Synthesis, Structural Characterization, and Luminescence of New Silver Aggregates Containing Short Ag−Ag Contacts Stabilized by Functionalized Bis(*N*-heterocyclic carbene) Ligands

Bin Liu, Wanzhi Chen,* and Shouwen Jin

Department of Chemistry, Zhejiang University, Xixi Campus, 148 Tianmushan Road, Hangzhou 310028, People's Republic of China

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The imidazolium salts bis(*N*-(pyridylmethyl)imidazoliumyl)methane hexafluorophosphate ($H_2L^1 \cdot (PF_6)_2$), 2,2′-bis(*N*-(pyridylmethyl)imidazoliumyl)ethyl ether ($H_2L^2 \cdot (PF_6)_2$), 2,6-bis(*N*-(pyridylmethyl)imidazoliumyl)pyridine ($H_2L^3 \cdot (PF_6)_2$), and 3,6-bis(*N*-(pyridylmethyl)imidazoliumyl)pyridazine ($H_2L^4 \cdot (PF_6)_2$) have been prepared and characterized. They reacted with Ag_2O in acetonitrile to produce the silver complexes $[Ag_4(L^1)_2(CH_3CN)_2](PF_6)_4 \cdot 2CH_3CN$ (**1**), $[Ag_4(L^2)_2](PF_6)_4 \cdot 2CH_3CN$ (**2**), $[Ag_4(L^3)_2](PF_6)_4 \cdot Et_2O \cdot CH_3CN$ (**4**), and $[Ag_6(L^4)_4](PF_6)_6$ (**5**), respectively. The reaction of **2** with 4 equiv of $Au(Et_2S)Cl$ afforded the dimetallic gold complex $[Au_2(L^2)](PF_6)_2 \cdot 2CH_3CN$ (**3**). Complexes **1**−**4** were characterized by ^1H NMR, ^{13}C NMR, luminescence spectroscopy, elemental analyses, and X-ray crystallography. Complex **1** is a tetrasilver complex consisting of a zigzag silver chain with silver−silver separations of 2.911(1) and 3.288(1) Å. Complexes **2** and **4** have orthogonal tetrasilver cores in which four silver atoms are held together by two L^2 or L^3 ligands with relatively short Ag−Ag contacts ranging from 2.790(1) to 3.293(2) Å. The digold complex consists of a macrometallocycle formed by two gold atoms and one L^2 ligand, and the intramolecular Au−Au bond distance is 3.267(1) Å. Complex **5** is a hexamer with six silver atoms bridged by four L^4 ligands forming three silver−silver bonds of distances 3.249(2), 3.014(2), and 3.089(2) Å. ESI-MS spectra show that these multinuclear silver cores are retained in acetonitrile solution. All of these silver complexes are intensely luminescent in their solid state.

Introduction

Extended metal systems especially those involving direct metal−metal interactions have raised a lot of interest over the past decades due to their versatile chemical and physical properties. Conductivity, magnetic properties, and electrochemical behavior of these metal aggregates have opened up potential applications in the field of nanoscale or molecular scale electronics.[1] Polynuclear molecular compounds containing monovalent coinage metals have demonstrated a remarkable tendency to aggregate despite their formally closed-shell d^{10} electronic configuration.[2] This behavior has been particularly well documented for gold, and the term "aurophilicity" is used to describe Au−Au interactions.[3] The metal−metal attractions can be either supported or unsupported by ancillary ligands. Experimental and theoretical evidence have also been accumulated for the analogous cuprophilicity[4] and argentophilicity[5] of the lighter congeners in recent years, although they are weaker than aurophilic interactions. The combination of d^8−d^{10}−s^2 closed-shell metallophilic interactions and ligand functionality has resulted in the formation and isolation of multinuclear aggregates with novel and diverse structures.[6]

N-Heterocyclic carbene (NHC) ligands constitute a valuable alternative to tertiary phosphines and form intriguingly stable bonds with transition metals.[7,8] Unique electronic properties such as high σ-basicity and low π-acidity give the transition metal complexes of NHCs enhanced catalytic activities in many organic transformation processes. A great number of metal−

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* Corresponding author. E-mail: chenwzz@zju.edu.cn. Tel & fax: 86-571-88273314.

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NHC complexes have been reported including NHCs with simple *N*-alkyl or aryl substituents[9] and *N*-functionalized NHCs bearing various functional groups such as pyridyl,[10] phosphinyl,[11] pyrazolyl,[12] thioether,[13] RO−,[14] and iminos.[15] Among these metal−NHC complexes, the family of silver−NHC complexes has been receiving continuous attention[8] since they are often used as carbene transfer reagents to make other metal−NHC complexes. However, so far only a few NHC-stabilized silver clusters have been reported.[8,12]

We have been interested in the construction of platinum aggregates containing short Pt−M (M = Pt, Tl, Ag, Pd) interactions.[16] Some of these materials show very interesting luminescence properties and are potentially useful precursors for optical sensors. Taking into account the strong σ-donating abilities of NHCs, the pyridyl-functionalized bis(NHC) ligands would be expected to be suitable candidates to connect transition metals into organometallic oligomers or polymers. Here we report the preparation and structural characterization of silver complexes of bis(NHC) ligands bearing rigid or flexible spacers of different lengths.

Experimental Section

All the chemicals were obtained from commercial suppliers and used without further purification. *N*-(2-Pyridylmethyl)imidazole, $H_2L^1\cdot(PF_6)_2$, was prepared according to the known procedure.[10c] ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) 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. Electrospray mass spectra were acquired using a Waters Micromass ZQ mass spectrometer (+mode, ESI source).

$H_2L^2\cdot(PF_6)_2$. To a solution of di(2-chloroethyl) ether (0.9 g, 6.3 mmol) in 20 mL of dried 1,4-dioxane was added *N*-(2-pyridylmethyl)imidazole (2.0 g, 12.6 mmol). The mixture was refluxed for 2 days. The brown viscous solid was isolated and dissolved in 10 mL of water. Addition of NH_4PF_6 (2.5 g, 15.3 mmol) to the aqueous solution precipitated a pale yellow liquid, which was isolated by decanting the solution and dried. Yield: 1.19 g, 27.5%. Anal. Calcd for $C_{22}H_{26}F_{12}N_6OP_2$: C, 38.83; H, 3.85; N, 12.35. Found: C, 38.57; H, 4.03; N, 12.02. ^1H NMR (dmso-d_6): 9.23 (s, NC*H*N, 2H), 8.54 (d, $J = 7.6$ Hz, 2H, *o*-C_6H_4N), 7.90 (dt, $J = 7.6$ Hz, $J = 1.8$ Hz, 2H, *p*-C_6H_4N), 7.76, 7.70 (both s, each 2H, NCHCHN), 7.48 (d, $J = 7.6$ Hz, 2H, *m*-C_6H_4N), 7.41 (dt, $J = 5.6$ Hz, $J = 1.2$ Hz, 2H, *m*-C_6H_4N) 5.57 (s, 4H, CH_2), 4.40 (t, $J = 4.8$ Hz, 4H, NCH_2CH_2O), 3.79 (t, 4H, NCH_2CH_2O). ^{13}C NMR (dmso-d_6): 153.90, 150.05, 138.01, 137.58, 124.15, 123.46, 123.26, 122.97, 68.49 (s, CH_2), 53.45 (s, CH_2), 49.23 (s, CH_2). ESI-MS *m/z* (%): 535.10 (100) $[M - PF_6^-]^+$.

