

# Synthesis, structural characterization, and luminescence properties of multinuclear silver complexes of pyrazole-functionalized NHC ligands containing Ag–Ag and Ag– $\pi$ interactions

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## Abstract

A few pyrazole-functionalized imidazolium salts have been prepared via the reactions of *N*-alkylimidazole and 3,5-bis(chloromethyl)pyrazole or 2-(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)-6-(5-methyl-1-vinyl-1H-pyrazol-3-yl) pyridine. Reactions of these imidazolium salts with Ag<sub>2</sub>O led to the successful isolation of tetranuclear [Ag<sub>4</sub>(L)<sub>2</sub>](X)<sub>2</sub> (X = PF<sub>6</sub><sup>−</sup> or BF<sub>4</sub><sup>−</sup>; H<sub>3</sub>L1 = 3,5-bis(*N*-benzylimidazoliumyl)pyrazole, H<sub>3</sub>L2 = 3,5-bis(*N*-(2,4,6-trimethylphenyl)imidazoliumyl)pyrazole, H<sub>3</sub>L3 = imidazolium cyclophane from the condensation of 3,5-bis(chloromethyl)pyrazole and 1,4-bis(imidazolyl)butane) and trinuclear silver clusters supported by *N*-heterocyclic carbene ligands in high yields. The molecular structures of these silver complexes have been confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, ESI-MS spectroscopy, and X-ray diffraction analyses. The tetranuclear complexes [Ag<sub>4</sub>(L1)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**1**) and [Ag<sub>4</sub>(L2)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**2**) consist of a pair of Ag–Ag contacts (ca. 3.11 Å) showing weak silver–silver interaction. [Ag<sub>4</sub>(L3)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**3**) has a square planar Ag<sub>4</sub> core sandwiched by two NHC cyclophanes with Ag–Ag distances of 3.22 Å. All the silver atoms in **1–3** are located in the same linear C–Ag–N coordination environment. [Ag<sub>3</sub>(L4)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> (HL4 = 2-(1-(2-methylimidazoliumylethyl)-5-methyl-1H-pyrazol-3-yl)-6-(5-methyl-1-vinyl-1H-pyrazol-3-yl) pyridine) (**4**) is a trinuclear complex in which the three silver are bridged by two L4 molecules, and the Ag<sub>3</sub> units form one-dimensional chain via Ag– $\pi$  interaction. The luminescence properties of the imidazolium salts and their silver complexes were also studied. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** *N*-heterocyclic carbene; Silver; Cluster; Metal–metal interaction

## 1. Introduction

The organometallic and coordination chemistry of *N*-heterocyclic carbene (NHC) ligands has been receiving great attention in recent years. A number of reports have proved that NHC ligand is a valuable alternative to tertiary phosphines and form intriguingly stable bonds with various metals from main group to transition metals [1,2]. The unique electronic properties such as high  $\sigma$ -basicity and low  $\pi$ -acidity make the transition metal complexes of

NHCs enhanced catalytic activities in various organic transformation processes. Furthermore, the steric and electronic properties can be easily tuned to optimize the selectivity and activity of metal–NHC complexes by variation of the *N*-substituents. So far many metal–NHC complexes have been reported including the NHCs with simple *N*-alkyl or aryl substituents [3] and *N*-functionalized NHCs bearing various functional groups such as pyridyl [4], phosphinyl [5], and pyrazolyl [6]. Among these metal–NHC complexes, the family of silver–NHC complexes have been receiving continuous attention [7] since they are often used as convenient carbene transfer reagents to make other metal–NHC complexes. The chemistry of silver–NHC complexes has been recently reviewed [8]. Although a large

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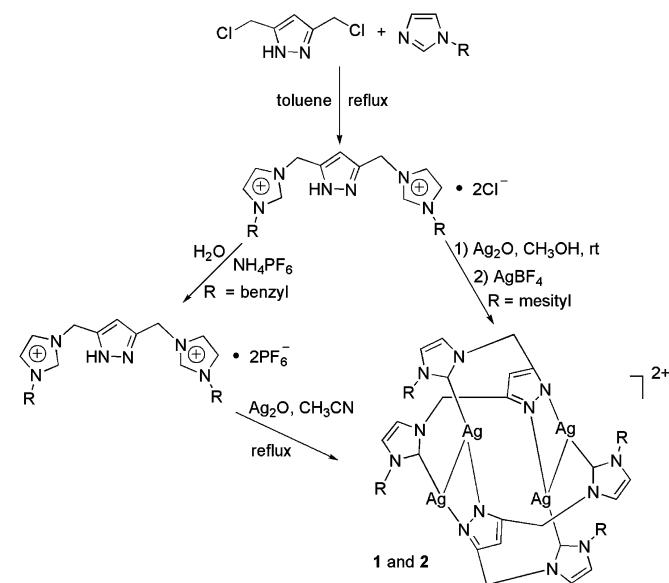
number of silver–NHC complexes have been known, so far only a few NHC-stabilized silver clusters have been reported [9].

We have been interested in the construction of metal aggregates consisting of short M–M (M = Pt, Tl, Ag, Pd) interactions [10] since these materials often show very interesting luminescence properties, and are potentially useful precursors for optical sensors or catalysts for some organic transformations. Recently our interest in this area has been focused on the design and synthesis of functionalized N-heterocyclic carbene ligands and their metal complexes [11]. Because of the strong  $\sigma$ -donating abilities of the NHC ligands, the heteroaryl-functionalized bis(NHC) ligands have shown to be suitable candidate to construct new organometallic clusters. Here in this paper we report the preparation, structural characterization, and emissive properties of a few new multidentate NHC precursors (imidazolium salts) and their corresponding silver complexes of the multidentate NHC ligands.

## 2. Results and discussion

### 2.1. Synthesis of the ligand precursors and the complexes

The direct reaction of 3,5-bis(chloromethyl)pyrazole with *N*-benzylimidazole or *N*-mesitylimidazole in toluene according to our previously reported procedure [11a] afforded the imidazolium chlorides  $[\text{H}_3\text{L1}]\text{Cl}_2$  and  $[\text{H}_3\text{L2}]\text{Cl}_2$  in high yields. Subsequent addition of  $\text{NH}_4\text{PF}_6$  to the aqueous solutions yielded their corresponding hexafluorophosphates via anion exchange reaction (Scheme 1).  $^1\text{H}$  NMR spectra of  $[\text{H}_3\text{L1}]\text{Cl}_2$  and  $[\text{H}_3\text{L2}]\text{Cl}_2$  shows downfield resonance signals at around 13.8 and 9.6 ppm, characteristic of the acidic NH and CH protons.



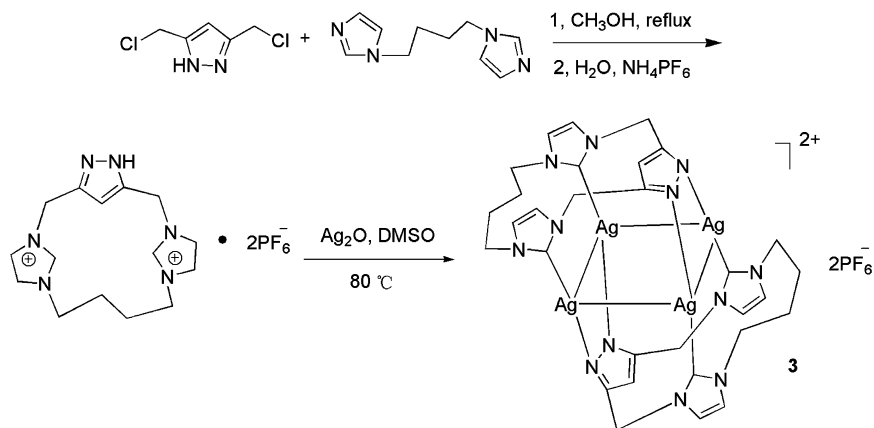
Scheme 1.

