 2 equiv of ligand **A** (Table 1). Here again, the Ag^{I} centers of **1** have extended their coordination sphere from tricoordinated to tetracoordinated during the self-assembly process, leading to **3b**. In metallocyclophane **3b**, the two aromatic rings of the organic linkers are coplanar (torsion angle $< 2^\circ$). The four Ag^{I} ions lie in the same plane, defining a rectangle ($14.174 \text{ \AA} \times 2.881 \text{ \AA}$) of type **C** (Figure 2b), in

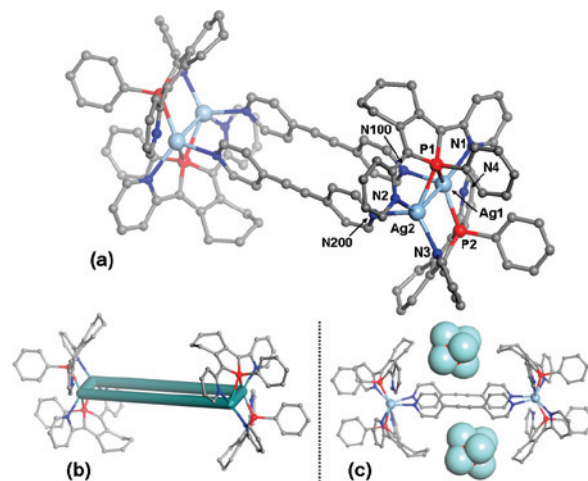


Figure 2. (a) Molecular structure of the tetracationic derivative **3b**. (b) Schematic view showing the topology of the metallacycle. (c) View with the PF_6^- counterion. Solvent molecules and hydrogen atoms have been omitted for clarity.

which the aromatic rings of the organic linkers are involved in face-to-face π interactions (intramolecular distances between each π system = ca. 3.5 \AA). The formation of **3b** demonstrates that the geometric change of the coordination sphere of the Ag^{I} ions of clip **1** has a general character and that this adaptive clip can be used for the rational design of assemblies **C** (Scheme 2).

In conclusion, the formation of self-assemblies **3a** and **3b** reveals two unexpected features. First, Ag^{I} ions are able to force face-to-face π stacking of aromatic derivatives upon coordination into supramolecular metalloparacyclophanes in spite of the repulsive interactions between the closed-shell π clouds.⁹ Second, it demonstrates that metal dimers having no programmed shape but adaptive coordination behavior can be used as molecular clips in coordination-driven self-assembly processes. In other words, the design of bimetallic clips according to the directional-bonding approach having coordination sites available to the incoming linkers arranged at the appropriate angle to form a target supramolecular assembly is not an absolute requirement. This novel approach, based on predictable rearrangement of the coordination spheres of a metal upon binding to organic linkers, can likely be extended to other metals and to weakly coordinating linkers.

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(10) Note that a similar structure is obtained with BF_4^- .