$H_2L^3\cdot(PF_6)_2$. A mixture of 2,6-di(chloromethyl)pyridine (1.32 g, 5 mmol) and *N*-(2-pyridylmethyl)imidazole (1.57 g, 10 mmol) in 20 mL of toluene was refluxed for 24 h to afford a deep brown solid, which was collected and dissolved in 10 mL of water. Subsequent addition of an excess of NH_4PF_6 (2.0 g, 12.2 mmol) led to an immediate white precipitation. The white solid was collected and washed with water and dried. Yield: 1.20 g, 33.7%. Anal. Calcd for $C_{25}H_{25}F_{12}N_7P_2$: C, 42.09; H, 3.53; N, 13.74. Found: C, 42.26; H, 3.47; N, 13.63. ^1H NMR (dmso-d_6): 9.33 (s, 2H, NCHN), 8.56 (d, $J = 4.0$ Hz, 2H, *o*-C_6H_4N), 8.00 (t, $J = 8.0$ Hz, 1H, *p*-C_6H_3N), 7.91 (dt, $J = 1.6$ Hz, $J = 7.6$ Hz, 2H, *p*-C_6H_4N), 7.78 (br, 2H, NC*H*CHN), 7.70 (br, 2H, NCHC*H*N), 7.50 (d, $J = 7.6$ Hz, 2H, *m*-C_6H_3N), 7.47 (d, $J = 7.6$ Hz, 2H, *m*-C_6H_4N), 7.41 (t, $J = 7.2$ Hz, 2H, *m*-C_6H_4N), 5.60 (s, 4H, CH_2), 5.59 (s, 4H, CH_2). ^{13}C NMR (dmso-d_6): 154.08, 153.88, 150.08, 139.39, 138.05, 124.18, 123.79, 123.55, 123.02, 122.44, 53.52 (s, CH_2), 53.16 (s, CH_2). ESI-MS *m/z* (%): 567.99 (100) $[M - PF_6^-]^+$.

$H_2L^4\cdot(PF_6)_2$. A mixture of 3,6-dichloropyridazine (0.58 g, 3.9 mmol) and *N*-(pyridylmethyl)imidazole (1.24 g, 7.8 mmol) in 20 mL of toluene was refluxed for 4 days to afford a deep brown solid, which was collected and dissolved in 5 mL of water. Subsequent addition of an excess of NH_4PF_6 (1.5 g, 9.2 mmol) led to an immediate white precipitation. The white solid was collected and washed with water and dried. Yield: 0.12 g, 4.5%. Anal. Calcd for $C_{22}H_{20}F_{12}N_8P_2$: C, 38.50; H, 2.94; N, 16.33. Found: C, 38.17; H, 2.89; N, 16.02. ^1H NMR (dmso-d_6): 10.45 (s, 2H, NCHN), 8.81 (s, 2H, $C_4N_2H_2$), 8.70 (s, 2H, NC*H*CHN), 8.59 (d, $J = 4.0$ Hz, 2H, *o*-C_6H_4N), 8.17 (s, 2H, NCHC*H*N), 7.94 (t, $J = 6.4$ Hz, 2H, *p*-C_6H_4N), 7.62 (d, $J = 7.6$ Hz, 2H, *m*-C_6H_4N), 7.44 (t, $J = 4.8$ Hz, 2H, *m*-C_6H_4N), 5.77 (s, 4H, CH_2). ^{13}C NMR (dmso-d_6): 153.34, 152.00, 150.03, 138.04, 137.09, 125.21, 124.28, 124.03, 123.16, 120.39, 54.20 (s, CH_2). ESI-MS *m/z* (%): 540.83 (100) $[M - PF_6^-]^+$.

$[Ag_4(L^1)_2(CH_3CN)_2](PF_6)_4\cdot 2CH_3CN$, 1. To a slurry of Ag_2O (24 mg, 0.1 mmol) in 20 mL of CH_3CN was added $H_2L^1\cdot(PF_6)_2$ (62 mg, 0.1 mmol). The mixture was protected from light and stirred at 50 °C until Ag_2O was dissolved. The solution was filtered through Celite to remove a small amount of precipitate. The clear filtrate was then evaporated to dryness. The residue was washed with diethyl ether and dried. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its CH_3CN solution. Yield: 70 mg, 83.7%. Anal. Calcd for $C_{46}H_{48}Ag_4F_{24}N_{16}P_4$: C, 30.09; H, 2.64; N, 12.20. Found: C, 31.00; H, 2.82; N, 11.65. ^1H NMR (dmso-d_6): 8.50 (d, $J = 4.4$ Hz, 2H, *o*-C_6H_4N), 7.95 (t, $J = 4.8$ Hz, 2H, *p*-C_6H_4N), 7.89 (s, 2H, NC*H*CHN), 7.67 (s, 2H, NCHC*H*N), 7.55 (d, $J = 6.0$ Hz, 2H, *m*-C_6H_4N), 7.46 (t, $J = 6.0$ Hz, 2H, *m*-C_6H_4N), 6.58 (s, 2H, NCH_2N), 5.50 (s, 4H, CH_2), 2.07 (s, CH_3CN, 6H). ^{13}C NMR (dmso-d_6): 180.29 (s, Ag−C), 155.23, 150.93, 139.19, 124.63, 124.45, 123.89, 123.31, 118.50 (s, CH_3CN), 65.33 (s, CH_2), 57.07 (s, CH_2), 1.54 (s, CH_3CN). ESI-MS *m/z* (%): 1528.03(3) $[M - PF_6^- - 4CH_3$-

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Table 1. Summary of X-ray Crystallographic Data for Complexes 1−5

	1	**2**	**3**	**4**	**5**
formula	$C_{46}H_{48}Ag_4F_{24}N_{16}P_4$	$C_{48}H_{54}Ag_4F_{24}N_{14}O_2P_4$	$C_{26}H_{32}Au_2F_{12}N_8O_2P_2$	$C_{56}H_{59}Ag_4F_{24}N_{15}OP_4$	$C_{88}H_{72}Ag_6P_6N_{32}F_{36}$
fw	1836.36	1870.41	1172.47	1969.54	3094.82
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1$
a, Å	11.537(2)	11.895(2)	8.288(2)	12.281(2)	25.520(5)
b, Å	11.903(2)	11.937(2)	24.503(3)	21.320(3)	16.800(3)
c, Å	15.777(3)	14.366(3)	20.007(2)	15.260(3)	30.530(6)
α, deg	102.710(3)	95.157(3)			
β, deg	99.325(3)	92.219(2)	98.271(2)	96.041(2)	113.76(3)
γ, deg	109.119(3)	104.290(3)			
V, Å^3	1931.4(6)	1964.8(6)	4021.1(12)	3973.4(10)	11980(4)
Z	1	1	4	2	4
D_{calcd}, Mg/m^3	1.579	1.581	1.937	1.646	1.716
no. of reflns collected	9888	9745	17 126	20 318	49 743
no. of indep reflns (R_{int})	6667 (0.0228)	6660 (0.0535)	6987 (0.2266)	6991 (0.0388)	28 468 (0.0422)
goodness-of-fit on F^2	0.925	0.873	0.953	1.065	0.837
R ($I > 2\sigma I$)	0.0375, 0.0890	0.0726, 0.1766	0.0945, 0.2238	0.0584, 0.1659	0.0467, 0.1051
R (all data)	0.0621, 0.0975	0.1338, 0.1982	0.1461, 0.2426	0.1087, 0.2417	0.0894, 0.1234

$CN]^+$, 1274.57 (16) $[Ag_3(L^1)_2(PF_6)_2]^+$, 1020.93 (100) $[Ag_2(L^1)_2(PF_6)]^+$, 438.21 (77) $[Ag(L^1)]^+$.