The synthesis of the imidazolium cyclophane  $[\text{H}_3\text{L3}]^{2+}$  is outlined in Scheme 2. The imidazolium cyclophane  $[\text{H}_3\text{L3}](\text{Cl})_2$  could be obtained from the reaction of 3,5-bis(chloromethyl)pyrazole and 1,4-bis(imidazolyl)butane in  $\text{CH}_3\text{OH}$ . The key to success is to maintain the reaction proceed at very dilute concentrations of both reactants. The dilute solution was allowed to mix very slowly, and the reactions in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{COCH}_3$ , or Toluene, etc. failed. Subsequent anion exchange with an excess of  $\text{NH}_4\text{PF}_6$  in water gave the final product  $[\text{H}_3\text{L3}](\text{PF}_6)_2$  (Scheme 2). The cyclophane was isolated as colorless crystals in 29% yield after purification.  $^1\text{H}$  NMR spectrum in  $\text{DMSO}-d_6$  shows a peak at 9.02 ppm assigned to the acidic CH proton, however, the NH resonance of the pyrazole was not observed.

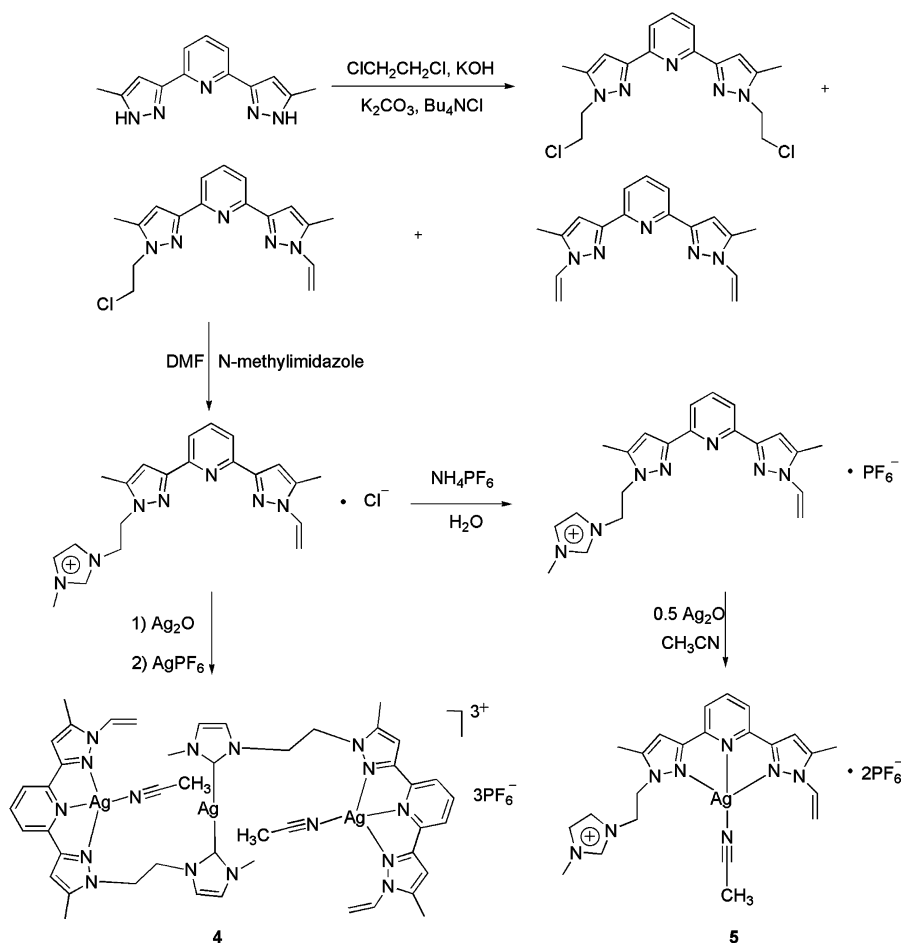
Attempts to prepare 2,6-bis(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)pyridine from the alkylation reaction of 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine with 1,2-dichloroethane under basic condition was made (Scheme 3). Two other products, 2-(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)-6-(5-methyl-1-vinyl-1H-pyrazol-3-yl)pyridine and 2,6-bis(5-methyl-1-vinyl-1H-pyrazol-3-yl)pyridine were also isolated due to further deprotonation of the resulted 2,6-bis(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)pyridine. The three compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.  $^1\text{H}$  NMR spectra of the two vinyl derivatives exhibit a doublet of doublet at ca. 7.3 ppm due to olefinic proton adjacent to nitrogen atom and two doublet at 5.7 and 4.9 ppm assignable to terminal olefinic protons.

The condensation reaction of 2-(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)-6-(5-methyl-1-vinyl-1H-pyrazol-3-yl)pyridine with excess of *N*-methylimidazole afforded the imidazolium salt  $[\text{HL4}]\text{Cl}$  as a pale yellow hygroscopic solid in excellent yield. Subsequent anion exchange with an excess of  $\text{NH}_4\text{PF}_6$  in water gave  $[\text{HL4}](\text{PF}_6)$  as a white powder (Scheme 3).  $^1\text{H}$  NMR appears a singlet at 8.95 ppm due to the acidic imidazolium CH proton. The chemical shifts of the olefinic protons are nearly the same as the starting compound.

The procedure developed by Lin et al. [12] is most popularly employed for the preparation of silver–NHC complexes [8]. As shown in Schemes 1–3, the direct reaction of the pyrazole-functionalized imidazolium salts and  $\text{Ag}_2\text{O}$  yielded tetranuclear and trinuclear complexes 1–4. Complex 1 and 3 were obtained from the reactions of  $\text{Ag}_2\text{O}$  with  $[\text{H}_3\text{L1}](\text{PF}_6)_2$  and  $[\text{H}_3\text{L3}](\text{PF}_6)_2$ , respectively, whereas 2 could be yielded by the reaction of  $[\text{H}_3\text{L2}](\text{Cl})_2$  and  $\text{Ag}_2\text{O}$  after subsequent anion exchange in methanol.  $[\text{HL4}]\text{Cl}$  reacted with  $\text{Ag}_2\text{O}$  in the presence of 1 equiv. of  $\text{AgPF}_6$  yielded a trinuclear complex 4. In contrast,  $[\text{HL4}](\text{PF}_6)$  and a half equivalent  $\text{Ag}_2\text{O}$  led to the isolation of the mononuclear complex 5. These complexes have been characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.  $^{13}\text{C}$  NMR spectra of 2 and 3 exhibit singlets at 180.5 and 184.4 ppm, respectively, characteristic of the resonance signals of carbene carbons. These chemical shifts are well consistent with those of our previously reported silver–NHC clusters [11].



Scheme 2.



Scheme 3.

However, in the <sup>13</sup>C spectra of **1** and **4**, the carbene resonance signals were not observed. The absence of the carbene carbon resonance is not unusual, and this phenomenon has been reported for a few silver–carbene complexes [8a]. Actually, many Ag–NHC complexes exhibit broad singlets or no carbene signal ascribed to the rapid carbene exchange process in solution.

## 2.2. ESI-MS spectra

Electrospray ionization mass spectrometry (ESI-MS) was used to identify the silver complexes. ESI-MS spectrum of **1** in acetonitrile shows the most intense peak at 622.45 amu corresponding to [Ag<sub>2</sub>(L1)-H]<sup>+</sup> (calc. 622.23 amu), whereas the peaks at 1390.67 amu can be

assignable to  $[\text{Ag}_4(\text{L1})_2(\text{PF}_6)\text{-H}]^+$  (calc. 1390.42 amu). Quite similar to **1**, ESI-MS spectrum of **2** displays two peaks at 678.74 and 1444.71 amu due to  $[\text{Ag}(\text{L2})\text{-H}]^+$  (calc. 678.33 amu) and  $[\text{Ag}_4(\text{L2})_2(\text{BF}_4)]^+$  (1445.4 amu). For **3** the peaks at 497.07 and 1138.49 amu were observed, arising from the fragments of  $[\text{Ag}(\text{L3})]^+$  (calc. 497.07 amu) and  $[\text{Ag}_4(\text{L3})_2(\text{PF}_6)\text{-H}]^+$  (1138.11 amu). The spectrum of the trinuclear silver complex **4** shows peaks of  $[\text{Ag}(\text{L4})]^+$ ,  $[\text{Ag}(\text{L4})(\text{PF}_6)]^+$ , and  $[\text{Ag}_2(\text{L4})_2(\text{PF}_6)]^+$  at 480.21, 625.67, and 1146.86 amu, respectively. The peak owing to  $\text{Ag}_3$  moiety was not observed.

### 2.3. Structural description

The molecular structure of  $[\text{Ag}_4(\text{L1})_2](\text{PF}_6)_2$  (**1**) is illustrated in Fig. 1. The asymmetric unit of the structure contains a half of the molecule. It shows that the four silver ions are bridged by two 3,5-bis((*N*-benzylimidazolide-nyl)methyl)pyrazolate ligands. The silver ions are each bicoordinated by one pyrazolate nitrogen atom and one carbenic carbon atom. Coordination geometries about each silver atom are basically linear with C–Ag–N angles of 175.6(3) and 171.5(3)° for Ag(1) and Ag(2), respectively. The average Ag–C distance and Ag–N distance are 2.082 Å and 2.109 Å, similar to those of silver complexes having the same C–Ag–N coordination environment. The other bond parameters are quite similar to those observed for the analogous silver–NHC–pyrazolate complex [11a]. The two five-membered rings, pyrazolate and imidazolidene, coordinated to the same silver atom are nearly perpendicular to each other with an average dihedral angle of 84.5°. The

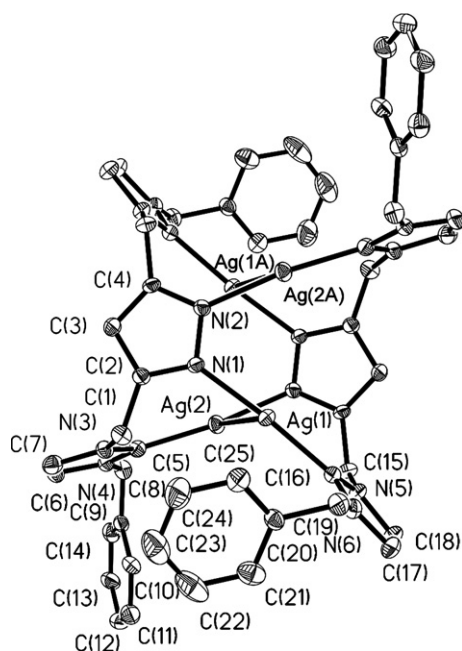


Fig. 1. Molecular structure of the cation of **1**. Selected bond distances (Å) and angles (°): Ag(1)–Ag(2) 3.113(1), Ag(1)–C(16) 2.083(8), Ag(1)–N(1) 2.100(6), Ag(2)–C(5) 2.082(8), Ag(2)–N(2A)#1 2.119(6), C(16)–Ag(1)–N(1) 175.6(3), C(5)–Ag(2)–N(2A)#1 171.5(3). Symmetry transformations used to generate equivalent atoms: #1  $-x + 1/2, -y + 3/2, -z + 1$ .

four silver atoms form two Ag–Ag bonds (Ag(1)–Ag(2) and Ag(1A)–Ag(2A), symmetry code: A #1  $-x + 1/2, -y + 3/2, -z + 1$ ) of distances at 3.113(1) Å, whereas the Ag(1)···Ag(1A) distance is 3.50 Å, and the latter is too long to be viewed as bonding. The relatively long Ag–Ag distances illustrate that the Ag–Ag interaction is weak and the framework is mainly stabilized by the multidentate NHC ligands other than argentophilic attraction.

Compound **2** is also a tetranuclear silver complex in which the four silver atoms are bonded together by two NHC ligands displaying U-shaped conformation. The molecular structure of complex **2** is very similar to complex **1**, which is shown in Fig. 2. The silver–silver distances are found to be 3.116(2) Å, comparable to those of **1**. Each of the four silver atoms is bonded by a carbenic carbon atom and a pyrazolate nitrogen atom in a typical linear coordination environment. The Ag–C and Ag–N distances in **2** do not show any significant differences compared to **1**.

The details of the molecular structure of **3** in the solid state were also established by an X-ray diffraction study. The molecular structure of **3** is depicted in Fig. 3. The complex is tetranuclear. The asymmetric unit is composed of one fourth of the molecule with one silver atom and a half L3 ligand. The compound features a square planar  $\text{Ag}_4$  core, and the  $\text{Ag}_4$  ring is sandwiched by two cyclophane ligands. Both L3 ligands link four different silver atoms by using two pyrazolate nitrogen and two NHC carbon atoms acting as monoanionic tetradentate ligands. The

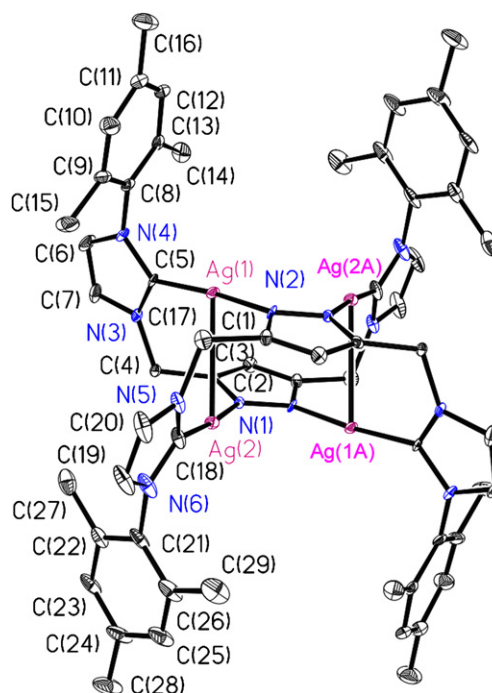


Fig. 2. Molecular structure of the cation of **2**. Selected bond distances (Å) and angles (°): Ag(1)–Ag(2) 3.116(2), Ag(1)–C(5) 2.078(1), Ag(1)–N(2) 2.091(10), Ag(2)–C(18) 2.065(17), Ag(2)–N(1) 2.111(12), C(5)–Ag(1)–N(2) 174.9(5), C(5)–Ag(1)–Ag(2) 104.3(4), N(2)–Ag(1)–Ag(2) 71.4(3), C(18)–Ag(2)–N(1) 175.4(6), C(18)–Ag(2)–Ag(1) 104.9(6), N(1)–Ag(2)–Ag(1) 71.5(3).

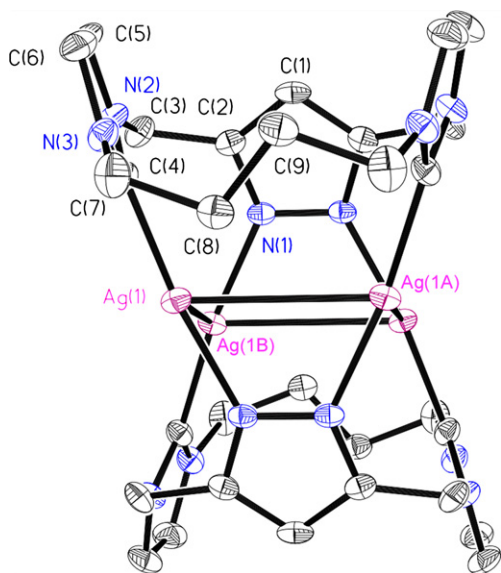


Fig. 3. Molecular structure of the cation of **3**. Selected bond distances (Å) and angles (°): Ag(1)–Ag(1A)#1 3.223(1), Ag(1)–Ag(1B)#2 3.232(1), Ag(1)–C(4) 2.068(9), Ag(1)–N(1A)#1 2.102(6), C(4)–Ag(1)–N(1A)#1 172.8(3), Ag(1A)#1–Ag(1)–Ag(1B)#2 90.0. Symmetry transformations used to generate equivalent atoms: #1  $-x + 1, y, -z + 1$ ; #2  $x, -y + 1, z$ .

four silver atoms are crystallographically equal and each is coordinated by a NHC and a pyrazolate nitrogen atom in nearly linear coordination geometry with C–Ag–C angles of 172.8(3)°. The silver–carbene distances are 2.068(9) Å, consistent with the known values of other silver–NHC complexes. The four silver atoms form a square-planar ring because of argentophilic attraction and the functionality of the pyrazolate-linked NHC ligands with relatively long Ag–Ag contacts at 3.223(1) Å, shorter than the sum of van der Waals radii (3.4 Å). These Ag–Ag bonds are significantly longer than those found in complexes **1** and **2**. The coplanarity of the silver atoms is evidenced by the sum of each two adjacent Ag–Ag–Ag angles equal to 180°. Actually, each Ag–Ag–Ag angle is perfectly 90.0°. The dihedral angles between pyrazolate rings and NHC rings across each silver atom are 79.2°, illustrating the two rings coordinated to the same metal are nearly perpendicular.