The complexes **2**, **4**, and **5** were prepared similarly to **1**.

$[Ag_4(L^2)_2](PF_6)_4$·$2CH_3CN$, 2. Yield: 73 mg, 78.1%. Anal. Calcd for $C_{46}H_{51}Ag_4F_{24}N_{13}O_2P_4$: C, 30.20; H, 2.81; N, 9.95. Found: C, 30.23; H, 3.04; N, 10.07. ^1H NMR (dmso-d_6): 8.95 (d, J = 4.4 Hz, 2H, *o*-C_6H_4N), 8.29 (dt, J = 6.0 Hz, J = 1.4 Hz, 2H, *p*-C_6H_4N), 8.06 (d, J = 7.6 Hz, 2H, *m*-C_6H_4N), 7.73 (t, J = 6.4 Hz, 2H, *m*-C_6H_4N), 7.62 (d, J = 1.2 Hz, 2H, NC*H*CHN), 7.38 (d, J = 1.2 Hz, 2H, NCHC*H*N), 5.75 (s, 4H, NCH_2Py), 4.34 (s, 4H, NC*H*$_2$-CH_2O), 3.60 (s, 4H, NCH_2C*H*$_2$O). ^{13}C NMR (dmso-d_6): 155.13, 153.87, 141.46, 127.46, 125.53, 123.94, 122.01, 68.57 (s, CH_2), 55.95 (s, CH_2), 51.76 (s, CH_2). ESI-MS *m/z* (%): 1642.41 (8) [M − PF_6^- − $2CH_3CN]^+$, 748.59 (42) $[Ag_2(L^2)(PF_6)]^+$, 495.17 (100) $[AgL^2]^+$.

$[Ag_4(L^3)_2](PF_6)_4$·Et_2O·CH_3CN, 4. Yield: 80 mg, 86.9%. Anal. Calcd for $C_{56}H_{59}Ag_4F_{24}N_{15}OP_4$: C, 34.15; H, 3.02; N, 10.67. Found: C, 33.70; H, 2.85; N, 10.22. ^1H NMR (dmso-d_6): 8.91 (d, J = 4.4 Hz, 2H, *o*-C_6H_4N), 8.27 (t, J = 7.4 Hz, 2H, *p*-C_6H_4N), 8.06 (d, J = 7.6 Hz, 2H, *m*-C_6H_4N), 7.90 (t, J = 7.6 Hz, 1H, *p*-C_6H_3N),7.72 (t, J = 6.8 Hz, 2H, *m*-C_6H_3N), 7.57 (s, 2H, NC*H*CHN), 7.49 (d, J = 8.0 Hz, 2H, *m*-C_6H_4N), 7.31 (s, 2H, NCHC*H*N), 5.83 (s, 4H, CH_2), 5.53 (s, 4H, CH_2), 2.08 (s, CH_3CN). ^{13}C NMR (dmso-d_6): 179.62 (s, Ag−C), 155.08, 155.06, 153.88, 141.36, 138.69, 138.02, 127.39, 125.38, 124.79, 122.42, 121.48 (s, CH_3*C*N), 56.23 (s, CH_2), 54.94 (s, CH_2), 1.47 (s, *C*H_3CN). ESI-MS *m/z* (%): 1708.36 (5) [M − PF_6^- − Et_2O − $CH_3CN]^+$, 781.67 (37) $[Ag_2(L^3)(PF_6)]^+$, 528.27 (100) $[AgL^3]^+$.

$[Ag_6(L^4)_4](PF_6)_6$, 5. Yield: 11 mg, 21.2%. Anal. Calcd for $C_{88}H_{72}Ag_6P_6N_{32}F_{36}$: C, 34.13; H, 2.41; N, 14.47. Found: C, 33.91; H, 2.27; N, 14.31.

$[Au_2(L^2)](PF_6)_2$·$2CH_3CN$, 3. To a solution of L^2 (100 mg, 0.15 mmol) was added Ag_2O (36 mg, 0.15 mmol) in 10 mL of CH_3CN. After the mixture was stirred at 50 °C for 2 days, $Au(SEt_2)Cl$ (97 mg) was added. The solution was continuously stirred for an additional 1 day, and then it was filtered through Celite to remove AgCl precipitate. The clear yellow solution was condensed to ca. 2 mL, and the product was precipitated by adding diethyl ether. Yield: 92 mg, 57.2%. Anal. Calcd for $C_{26}H_{32}Au_2F_{12}N_8O_2P_2$: C, 27.05; H, 2.62; N, 9.71. Found: C, 26.74; H, 2.55; N, 9.24. ^1H NMR (dmso-d_6): 9.00 (d, J = 5.6 Hz, 2H, *o*-C_6H_4N), 8.46 (t, J = 7.2 Hz, 2H, *m*-C_6H_4N), 8.25 (d, J = 8.0 Hz, 2H, *m*-C_6H_4N), 7.89 (t, J = 6.4 Hz, 2H, *p*-C_6H_4N), 7.66 (d, J = 2.0 Hz, 2H, NC*H*CHN), 7.37 (d, J = 2.0 Hz, 2H, NC*H*CHN), 6.38, 5.49 (both d, J = 14.0 Hz, each 2H, NC*H*$_2$Py), 4.57 (dt, J = 14.0 Hz, J = 3.6 Hz, 2H, NC*H*$_2$CH$_2$O), 4.17 (d, J = 14.0 Hz, 2H, NC*H*$_2$CH$_2$O), 3.70 (t, J = 9.8 Hz, 2H, NCH$_2$C*H*$_2$O), 3.59 (d, J = 9.8 Hz, 2H, NCH$_2$C*H*$_2$O). ^{13}C NMR (dmso-d_6): 166.30 (s, Au−C), 154.63, 154.56, 143.03, 129.55, 126.93, 123.67, 122.16, 118.49, 68.10, 55.04 (s, CH_2), 51.34 (s, CH_2). ESI-MS *m/z* (%): 926.78 (100) [M − $PF_6^-]^+$, 391.35 (44) [M − 2Au − $2PF_6^-]^+$.