Although a large number of Ag–NHC complexes have been structurally characterized, only a few trinuclear [9a,9b] and tetranuclear [9c,9d] silver clusters stabilized by NHC ligands were reported by Youngs and Catalano's groups, respectively. For all these reported clusters the silver atoms are all bonded to two NHCs with an average Ag–C bond distance of 2.259(9) Å. The silver–carbene bond distances of the silver clusters seem to be longer than other Ag–NHC complexes [7,8]. However, the Ag–C bond distances of **3** together with **1** and **2** are considerably shorter than those of the previously reported silver clusters [9], but are consistent with the majority of Ag–NHC complexes [7]. The Ag–N distances of **3** are 2.102(6) Å are well consistent with those of **1** and **2**, but are significantly shorter than those in our previously reported Pt–Ag coordination polymers [10b]. In contrast to the shorter Ag–C

bonds of **1–3**, the Ag–Ag distances of **1–3** are remarkably longer than those of the known teranuclear clusters (2.768(1)–2.971(1) Å) and trinuclear clusters (2.725(1)–2.851(1) Å) containing NHC ligands.

So far, most of the structurally characterized silver NHC complexes can be classified into categories of C<sub>2</sub>–Ag, C–Ag–X<sub>n</sub> (X = halides,  $n = 1–3$ ), and C–Ag–Ag, respectively [8]. The C–Ag–Y (Y = coordinating anions other than halides) type complexes are relatively rare, only few mono-N-heterocyclic carbene complexes have been reported with silver linearly bound to a carbene moiety and aryloxy anion [13]. Thus the complexes **1–3** represent new structural motif of silver–NHC complexes.

X-ray diffraction analysis showed that complex **4** is a trinuclear complex, and its structure is shown in Fig. 4. The asymmetric unit contains only a half of the molecule with an inversion center at Ag(1) atom. Two neighboring silver atoms are bridged by one ligand molecule in tetradentate fashion. Ag(1) is bicoordinated by two NHC carbon atoms, and the dihedral angle between the two imidazolidene rings is 20.21°. The Ag–C bond distances of the Ag(NHC)<sub>2</sub> are 2.093(7) Å, similar to those of the C–Ag–N moieties in complexes **1–3** presented above. Ag(2) is coordinated by an acetonitrile molecule, two pyrazole rings, and one pyridine in a disordered square geometry. The Ag–N<sub>acetonitrile</sub> bond distance of 2.193(8) Å is approximately comparable to the normal Ag–N bonds, whereas the other three Ag–N bonds in the range of 2.302(6)–2.594(6) Å are significantly longer. The Ag–Ag separation is 4.84 Å excluding any Ag–Ag interaction.

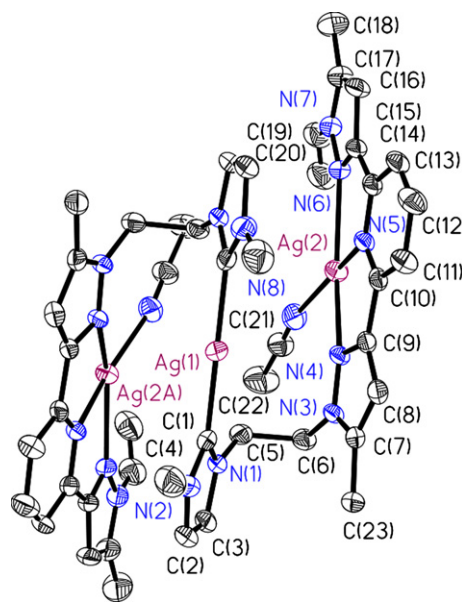


Fig. 4. Molecular structure of the cation of **4**. Selected bond distances (Å) and angles (°): Ag(1)–C(1) 2.093(7), Ag(2)–N(8) 2.193(8), Ag(2)–N(5) 2.302(6), Ag(2)–N(6) 2.450(6), Ag(2)–N(4) 2.594(6), C(1A)#1–Ag(1)–C(1) 177.8(5), N(8)–Ag(2)–N(5) 159.0(3), N(8)–Ag(2)–N(6) 124.3(3), N(5)–Ag(2)–N(6) 70.2(2), N(8)–Ag(2)–N(4) 94.6(2), N(5)–Ag(2)–N(4) 67.6(2), N(6)–Ag(2)–N(4) 137.0(2). Symmetry transformations used to generate equivalent atoms: #1  $-x + 1, y, -z + 1$ ; #2  $x, -y + 1, z$ .

Interestingly, the trinuclear complex stacks via intermolecular Ag– $\pi$  interaction forming infinite one-dimensional chain, shown in Fig. 5. The  $[\text{Ag}_3(\text{L4})_2]$  moieties are doubly linked by Ag–pyrazole interaction. The nearly planar  $\text{Ag}(2)$  coordination plane allows the close approach of  $[\text{Ag}_3(\text{L4})_2]$  units. The nearest Ag– $\text{C}_{\text{pyrazole}}$  distance is 2.928 Å, significantly shorter than those of the Ag–C distances being 2.965 and 3.040 Å between Ag and adjacent benzene rings in silver-di-2-pyridylamine complexes [14]. The silver cation is known to form comparatively weak interactions with aromatic molecules. The average distance for Ag–arene interactions are typically in the range 2.4–2.9 Å [15]. The present value is thus at the upper borderline of the range normally considered as bonding. The weak Ag– $\pi$  interaction also plays some role in determining the overall shape of the resulting structures.

Complex **5** is a mononuclear complex with the central silver atom surrounded by four nitrogen atoms from one

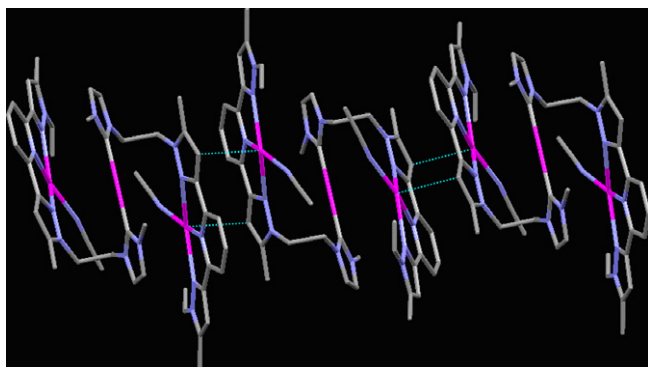


Fig. 5. One-dimensional chain showing the Ag– $\pi$  interaction.

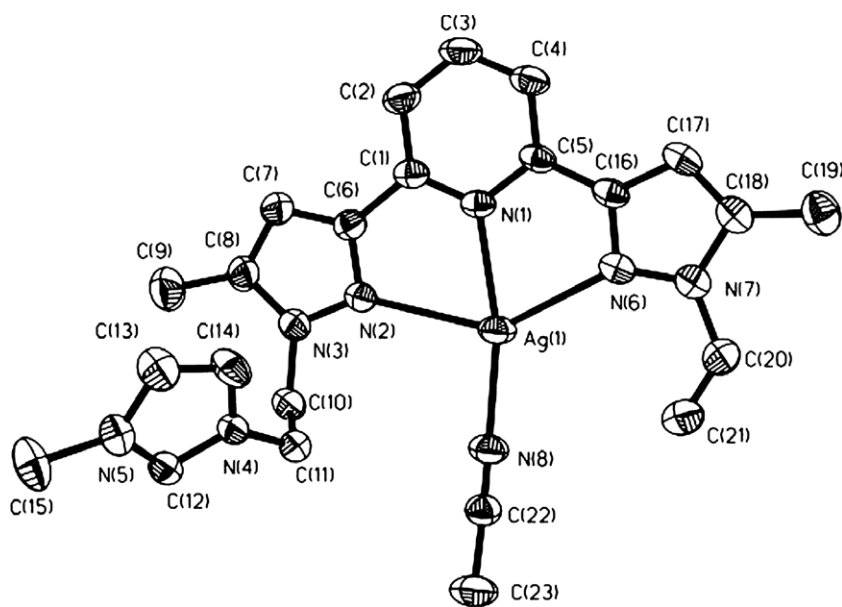


Fig. 6. Molecular structure of  $[\text{Ag}(\text{HL4})](\text{PF}_6)_2$  (**5**). Selected bond distances (Å) and angles (°): Ag(1)–N(8) 2.169(5), Ag(1)–N(1) 2.299(4), Ag(1)–N(6) 2.459(4), Ag(1)–N(2) 2.587(4), N(8)–Ag(1)–N(1) 167.21(17), N(8)–Ag(1)–N(6) 120.97(17), N(1)–Ag(1)–N(6) 70.86(15), N(8)–Ag(1)–N(2) 99.01(16), N(1)–Ag(1)–N(2) 68.78(14), N(6)–Ag(1)–N(2) 139.51(13).

$[\text{HL4}]^+$  and one acetonitrile molecule in an square-planar environment (see Fig. 6). Because of the Ag– $\pi$  interaction, the compound exists as a dimer in its solid state (Fig. 7). The Ag–C distances being 3.412 Å are remarkably longer than those found in compound **4**.

#### 2.4. Luminescence properties

The imidazolium salts  $[\text{H}_3\text{L1}](\text{PF}_6)_2$ ,  $[\text{HL4}](\text{PF}_6)$ , and their corresponding silver complexes **1** and **4** are emissive in their solid states. The emission spectra are shown in Figs. 8 and 9, respectively. In the emission spectrum of  $[\text{H}_3\text{L1}](\text{PF}_6)_2$ , a single broad band at 401 nm was observed when excited at 363 nm. The tetranuclear complex **1** shows two broad emission bands centered at 362 and 463 nm upon excitation at 318 nm. The emission spectrum of  $[\text{HL4}](\text{PF}_6)$  exhibits 371 and 461 nm upon excitation at 345 nm, whereas its silver complex emits a broad band at 442 nm upon excitation at 368 nm. The low-energy emission bands for both **1** and **4** are similar to those of our previously reported silver complexes having orthogonal  $\text{Ag}_4$  cores [11b]. Similar emission properties of  $[\text{Ag}_3(\text{CH}_3\text{im}(\text{CH}_2\text{py}))_3(\text{NCCH}_3)_2](\text{BF}_4)_3$  have been previously reported by Catalano and Moore [9d], which also shows a very broad and intense emission band centered at 445 nm. The intense emission of the Ag(I)–NHC complexes can be originated from intraligand excited states or metal-centered excited states. We are not able to assign the nature of the excited states due to the complexity brought by metallophilic attractions existed in the complexes. Although a great number of transition metal complexes of Ag–NHC have been structurally characterized in the recent decade [8], the solid state photoluminescent properties of these

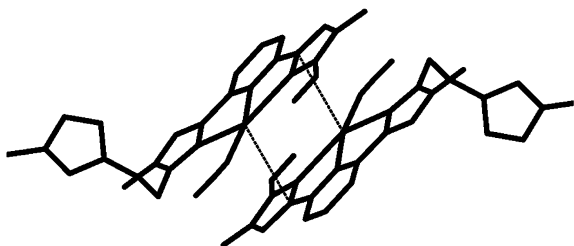


Fig. 7. The dimerized structure of **5** showing the Ag- $\pi$  interaction.

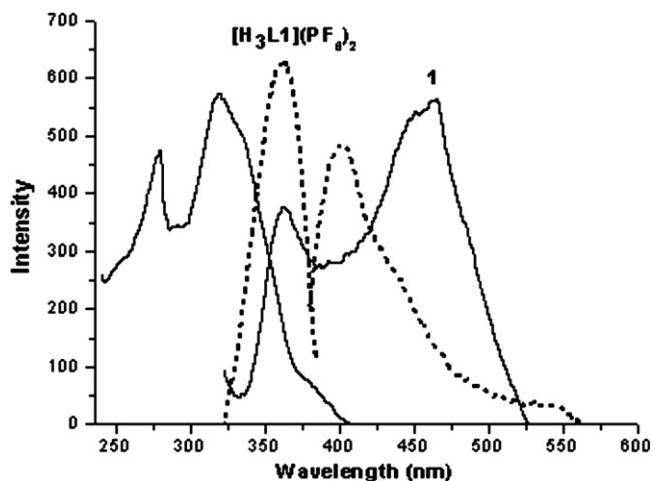


Fig. 8. The solid-state emission (right) and excitation (left) spectra of  $[H_3L1](PF_6)_2$  (dashed) and complex **1** (solid).

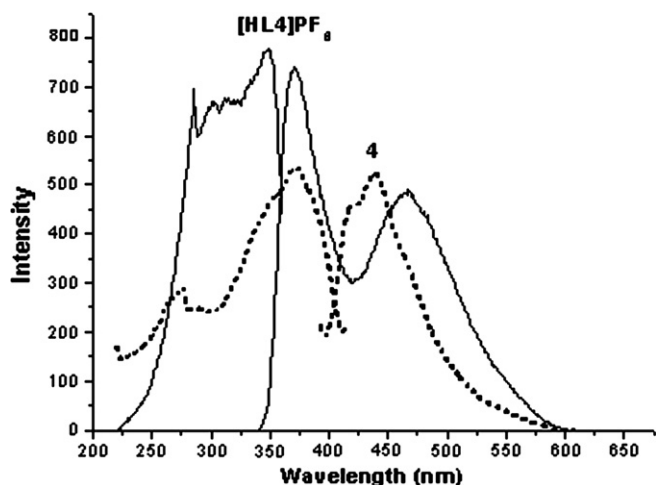


Fig. 9. The solid-state emission (right) and excitation (left) spectra of  $[HL4](PF_6)$  (dashed) and complex **4** (solid).

materials have not been well explored and more work is needed to elucidate the nature of the emission.

In summary, we have successfully prepared a few pyrazole linked bis(imidazolium) salts which act as multidentate mixed N,C-ligands upon deprotonation. The corresponding tetranuclear and trinuclear silver-NHC clusters were obtained and structurally characterized. Variation of the

N-alkyl groups lead to the silver clusters **1** and **4** show interesting photoluminescent properties originated either from intraligand or metal-based excitation states. However, the nature of emissive mechanism has not been clarified.

### 3. Experimental section

#### 3.1. General procedures

All the chemicals were obtained from commercial suppliers and used without further purification. 3,5-Bis(chloromethyl)pyrazole [11a], *N*-benzylimidazole [16], *N*-mesitylimidazole [17], 1,4-bis(imidazolyl)butane [18], and 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine [19] were prepared according to the known procedures.  $^1H$  and  $^{13}C$  NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm downfield to TMS at  $\delta = 0$  ppm and coupling constants ( $J$ ) are expressed in Hz. The photoluminescence study was carried out on powdered samples in the solid state at room temperature using a Hitachi 850 spectrometer. Mass spectral data were acquired using a Waters Micromass ZQ mass spectrometer (+ mode, ESI source).

#### 3.2. Synthesis of ligands and complexes

##### 3.2.1. Synthesis of $[H_3L1](PF_6)_2$

A solution of 3,5-bis(chloromethyl)pyrazole (0.33 g, 2 mmol) and *N*-benzylimidazole (0.66 g, 4.2 mmol) in 10 mL of toluene was refluxed for 2 days. The solvent was removed and the residue was washed with 10 mL of  $Et_2O$ . Then the pale yellow residue was dissolved into 5 mL of water. Addition of  $NH_4PF_6$  (1.63 g, 10 mmol) to the aqueous solution led to a white precipitation, which was washed by water and ethanol. Yield: 0.96 g (69%). Anal. Calc. for  $C_{25}H_{26}F_{12}N_6P_2$ : C, 42.87; H, 3.74; N, 12.00. Found: C, 42.58; H, 3.91; N, 12.17%.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ): 13.30 (s, 1H, NH), 9.35, 9.30 (both s, each 1H, NCHN), 7.82, 7.75 (both s, each 2H,  $CH_{imid}$ ), 7.49–7.38 (m, 10H,  $C_6H_5$ ), 6.48 (s, 1H,  $CH_{pyrazole}$ ), 5.44 (br s, 8H,  $CH_2$ ).  $^{13}C$   $\{^1H\}$  NMR (100.6 MHz,  $DMSO-d_6$ ): 162.7, 146.4, 137.8, 136.7, 135.1, 129.4, 129.2, 128.7, 128.6, 123.5, 123.3, 123.2, 123.0, 105.6, 46.5, 43.5.