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 Mo Kα radiation (λ = 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.[17] The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTXL package.[18] 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_{iso}(H) = (−1.2 to −1.5)U_{eq}(C). Hydrogen atoms bound to water molecules or N atoms were located in the Fourier difference map, and their distances were fixed. Disordered solvents in the lattice for **1**−**3** could not be modeled successfully and were removed from their reflection data with SQUEEZE[19] (solvent accessible void volumes of **1**−**3** are 601.6, 622.4 (2), and 1221.1 Å^3). The fluorine atoms of the hexafluorophosphate anions for compound **2** are disordered over two positions, which were modeled successfully at 50% occupancy for each atom. Further details of the structural analysis are summarized in Table 1. CCDC635181−635186 (**1**−**5** and **1′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and Characterization. The imidazolium salts could be easily prepared by the reactions of the corresponding organic halides with *N*-(2-pyridylmethyl)imidazole in refluxing toluene or dioxane and subsequent anion exchange with NH_4PF_6. This procedure yielded H_2L^1•$(PF_6)_2$, H_2L^2•$(PF_6)_2$, and H_2L^3•$(PF_6)_2$ in moderate yields. However, H_2L^4•$(PF_6)_2$ was obtained

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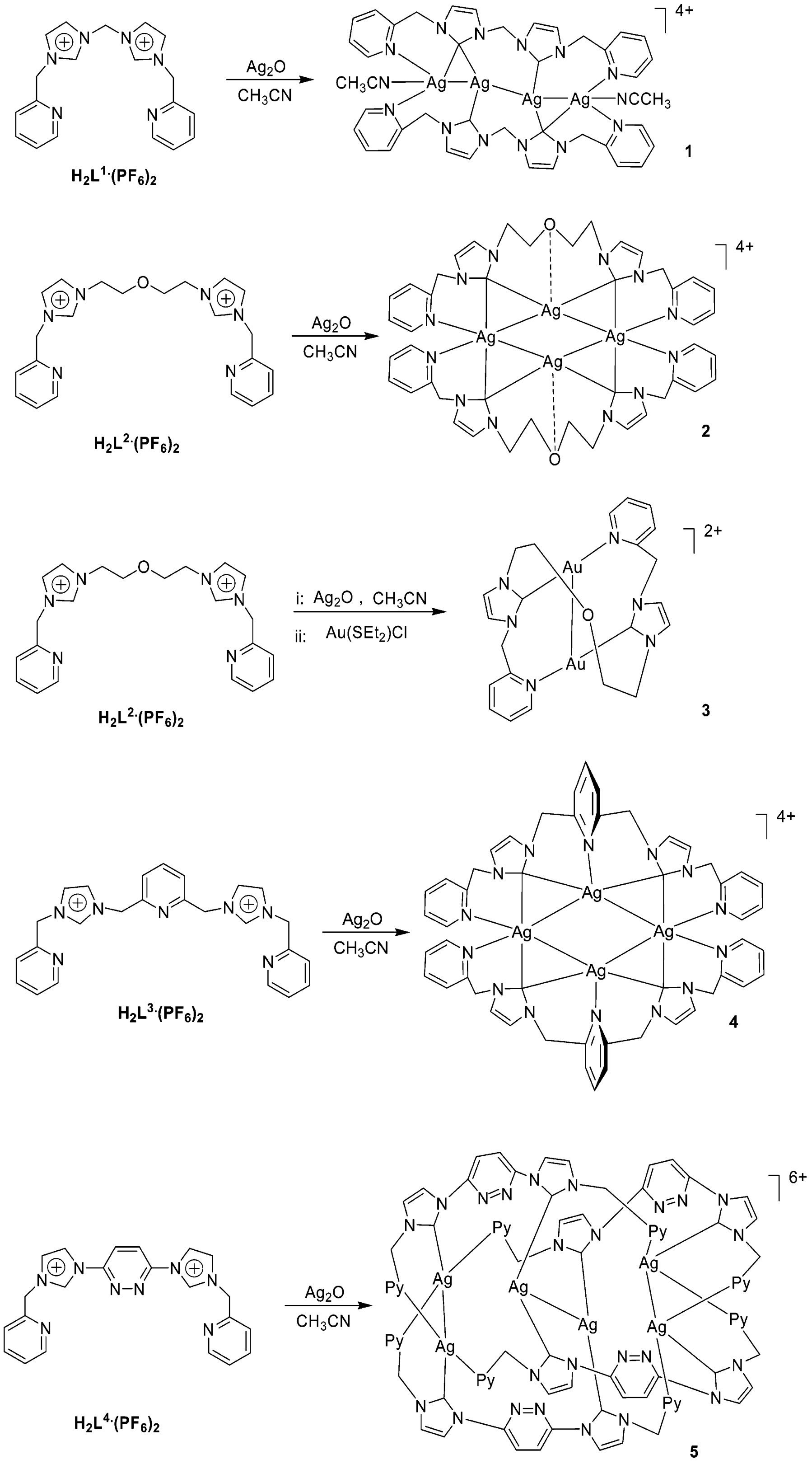
[17] *SMART-CCD* Software, version 4.05; Siemens Analytical X-ray Instruments: Madison, WI, 1996.

[18] Sheldrick, G. M. *SHELXS-97* and *SHELXL-97*, Program for X-ray Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

[19] Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; University of Utrecht: Utrecht, The Netherlands, 1998.

Scheme 1. Synthesis of the Silver−Carbene Complexes



in very poor yield due to the decomposition of 3,6-dichloropyridazine at the refluxing temperature. Treatment of the imidazolium hexafluorophosphate salts in acetonitrile at 50 °C with a slight excess of Ag_2O yielded complexes $[Ag_4(L^1)_2(CH_3CN)_2](PF_6)_4\cdot 2CH_3CN$ (**1**), $[Ag_4(L^2)_2](PF_6)_4\cdot 2CH_3CN$ (**2**), $[Ag_4(L^3)_2](PF_6)_4\cdot Et_2O\cdot CH_3CN$ (**4**), and $[Ag_6(L^4)_4](PF_6)_6$ (**5**), respectively, which are illustrated in Scheme 1. $[Au_2(L^2)](PF_6)_2\cdot 2CH_3CN\cdot H_2O$ (**3**) was prepared by reacting $[Au(Et_2S)Cl]$ and **2**, acting as the carbene transfer reagent.

The imidazolium salts and the metal−NHC complexes were studied by ^1H and ^{13}C NMR spectroscopy, and their spectra are consistent with their proposed formulation. The elemental analysis of **1** does not satisfy the composition of $[Ag_4(L^1)_2(CH_3CN)_2](PF_6)_4\cdot 2CH_3CN$ because of partial loss of solvent molecules. The NMR spectrum of **5** was not recorded owing to its poor solubility in common commercially available deuterated solvents. The most remarkable features in the ^{1}H NMR spectra of the imidazolium salts are the appearance of the downfield resonance signals at 9−11 ppm, assignable to the acidic NC*H*N protons of the imidazolium groups. ^{1}H NMR spectra of complexes **1**−**4** in DMSO-d_6 show the complete disappearance of acidic 2H-imidazolium protons, which is diagnostic for the loss of the carbonium protons and the formation of silver−carbene complexes. The ^{1}H NMR spectra of **1**−**4** give two doublets or two broad singlets in the range 7.16−7.89 ppm due to the two imidazolidene backbone protons. The three methylene resonances of **1** appear as two broad singlets at 6.58 and 5.50 ppm in the intensity ratio of 2:4. Two broad singlets for **2** were observed at 4.34 and 3.60 ppm due to ethylene units, and the methylene resonance signal appears at 5.75 ppm as a broad singlet. The two protons of each methylene group for **1**, **3**, and **4** are magnetically equivalent, whereas the methylene groups for **2** display two sets of resonance signals illustrating that the two achiral protons of each CH_2 moiety become magnetically inequivalent.