##### 3.2.2. Synthesis of $[H_3L2](Cl)_2$

A solution of 3,5-bis(chloromethyl)pyrazole (0.50 g, 3 mmol) and *N*-mesitylimidazole (1.17 g, 6.3 mmol) in 15 mL of toluene was refluxed for 2 days. The solvent was removed and the residue was washed with 15 mL of  $Et_2O$ . Then the residue was dissolved into 10 mL of ethanol. Addition of 50 mL of diethyl ether afforded a colorless solid. Yield: 1.32 g (81.9%).  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ): 14.2 (s, 1H, NH), 9.92, 9.74 (both br. s, each 1H, NCHN), 8.21, 8.09, 8.00 (all br. total 4H,  $NCHCN$ ), 7.14 (s, 4H,  $CH_{mesityl}$ ), 6.61 (s, 1H,  $C3N2H$ ), 5.72, 5.58

(both s, each 2H, CH<sub>2</sub>), 2.33 (s, 6H, CH<sub>3</sub>), 2.01 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): 140.6, 138.3, 134.6, 131.5, 129.6, 129.3, 124.3, 105.3, 56.3, 20.9, 17.3. The solid is highly hygroscopic and thus no satisfactory elemental analysis was obtained.

### 3.2.3. Synthesis of [H<sub>3</sub>L3](PF<sub>6</sub>)<sub>2</sub>

To a flask charged with 200 mL methanol was dropped gradually and simultaneously the solution of 3,5-bis(chloromethyl)pyrazole (0.33 g, 2 mmol) in 200 mL methanol and the solution of 1,4-bis(imidazolyl)butane (0.38 g, 2 mmol) in 200 mL of methanol within 36 h at reflux. The mixture was allowed to reaction for a further 36 h. The mixture was filtered and condensed to ca. 10 mL. Addition of 30 mL of diethyl ether to the filtrate, and the resulted precipitate was dissolved in 20 mL of water and filtered. Addition of NH<sub>4</sub>PF<sub>6</sub> in 5 mL water (0.82 g, 5 mmol) to the aqueous solution led to a white precipitation, which was washed by water and dried. Yield: 0.18 g (29%). Anal. Calc. for C<sub>15</sub>H<sub>20</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>: C, 31.37; H, 3.51; N, 14.63. Found: C, 31.12; H, 3.67; N, 14.51%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 9.02 (s, 2H, NCHN), 7.72, 7.65 (both s, each 2H, NCH=CHN), 7.21, 7.08, 6.95 (all s, total 5H, 2CH<sub>2</sub> + CH<sub>pyrazole</sub>), 4.20 (s, 4H, CH<sub>2</sub>), 1.77 (s, 4H, CH<sub>2</sub>).

### 3.2.4. Reaction of 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine with 1,2-dichloroethane

A mixture of 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine (7.18 g, 30 mmol), KOH (6.72 g, 120 mmol), K<sub>2</sub>CO<sub>3</sub> (6.56 g, 120 mmol), and Bu<sub>4</sub>NCl (0.6 g) in 300 mL of 1,2-dichloroethane was heated at 60 °C for 4 days. The residue was washed with water and the organic phase was dried. The residue was dissolved in a small amount of ethyl acetate and passed through a silica column eluted with EA:PE = 1:5. 2,6-Bis(5-methyl-1-vinyl-1H-pyrazol-3-yl)pyridine, 2,6-bis(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)pyridine, and 2-(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)-6-(5-methyl-1-vinyl-1H-pyrazol-3-yl)pyridine were isolated, respectively.

2,6-Bis(5-methyl-1-vinyl-1H-pyrazol-3-yl)pyridine. Yield: 0.72 g (8.3%). Anal. Calc. for C<sub>17</sub>H<sub>17</sub>N<sub>5</sub>: C, 70.08; H, 5.88; N, 24.04. Found: C, 69.89; H, 5.95; N, 23.83%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.89–7.94 (m, 3H, C<sub>5</sub>H<sub>3</sub>N), 7.27 (dd, 2H, *J* = 6.3, 14.2 Hz, CH<sub>2</sub>=CHN), 6.86 (s, 2H, CH<sub>pyrazole</sub>), 5.70 (d, 2H, *J* = 14.2 Hz, *trans*-CH<sub>2</sub>=CHN), 4.93 (d, 2H, *J* = 6.3 Hz, *cis*-CH<sub>2</sub>=CHN), 2.41 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, CDCl<sub>3</sub>): 151.75, 151.31, 140.83, 137.91, 130.57, 118.90, 105.75, 101.18, 10.96.

2,6-Bis(1-(2-chloroethyl)-5-methyl-1H-pyrazol-3-yl)pyridine. Yield: 1.82 g (16.7%). Anal. Calc. for C<sub>17</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>5</sub>: C, 56.05; H, 5.26; N, 19.23. Found: C, 56.10; H, 5.34; N, 18.97%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.81–7.76 (m, 3H, C<sub>5</sub>H<sub>3</sub>N), 6.71 (s, 2H, CH<sub>pyrazole</sub>), 4.44 (t, 4H, *J* = 6.0 Hz, CH<sub>2</sub>CH<sub>2</sub>), 4.04 (t, *J* = 6.0 Hz, CH<sub>2</sub>CH<sub>2</sub>), 2.37 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, CDCl<sub>3</sub>): 151.8, 150.7, 141.2, 137.6, 118.0, 104.2, 50.2, 44.1, 11.2.

2-(1-(2-Chloroethyl)-5-methyl-1H-pyrazol-3-yl)-6-(5-methyl-1-vinyl-1H-pyrazol-3-yl)pyridine: Yield: 2.15 g (21.9%). Anal. Calc. for C<sub>17</sub>H<sub>18</sub>ClN<sub>5</sub>: C, 62.29; H, 5.53; N, 21.36. Found: C, 62.24; H, 5.62; N, 21.17%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.88–7.83 (m, 3H, C<sub>5</sub>H<sub>3</sub>N), 7.30 (dd, 1H, *J* = 15.6, 7.2 Hz, CH<sub>2</sub>=CHN), 6.84, 6.74 (both s, each H, CH<sub>pyrazole</sub>), 5.70 (d, 1H, *J* = 15.6 Hz, *trans*-CH<sub>2</sub>=CHN), 4.92 (d, 1H, *J* = 7.2 Hz, *cis*-CH<sub>2</sub>=CHN), 4.44 (t, 2H, *J* = 6.0 Hz, CH<sub>2</sub>CH<sub>2</sub>), 4.04 (t, 2H, *J* = 6.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.40, 2.37 (both s, each 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, CDCl<sub>3</sub>): 151.9, 151.8, 151.2, 150.6, 141.2, 140.8, 137.7, 130.6, 118.5, 118.4, 105.7, 104.2, 101.1, 50.2, 44.1, 11.1, 10.9.