^{13}C NMR spectra of **1** and **4** exhibit singlets at 180.29 and 179.62 ppm, respectively, attributed to carbenic carbons, and no Ag−C coupling was observed. In the ^{13}C spectrum of **2**, the carbene resonance signal was not observed. The NMR data have shown that many Ag−NHC complexes exhibit broad singlets or no carbene signal because of a rapid carbene exchange process in solution.[8] The absence of the carbenic carbon resonance is not unusual, and this phenomenon has been reported for a few silver−carbene complexes. The reason is not yet clear, but the dynamic behavior and the poor relaxation of the carbenic carbon were thought to be important factors. Actually, the majority of Ag−NHC complexes undergo rapid carbene exchange in solution and only a few Ag−NHC complexes give well-resolved J_{AgC}.[9f,g,20] Although the cationic complex **1** consists of two kinds of imidazolidene rings in its solid state (see Figure 1), only one set of ^{1}H and ^{13}C resonances was observed, assignable to imidazolidene moieties. This phenomenon together with lack of coupling between the carbon and silver illustrates that the carbene exchange processes are rapid for these silver complexes.

These silver and gold complexes are quite stable toward air and moisture. An ESI-MS spectrum of **1** in acetonitrile shows the most intense peak at 1020.93 amu corresponding to $[Ag_2(L^1)_2(PF_6)]^+$ (calcd 1021.09 amu), whereas the peaks at 1274.57 and 1528.03 amu can be assigned to $[Ag_3(L^1)_2(PF_6)_2]^+$ (calcd 1274.31 amu) and $[Ag_4(L^1)_2(PF_6)_3]^+$ (calcd 1527.14), respectively. The ESI-MS spectrum of **2** displays peaks at 495.17, 748.59, and 1642.41 amu due to $[Ag(L^2)]^+$ (495.11 amu), $[Ag_2(L^2)(PF_6)]^+$ (748.98 amu), and $[Ag_4(L^2)_2(PF_6)_3]^+$ (1642.91 amu). Quite similar to **2**, the peaks at 528.27, 781.67, and 1708.36 amu are seen for **4**, arising from the fragments $[Ag(L^3)]^+$ (528.27 amu), $[Ag_2(L^3)(PF_6)]^+$ (781.98 amu), and $[Ag_4(L^3)_2(PF_6)_3]^+$ (1708.92 amu). The spectrum of **5** shows peaks of $[Ag(L^4)(CH_3CN)]^+$, $[Ag_3(L^4)_2(CH_3CN)(H_2O)_2(PF_6)]^+$, $[Ag_2(L^4)_3(PF_6)2]^+$, and $[Ag_4(L^4)_3(H_2O)(PF_6)_2]^+$ at 540.83, 1226.93, 1684.86, and 1913.85 amu, respectively. In the ESI-MS spectrum of the gold complex, the most intense peak, at 926.78 amu, is obviously ascribed to $[Au_2(L^2)(PF_6)]^+$ (927.36 amu). These results suggest that the multinuclear cores supported by the NHC ligands are maintained in solution.

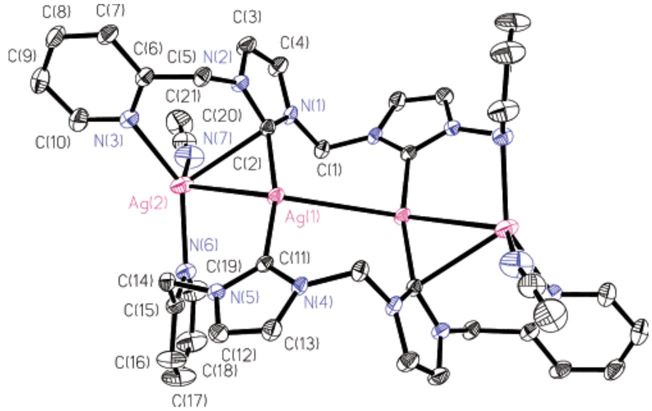


Figure 1. Molecular structure of the cationic chain of **1**. Selected bond distances (Å) and angles (deg): Ag(1)−Ag(2) 2.911(1), Ag(1)−Ag(1)#1 3.288(1), Ag(1)−C(11) 2.087(4), Ag(1)−C(2) 2.108(4), Ag(2)−C(2) 2.671(4), Ag(2)−N(6) 2.230(4), Ag(2)−N(3) 2.247(4), Ag(2)−N(7) 2.361(5), C(11)−Ag(1)−C(2) 166.32(14), N(6)−Ag(2)−N(3) 140.16(14), N(6)−Ag(2)−N(7) 107.53(15), N(3)−Ag(2)−N(7) 97.61(16), N(6)−Ag(2)−C(2) 120.97(18), N(3)−Ag(2)−C(2) 89.58(13), N(7)−Ag(2)−C(2) 88.08(16), Ag(2)−Ag(1)−Ag(1)#1 133.26(2). Symmetry codes: #1 $-x+2$, $-y+2$, $-z+1$.

Structural Description. Complexes **1**−**5** were additionally characterized by X-ray crystallography. The crystallographic information is summarized in Table 1.

Single crystals of **1** were grown by diffusing diethyl ether into its CH_3CN solution. Crystallization of **1** in CH_2Cl_2 yielded $[Ag_4(L^1)_2](PF_6)_4 \cdot 2H_2O$ (**1′**). X-ray diffraction analysis shows that **1** is a linearly arranged tetranuclear complex and crystallizes in the monoclinic space group $P\bar{1}$. A structural drawing of the cation is presented in Figure 1. In the asymmetric unit there are two independent silver atoms. The four silver atoms are held together by two L^1 ligands with short Ag−Ag contacts, in which the Ag−Ag bond distances are 3.288(1) and 2.911(1) Å. These short Ag−Ag contacts have been observed for several silver−NHC complexes,[8] and the Ag−Ag distances in **1** are comparable to the known values. The two internal silver atoms are bicoordinated by two usual carbenic carbon atoms with normal Ag−C bond distances in a bent geometry with a C(11)−Ag(1)−C(2) angle of 166.32(14)° and Ag(1)−C(11) and Ag(1)−C(2) bond distances of 2.087(6) and 2.108(6) Å, respectively. The reason for the deviation from linearity is probably due to the restriction imposed by the linking methylene group on the NHC rings and the silver−silver interactions. The NHC plane is nearly perpendicular to the AgAgC plane with a dihedral angle of ca. 81°. The two terminal silver atoms are tetracoordinated by two pyridyl nitrogen atoms, a carbenic carbon atom, and an acetontrile molecule in a distorted tetrahedron geometry. The Ag−N_{pyridyl} and Ag−$N_{\mathrm{acetonitrile}}$ bond distances in the range 2.304(4)−2.361(5) Å are longer than the normal Ag−N bonds. Interestingly, one of the NHC acts as a bridging ligand to link unsymmetrically two silver atoms, forming a triangular AgAgC ring, whereas the second imidazolidene unit is bonded in a common monodentate fashion. The bridging coordination mode of NHC is rarely observed, and so far it is only seen for a few silver(I)[21] and copper(I)[22] complexes. The Ag(1)−C(2) bond distance (2.108(4) Å) is normal, whereas Ag(2)−C(2) (2.671(4) Å) is at the upper extreme of the Ag−NHC distances.

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Previously, it was reported that the reaction of Ag_2O and a dicationic imidazolium-linked cyclophane gave the silver *N*-heterocyclic carbene complex $[Ag_4(L)_2][PF_6]_4$, where L denotes a bis-carbene-linked cyclophane.[21a] This tetranuclear complex was reported to be the first silver complex that has an *N*-heterocyclic carbene ligand involved in a π-bonding interaction. The bonding situation of Ag(1)Ag(2)C(2) in **1** is similar to the reported one and can be described as 3c2e bonding.

The structure of $[Ag_4(L^1)_2](PF_6)_4 \cdot 2H_2O$ (**1′**) consists of a similar Ag_4 chain. Unlike **1**, the solvent molecules are not coordinated to the terminal silver atoms, as evidenced by the long Ag−O distance of 2.761 Å. The Ag−Ag contacts in **1′** do not show any significant differences when compared to those of **1**. Thus the structure of **1′** is not discussed in detail here.

Dinuclear complexes of the formula $[Ag_2L_2]^{2+}$ (L = bis(1,1′-dialkylimidazolidene)-3,3′-methylene) have been known,[23] in which two silver atoms are held together by two bidentate NHC ligands. The chain compound **1** may be viewed as an adduct of $[Ag_2L_2]^{2+}$ (L = bis(2-pyridylmethylimidazolidene)methane) and two Ag^+ ions bridged by pyridine rings.

Compound **2** is a tetranuclear complex. The asymmetric unit consists of half of the cationic section of the molecule with two independent silver atoms and one L^2 ligand. Interestingly, the four silver atoms form a square-planar core surrounded by two L^2 ligands. The four side lengths of the square ring are nearly equal with very short Ag−Ag bond distances of 2.790(1) and 2.791(2) Å. The long diagonal Ag−Ag distance is 3.316(2) Å, significantly longer than the other Ag−Ag bonds, indicating much weaker interaction between Ag(1) and Ag(1)#1 (symmetry code: #1 $-x+2$, $-y+2$, $-z+1$) atoms.

Each NHC interacts symmetrically with two neighboring silver atoms, forming four three-membered rings. The four NHC planes are approximately perpendicular to the Ag_4 plane, as indicated by the dihedral angles (82.40−84.71°) between them. The four silver atoms are nearly perfectly coplanar, which is illustrated by the dihedral angle close to 0° between two triangular Ag_3 subunit planes. The two pairs of Ag−C(1) and Ag−C(12) bond distances are almost equal, at Ag−C lengths of ca. 2.2 Å. The two NHC ligands around Ag(2) are nearly linearly arranged with a C(1)#1−Ag(2)−C(12) angle of 173.7(3)°. The Ag(2) atom also weakly interacts with two pyridyl rings with Ag(2)−N(3)#1 and Ag(2)−N(6) being 2.380(9) and 2.422(9) Å, respectively, whereas C(1)−Ag(1)−C(12) is quite bent with an angle of 151.2(3)°, probably because of the geometry constraints arising from the formation of the 10-membered ring involving two NHC and a $-CH_2CH_2OCH_2CH_2-$ group. The Ag···O contact is 2.674(6) Å, showing that the Ag−O interactions can be neglected. We have noted that tetranuclear silver cluster-stabilized mixed-donor *N*-heterocyclic carbine linked cyclophanes have been reported,[21a,d] and the Ag_4 cores are similar.

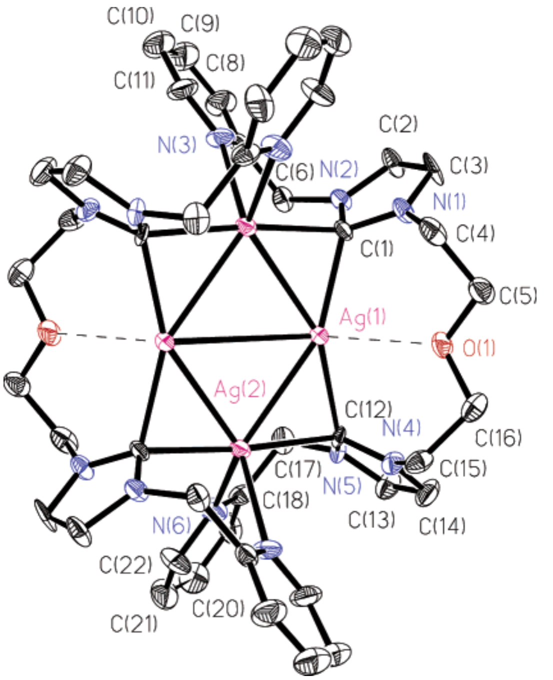

Figure 2. Molecular structure of **2** showing atomic numbering scheme at 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Ag(1)−Ag(2) 2.790(1), Ag(1)−Ag(2)#1 2.791(1), Ag(1)−Ag(1)#1 3.316(2), Ag(2)−Ag(1)#1 2.792(2), Ag(1)−C(1) 2.186(9), Ag(1)−C(12) 2.215(9), Ag(1)−O(1) 2.674(6), Ag(2)−C(1)#1 2.208(12), Ag(2)−C(12) 2.197(8), Ag(2)−N(3)#1 2.380(9), Ag(2)−N(6) 2.422(9), C(1)−Ag(1)−C(12) 151.2(3), C(1)#1−Ag(2)−C(12) 173.7(3), C(1)#1−Ag(2)−N(3)#1 86.2(3), C(12)−Ag(2)−N(3)#1 96.3(3), C(1)#1−Ag(2)−N(6) 99.8(4), C(12)−Ag(2)−N(6) 86.0(4), N(3)#1−Ag(2)−N(6) 93.4(4), Ag(2)−Ag(1)−Ag(2)#1 107.10(3), Ag(1)−Ag(2)−Ag(1)#1 72.90(4), Ag(2)−Ag(1)−Ag(1)#1 53.57(3), Ag(2)#1−Ag(1)−Ag(1)#1 53.53(3). Symmetry code: #1 $-x+2$, $-y+2$, $-z+1$.