### 3.2.5. Synthesis of [HL4]Cl

A solution of vinylchloroethyl (0.66 g, 2.0 mmol) and *N*-methylimidazole (0.65 g, 8.0 mmol) in 5 mL of dimethylformamide heated at 120 °C for 36 h and filtered. Addition of 30 mL of diethyl ether to the resulted mixture afforded oily precipitate. It was washed with acetone and diethyl ether. Yield: 0.74 g (90%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 9.06 (s, 1H, NCHN), 7.89–7.71 (m, 3H, Py), 7.69, 7.64 (s, each 1H, NCHCHN) 7.27 (dd, 1H, *J* = 8.4, 14.8 Hz, CH<sub>2</sub>=CHN), 6.81, 6.72 (both s, each 1H, CH<sub>pyrazole</sub>), 5.69 (d, 1H, *J* = 14.8 Hz, *trans*-CH<sub>2</sub>=CHN), 4.92 (d, 1H, *J* = 8.4 Hz, *cis*-CH<sub>2</sub>=CHN), 4.68 (t, 2H, *J* = 6.8 Hz, CH<sub>2</sub>CH<sub>2</sub>), 4.58 (t, *J* = 6.8 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.80 (s, 3H, NCH<sub>3</sub>), 2.40, 2.25 (both s, each 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): 151.8, 151.7, 151.2, 150.7, 141.0, 140.8, 137.8, 137.5, 130.6, 123.9, 123.1, 118.5, 105.7, 104.6, 101.2, 48.8, 48.3, 36.1, 11.0, 10.8. The solid is highly hygroscopic and thus no satisfactory elemental analysis was obtained.

### 3.2.6. Synthesis of [HL4]PF<sub>6</sub>

To 5 mL aqueous solution of [H<sub>3</sub>L<sub>4</sub>](Cl)<sub>2</sub> (0.41 g, 1.0 mmol) was added NH<sub>4</sub>PF<sub>6</sub> (0.82 g, 5.0 mmol) in 2 mL H<sub>2</sub>O. The resulted precipitate was collected and washed with water and a small amount of ethanol. Yield: 0.34 g (65%). Anal. Calc. for C<sub>21</sub>H<sub>24</sub>F<sub>6</sub>N<sub>7</sub>P: C, 48.56; H, 4.66; N, 18.88. Found: C, 48.30; H, 4.87; N, 18.67%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 8.95 (s, 1H, NCHN), 7.88(t, 1H, *J* = 7.2, 4-positioned C<sub>5</sub>H<sub>3</sub>N), 7.72, 7.70 (both d, *J* = 7.2 Hz, 3,5-positioned C<sub>5</sub>H<sub>3</sub>N), 7.66, 7.62 (both s, each 1H, NCHCHN), 7.27 (dd, *J* = 8.8, 14.4 Hz, CH<sub>2</sub>=CHN), 6.82, 6.73 (both s, each 1H, C<sub>3</sub>N<sub>2</sub>H), 5.69 (d, 1H, *J* = 14.4 Hz, *trans*-CH<sub>2</sub>=CHN), 4.92 (d, 1H, *J* = 8.8 Hz, *cis*-CH<sub>2</sub>=CHN), 4.67 (br., 2H, CH<sub>2</sub>CH<sub>2</sub>), 4.57 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.80 (s, 3H, NCH<sub>3</sub>), 2.40, 2.24 (both s, each 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): 151.5, 151.4, 150.9, 150.4, 140.7, 140.5, 137.4, 137.1, 130.2, 123.6, 122.8, 118.2, 118.1, 105.4, 104.3, 100.8, 48.5, 47.9, 35.7, 10.6, 10.4.

### 3.2.7. Synthesis of [Ag<sub>4</sub>(L<sub>1</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> · 4CH<sub>3</sub>CN (I)

A slurry of Ag<sub>2</sub>O (92 mg, 0.4 mmol) in 7 mL of CH<sub>3</sub>CN was treated with [H<sub>3</sub>L<sub>1</sub>](PF<sub>6</sub>)<sub>2</sub> (140 mg, 0.2 mmol). After



the mixture was refluxed with exclusion of light for 12 h, the resulted mixture was filtered through a plug of Celite. Et<sub>2</sub>O was added to the clear solution, the resulted precipitate was collected and washed with methanol and complex **1** was collected as a colorless powder. Yield: 85 mg (55%). Anal. Calc. for C<sub>50</sub>H<sub>46</sub>Ag<sub>4</sub>F<sub>12</sub>N<sub>12</sub>P<sub>2</sub>: C, 39.09; H, 3.02; N, 10.94. Found: C, 39.45; H, 3.16; N, 11.27%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 7.66, 7.54 (both s, each 2H, NCHCHN), 7.36–7.30 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 6.29 (s, 1H, C<sub>3</sub>N<sub>2</sub>H), 5.41 (d, *J* = 14.8 Hz, 2H, CH<sub>2</sub>), 5.30 (s, 4H, CH<sub>2</sub>), 5.02 (d, *J* = 14.8 Hz, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): 151.7, 137.4, 129.2, 128.6, 128.5, 124.7, 121.5, 103.4, 55.2, 48.5. The crystals suitable for X-ray single diffraction were grown by slow diffusion of Et<sub>2</sub>O to the solution of the complex in CH<sub>3</sub>CN.

### 3.2.8. Synthesis of [Ag<sub>4</sub>(L2)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> · 4CH<sub>3</sub>OH (**2**)

A slurry of [H<sub>3</sub>L2](Cl)<sub>2</sub> (108 mg, 0.2 mmol) in 5 mL of CH<sub>3</sub>OH was treated with Ag<sub>2</sub>O (92 mg, 0.4 mmol). After the mixture was stirred with exclusion of light for 12 h at room temperature, it was filtered. To the filtrate was added AgBF<sub>4</sub> (398 mg, 0.2 mmol) in 5 mL. The resulted precipitate was collected by filtration and then dissolved in 8 mL CH<sub>3</sub>CN. After filtration through a plug of Celite, Et<sub>2</sub>O was added to the clear solution, the resulted precipitate was collected and washed with methanol and complex **2** was collected as a colorless powder. Yield: 102 mg (64%). Anal. Calc. for C<sub>58</sub>H<sub>62</sub>Ag<sub>4</sub>B<sub>2</sub>F<sub>8</sub>N<sub>12</sub>: C, 45.46; H, 4.08; N, 10.97. Found: C, 45.10; H, 4.34; N, 10.62%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 7.85, 7.72, 7.51, 7.39 (all s, each 2H, NCHCHN), 7.08, 7.03, 6.87, 6.81 (all s, each 2H, CH<sub>mesityl</sub>), 6.47 (s, 2H, CH<sub>pyrazole</sub>), 5.51 (d, *J* = 14.4 Hz, CH<sub>2</sub>), 4.91 (d, *J* = 14.4 Hz, CH<sub>2</sub>), 2.37 (s, 6H, CH<sub>3</sub>), 2.29 (s, 6H, CH<sub>3</sub>), 1.91 (s, 6H, CH<sub>3</sub>), 1.77 (s, 6H, CH<sub>3</sub>), 1.64 (s, 6H, CH<sub>3</sub>), 1.57 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): 180.5, 150.9, 150.2, 139.2, 138.6, 136.8, 135.4, 135.0, 134.7, 134.3, 129.2, 124.5, 122.9, 104.2, 48.5, 21.1, 20.9, 17.9, 17.6, 17.5. The crystals suitable for X-ray single diffraction were grown by slow diffusion of Et<sub>2</sub>O to the solution of the complex in CH<sub>3</sub>CN and CH<sub>3</sub>OH (5:1).

### 3.2.9. Synthesis of [Ag<sub>4</sub>(L3)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**3**)

A slurry of Ag<sub>2</sub>O (69 mg, 0.3 mmol) in 3 mL of dry DMSO was treated with [H<sub>3</sub>L3](PF<sub>6</sub>)<sub>2</sub> (58 mg, 0.1 mmol). The mixture was stirred at 80 °C with exclusion of light for 12 h and the resulted mixture was filtered through a plug of Celite. To the filtrate was added 5 mL of methanol and 30 mL of diethyl ether, colorless solid was obtained. Yield: 28 mg (43%). Anal. Calc. for C<sub>30</sub>H<sub>34</sub>Ag<sub>4</sub>P<sub>2</sub>F<sub>12</sub>N<sub>12</sub>: C, 28.06; H, 2.67; N, 13.09. Found: C, 27.91; H, 2.71; N, 13.19%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 7.57, 7.32 (both s, NCHCHN, each 2H), 5.43 (s, C<sub>3</sub>HN<sub>2</sub>, 1H), 5.33 (m, NCH<sub>2</sub>N, 4H), 4.04 (br. NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, 4H), 2.54 (m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, 4H). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): 184.4, 183.7, 155.1, 123.3, 122.1, 50.6, 49.1, 30.8. The crystals suitable for X-ray single dif-

fraction were grown by slow diffusion of Et<sub>2</sub>O to the solution of the complex in CH<sub>3</sub>CN.