Complex **4** is also a tetranuclear complex consisting of a square-planar Ag_4 core, which is stabilized by two L^3 ligands. The molecular structure of **4** is depicted in Figure 3. The Ag_4 core is essentially the same as that of complex **2**, but $-CH_2CH_2OCH_2CH_2-$ groups are replaced by $-CH_2C_6H_3NCH_2-$ groups. Similarly to compound **2**, each side of the square is buttressed by a bridging NHC ligand. The silver−silver contacts are 2.784(1), 2.820(1), and 3.293(2) Å, respectively, comparable to those of complex **2**. The Ag(1) is almost linearly coordinated by two NHC ligands with a C−Ag−C angle of 173.5(3)°, whereas the C−Ag(2)−C is more bent, with an angle of 142.7(3)° owing to the geometrical constraint of the pincer-like ligand. The Ag−C distances of 2.205(8) and 2.215(9) Å for Ag(1) and 2.261(8) and 2.265(9) Å for Ag(2), respectively, are relatively longer. Each NHC carbenic carbon almost symmetrically binds two silver atoms. In this case, the interaction between two silver atoms and the carbene carbon atom may also be viewed as a 3c2e bond as found in **1** and other known complexes.[21d] The two central pyridyl rings of the bis(NHC)pyridine are parallel to each other, and they are tilted upward and downward from the Ag_4 plane with a dihedral angles of 28° between the Ag_4 ring and the pyridine rings. In such a way, a molecular chair is formed.

The carbene transfer reaction of **2** with $Au(Et_2S)Cl$ did not afford the analogous tetragold complex but a dinuclear complex of the formula $[Au_2(L^2)](PF_6)_2$, **3**. Despite repeated and varied attempts, the poor-quality crystal and the disorder of solvents and anions resulted in a very weak data set, limiting the resolution of the structure. Fortunately the core section can be well resolved. A view of the cation is presented in Figure 4.

The gold−carbene complex is dinuclear. Both gold atoms adopt a linear geometry with an imidazolidene ligand in a monodentate fashion and a pyridine completing their coordina-

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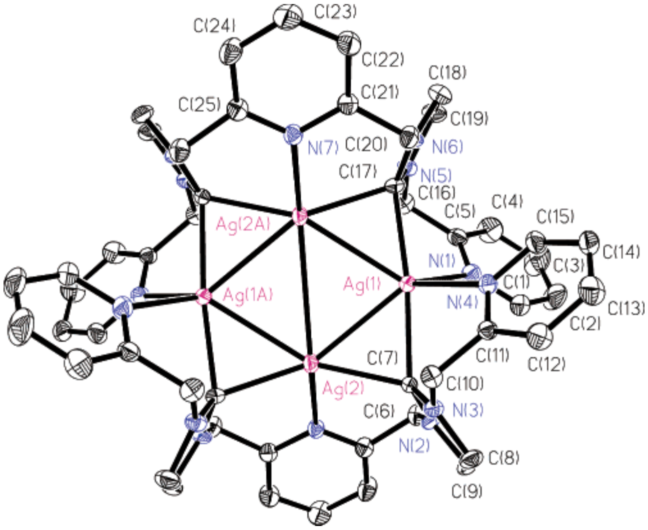

Figure 3. ORTEP drawing of the tetrametallic cation of **4**. Selected bond distances and angles (deg): Ag(1)−Ag(2) 2.784(1), Ag(1)−Ag(2)#1 2.820(1), Ag(2)−Ag(2)#1 3.293(2), Ag(1)−C(17) 2.205(8), Ag(1)−C(7) 2.215(9), Ag(1)−N(4) 2.406(8), Ag(1)−N(1) 2.427(8), Ag(2)−C(7) 2.261(8), Ag(2)−C(17)#1 2.265(9), Ag(2)−N(7)#1 2.491(8), C(17)−Ag(1)−C(7) 173.5(3), C(17)−Ag(1)−N(4) 99.0(3), C(7)−Ag(1)−N(4) 85.9(3), C(17)−Ag(1)−N(1) 85.6(3), C(7)−Ag(1)−N(1) 97.9(3), N(4)−Ag(1)−N(1) 97.7(3), C(7)−Ag(2)−C(17)#1 142.7(3), C(7)−Ag(2)−N(7)#1 88.1(3), C(17)#1−Ag(2)−N(7)#1 90.1(3), Ag(2)−Ag(1)−Ag(2)#1 72.0(1), Ag(1)−Ag(2)−Ag(1)#1 108.0(1), Ag(1)−Ag(2)−Ag(2)#1 54.5(1), Ag(1)#1−Ag(2)−Ag(2)#1 53.5(1). Symmetry code: #1 −*x*+1, −*y*+1, −*z*+1.

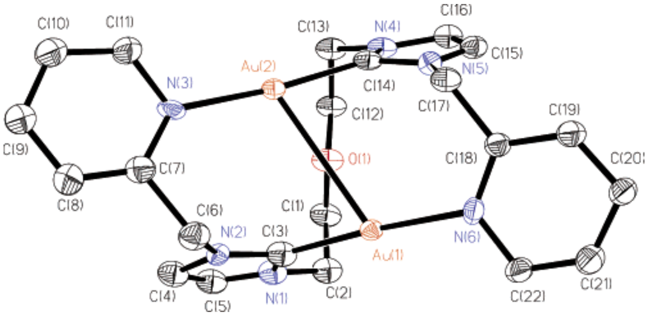

Figure 4. Molecular structure of $[Au_2(L^2)](PF_6)_2$. Selected bond distances (Å) and angles (deg): Au(1)−Au(2) 3.267(1), Au(1)−C(3) 2.01(2), Au(1)−N(6) 2.092(15), Au(2)−C(14) 2.00(2), Au(2)−N(3) 2.040(17), C(3)−Au(1)−N(6) 175.9(8), C(3)−Au(1)−Au(2) 72.5(7), N(6)−Au(1)−Au(2) 111.6(5), C(14)−Au(2)−N(3) 174.3(8), C(14)−Au(2)−Au(1) 75.2(5), N(3)−Au(2)−Au(1) 109.6(4).

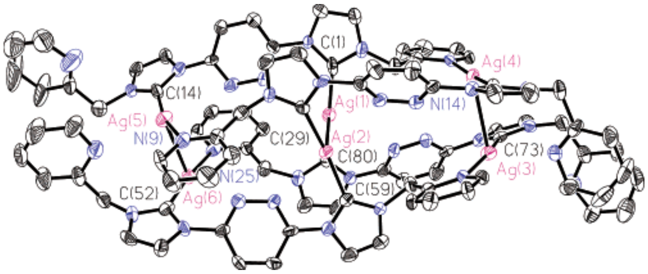

Figure 5. Crystal structure of **5** showing 20% probability ellipsoids. Selected bond distances (Å) and angles (deg): Ag(1)−Ag(2) 3.249(2), Ag(3)−Ag(4) 3.014(2), Ag(5)−Ag(6) 3.089(2), Ag(1)−C(80) 2.032(13), Ag(1)−C(1) 2.041(13), Ag(2)−C(59) 2.088(10), Ag(2)−C(29) 2.082(9), Ag(3)−C(73) 2.140(12), Ag(3)−N(24) 2.232(9), Ag(4)−C(38) 2.110(12), Ag(4)−N(8) 2.186(9), Ag(5)−C(14) 2.116(14), Ag(5)−N(9) 2.230(10), Ag(6)−C(52) 2.125(14), Ag(6)−N(25) 2.164(11), C(80)−Ag(1)−C(1) 174.2(5), C(59)−Ag(2)−C(29) 170.4(5), C(73)−Ag(3)−N(24) 165.1(4), C(38)−Ag(4)−N(8) 173.3(4), C(14)−Ag(5)−N(9) 166.3(4), C(52)−Ag(6)−N(25) 174.1(4).

tion sphere. The two Au−C bond distances are 2.01(2) and 2.00(2) Å, respectively, lying in the range of the known values of other Au−NHC complexes.[21c,24] The Au−N bond distances are 2.092(15) and 2.040(17) Å. The two C−Au−N are only slightly bent from 180°. Because of the high flexibility, the ligand twists in such a way that the pyridine group coordinated to the gold atom that is linked to the other imidazolidene holds the two gold atoms together, forming metallocyclic rings. The NHC and pyridine rings around Au(1) and Au(2) are bisected with dihedral angles of 65.3° and 59.5°, respectively.