### 3.2.10. Synthesis of [Ag<sub>3</sub>(L4)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> · 2CH<sub>3</sub>CN (**4**)

A slurry of Ag<sub>2</sub>O (115 mg, 0.5 mmol) in 3 mL of dry DMSO was treated with [HL4]Cl<sub>2</sub> (123 mg, 0.3 mmol). The mixture was stirred at 80 °C with exclusion of light for 12 h for 15 h which was filtered. To the filtrate was added AgPF<sub>6</sub> (228 mg, 0.9 mmol) in 5 mL of methanol. Subsequent addition of 40 mL diethyl ether afforded colorless solids, then it was dissolved in 8 mL CH<sub>3</sub>CN. After filtration through a plug of Celite, Et<sub>2</sub>O was added to the clear solution, and the resulted precipitate was collected and washed with methanol and complex **4** was collected as a colorless powder. Single crystals were obtained by slow diffusion of diethyl ether to its acetonitrile solution. Yield: 93 mg (39%). Anal. Calc. for C<sub>46</sub>H<sub>52</sub>Ag<sub>3</sub>F<sub>18</sub>N<sub>16</sub>P<sub>3</sub>: C, 34.80; H, 3.30; N, 14.12. Found: C, 34.53; H, 3.20; N, 13.89%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 7.79–7.65 (m, 3H, C<sub>5</sub>NH<sub>3</sub>), 7.34, 7.28 (both s, each 1H, NCHCHN), 7.22 (m, *J* = 7.2, 15.2 Hz, NCH=CH<sub>2</sub>), 6.82, 6.60 (both s, each 1H, C<sub>3</sub>N<sub>2</sub>H), 5.85 (d, 1H, *J* = 15.2 Hz, NCH=CH<sub>2</sub>), 4.90 (d, 1H, *J* = 7.2 Hz, NCH=CH<sub>2</sub>), 4.58, 4.44 (both br. each 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.91, 2.38, 1.91 (all s, each 3H, CH<sub>3</sub>), 2.07 (s, 3H, CH<sub>3</sub>CN). <sup>13</sup>C{<sup>1</sup>H}NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): 149.8, 149.7, 149.3, 148.8, 142.5, 142.3, 139.7, 136.5, 130.0, 123.1, 123.0, 122.6, 121.3, 118.2, 106.3, 105.0, 49.0, 48.4, 31.7, 19.0, 13.5, 1.42.

### 3.2.11. Synthesis of [Ag(HL4)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> · CH<sub>3</sub>CN (**5**)

A slurry of Ag<sub>2</sub>O (35 mg, 0.15 mmol) in 8 mL of dry CH<sub>3</sub>CN was treated with [HL4]PF<sub>6</sub> (156 mg, 0.3 mmol). After the mixture was refluxed with exclusion of light for 12 h, it was filtered through a plug of Celite. Slow vapor diffusion of diethyl ether to the filtrate afforded colorless crystals. Yield: 110 mg (45%). Anal. Calc. for C<sub>23</sub>H<sub>27</sub>AgF<sub>12</sub>N<sub>8</sub>P<sub>2</sub>: C, 33.97; H, 3.35; N, 13.78. Found: C, 33.69; H, 3.48; N, 13.54%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 8.85 (s, 1H, NCHN), 8.12 (t, *J* = 7.6 Hz, 4-positioned C<sub>5</sub>H<sub>3</sub>N), 8.01, 7.94 (both d, *J* = 7.6 Hz, 3,5-positioned C<sub>5</sub>H<sub>3</sub>N), 7.63, 7.37 (both s, each 1H, NCHCHN), 7.30 (m, 1H, *J* = 8.8, 15.2 Hz, NCH=CH<sub>2</sub>), 7.06, 6.89 (both s, each 1H, C<sub>3</sub>HN<sub>2</sub>), 5.96 (d, 1H, *J* = 15.2 Hz, NCH=CH<sub>2</sub>), 5.01 (d, *J* = 8.8 Hz, NCH=CH<sub>2</sub>), 4.68, 4.49 (both br, each 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.79 (s, 3H, NCH<sub>3</sub>), 2.43, 2.10 (both s, each 3H, C<sub>3</sub>HN<sub>2</sub>CH<sub>3</sub>), 2.07 (s, 3H, CH<sub>3</sub>CN).

## 3.3. X-ray structural determination

Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with a Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) by using an  $\omega$ -2 $\theta$  scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software [20]. The structures were solved by direct methods, and

Table 1  
Summary of X-ray crystallographic data for complexes **1–5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Formula	C <sub>58</sub> H <sub>58</sub> Ag <sub>4</sub> F <sub>12</sub> N <sub>16</sub> P <sub>2</sub>	C <sub>62</sub> H <sub>78</sub> Ag <sub>4</sub> B <sub>2</sub> F <sub>8</sub> N <sub>12</sub> O <sub>4</sub>	C <sub>30</sub> H <sub>34</sub> Ag <sub>4</sub> F <sub>12</sub> N <sub>12</sub> P <sub>2</sub>	C <sub>46</sub> H <sub>52</sub> Ag <sub>3</sub> F <sub>18</sub> N <sub>16</sub> P <sub>3</sub>	C <sub>23</sub> H <sub>27</sub> AgF <sub>12</sub> N <sub>8</sub> P <sub>2</sub>
<i>F</i> <sub>w</sub>	1700.62	1660.46	1284.11	1587.56	813.34
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/m</i>	<i>C2/m</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	18.545(3)	20.976(3)	13.868(2)	18.229(4)	8.4920(10)
<i>b</i> (Å)	15.135(2)	15.915(2)	17.475(2)	26.898(5)	12.500(2)
<i>c</i> (Å)	23.583(3)	23.200(3)	8.8420(17)	16.503(3)	15.427(2)
$\alpha$ (°)					91.271(2)
$\beta$ (°)	96.894(2)	115.595(3)	100.709(2)	120.00(3)	96.737(2)
$\gamma$ (°)					103.646(3)
<i>V</i> (Å <sup>3</sup> )	6571.0(16)	6985.1(15)	2105.5(6)	7007(2)	1578.3(4)
<i>Z</i>	4	4	2	4	2
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.719	1.579	2.025	1.505	1.711
$\mu$ (mm <sup>-1</sup> )	1.308	1.179	2.002	0.988	0.841
<i>F</i> (000)	3376	3344	1248	3152	812
$\theta$ Range	1.74–25.01	1.67–25.01	1.90–25.01	1.42–25.01	1.68–25.00
Reflections collected	16748	16162	5495	18235	8290
Unique, <i>R</i> <sub>int</sub>	5781, 0.0224	6001, 0.1585	1917, 0.0245	6297, 0.0491	5476, 0.0167
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.103	1.030	1.078	0.914	1.028
<i>R</i> , [ <i>I</i> > 2 $\sigma$ <i>I</i> ]	0.0518, 0.1319	0.0815, 0.1635	0.0480, 0.1407	0.0609, 0.1544	0.0497, 0.1293
<i>R</i> , (all data)	0.0730, 0.1545	0.2217, 0.2351	0.0614, 0.1629	0.1236, 0.1829	0.0765, 0.1513
Largest differences in peak and hole (e Å <sup>-3</sup> )	1.011, -1.008	1.004, -1.090	2.311, -1.973	0.849, -0.553	0.852, -0.538

the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on *F*<sub>2</sub> using SHELXTXL package [21]. Disordered solvent molecules for **3** and **4** could not be modeled successfully and were removed from their reflection data with SQUEEZE [22] (total potential solvent accessible void volume 76.0 Å<sup>3</sup> for **3** and solvent accessible void volume 753.00 Å<sup>3</sup> for **4**). Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C–H distances of 0.93–0.97 Å and *U*<sub>iso</sub>(H) = -1.2–1.5*U*<sub>eq</sub>(C). Further details of the structural analysis are summarized in Table 1.

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### Appendix A. Supplementary material

CCDC 656556, 656557, 656558, 656559 and 659518 contains the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.10.042](https://doi.org/10.1016/j.jorganchem.2007.10.042).

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