The compound is quite similar to $[Au_2(L)_2](BF_4)_2$ (L = 1-methyl-3-(2-pyridinylmethyl)imidazolidene), in which each Au atom is also coordinated by a NHC and a pyridine, recently reported by Catalano et al.[21c] The NHC ligands in **3** are also arranged in a head-to-tail fashion, and the two gold atoms are coordinated to one carbene and one pyridyl group in an almost linear geometry with C(3)−Au(1)−N(6) and C(14)−Au(2)−N(3) bond angles of 176.0(9)° and 174.6(7)°, respectively. The C(3)−Au(1)−Au(2)−C(14) and N(6)−Au(1)−Au(2)−N(3) torsion angles of 132.4(8)° and 131.1(8)° reflect that the gold atoms are slightly twisted with respect to each other by ca. 50°. The Au(1)−Au(2) separation at 3.267(1) Å is longer than the metal−metal separation in the similar compound $[Au_2(CH_3im(CH_2\text{-}Py))_2](BF_4)_2$ (3.173 Å).[21c] The intermolecular gold···gold distance is greater than 5.043 Å, excluding any metallophilic interaction between the dimeric molecules.

Single crystals of **5** were obtained by slow diffusion of diethyl ether into its CH_3CN solution. The complex is a hexanuclear compound in which six independent silver atoms are held together by four L^4 ligands. The asymmetric unit of the complex consists of two essentially the same $[Ag_6(L^4)_4]^{6+}$ units and 12 hexafluorophosphate anions, and thus only one cation is illustrated and discussed. An ORTEP drawing of the cationic structure of **5** is shown in Figure 5. Each L^4 ligand links four different silver atoms acting as a tetradentate bridge. The pyridazine rings stay uncoordinated, as evidenced by the long Ag−N distances, where the closest $Ag-N_{pyridazine}$ distance is 2.801 Å excluding the bonding interactions. Six silver atoms form three silver−silver bonds with distances of 3.249(2), 3.014(2), and 3.089(2) Å for Ag(1)−Ag(2), Ag(3)−Ag(4), and Ag(5)−Ag(6), respectively. The complex has two two-coordinate silver(I) atoms, Ag(1) and Ag(2), in an essentially linear environment with C−Ag−C angles close to 180°. Both are bonded by two NHC ligands with C−Ag−C angles of 174.2(5)° and 170.4(5)°, respectively. The remaining four silver atoms are also bicoordinated, and each silver atom is surrounded by a pyridine and one NHC ligand. The Ag−C bond distances, being in the range 2.071(15) to 2.088(10) Å, for the $[Ag(NHC)_2]$ units are not very different from those of [Ag(NHC)(Py)] units, which are in the range 2.110(12)−2.125(14) Å. For the [Ag(NHC)-

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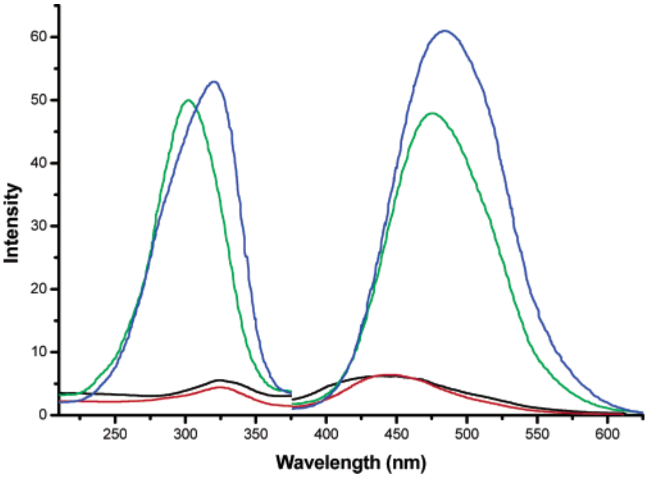

Figure 6. Excitation (left) and emission (right) spectra of complexes **1** (black), **2** (green), **3** (red), and **4** (blue).

(Py)] silver atoms, pyridine groups are bonded with the Ag−N bond approximately 2.164(11)−2.232(9) Å. The other four pyridines interact very weakly with silver atoms of the [Ag(NHC)(Py)] groups with relatively long Ag−N bonds, in the range 2.6−2.8 Å, which are not viewed as bonding. Ag(1) and Ag(2) centers are twisted with respect to each other by approximately 30°, as evidenced by the C(1)−Ag(1)−Ag(2)−C(59) and C(80)−Ag(1)−Ag(2)−C(29) torsion angles of −153.9(4)° and −151.8(4)°, respectively. The two NHC rings around Ag(1) and Ag(2) are tilted away from each other with dihedral angles of ca. 16.82° and 22.28°, respectively.

Solid-State Emission. The solid-state emission of the tetrametallic NHC complexes **1**, **2**, and **4** was studied at room temperature, and the emission spectra are given in Figure 6. Complex **1**, having a linear Ag_4 array, exhibits a single broad, structureless emission band at 442.8 nm when irritated at 326.1 nm. Complexes **2** and **4**, having similar orthogonal Ag_4 cores, show symmetrical broad bands centered at 475.9 and 486.7 nm, and both tail out to ca. 600 nm upon excitation at 304.1 and 332.5 nm, respectively. Compared to **2**, the red shift of **4** is certainly a result of the complexation of the central pyridyl rings. The dinuclear gold complex displays an emission band centered at 445.5 nm upon excitation at 326.5 nm. We are not able to compare the emission properties of the silver complexes with their corresponding ligands because of the unavailability of the free NHC compounds.

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 materials have not been well explored.[9f,10c,21c,25] Similar emission properties of $[Ag_3(CH_3im(CH_2py))_3(NCCH_3)_2](BF_4)_3$ have been previously reported by Catalano et al.;[21c] it 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 states or metal-centered states. We are not able to assign the nature of the excited states due to the complexity brought by metallophilic attractions existing in the complexes.

Conclusion

In this work, we have demonstrated that the bis(NHC) ligands bearing rigid and flexible spacers are useful for construction of d^{10} metal aggregates having metal−metal interactions. The compounds are air stable and easily prepared. Modification of the *N*-substituents at NHC rings may lead to silver−NHC materials of new structural motif and unique properties. These silver clusters show interesting photoluminescent properties, and further work is required to clarify the nature of emissive mechanism. Efforts to make new transition metal aggregates by using these Ag−NHC complexes as carbene transfer reagents are in progress.

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Supporting Information Available: Structural parameters for **1**−**5** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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