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Manuscript ID CE-ART-03-2012-025365

N-Heterocyclic carbene silver(I), palladium(II) and mercury(II) complexes: synthesis, structural studies and catalytic activity

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The bis-benzimidazolium salts, 1,2-bis[2-(N-R-benzimidazolemethyl)phenoxy]ethane $(L^{1}H_{2})$ L^2H_2 : chloride R Et, R ⁿBu). = 1,3-bis[2-(N-R-benzimidazolemethyl)phenoxy]propane chloride ($L^{3}H_{2}$: R = ⁿPr, $L^{4}H_{2}$: $R = {}^{n}Bu$) and bis[N-R-benzimidazolemethyl]mesitylene 2X ($L^{5}H_{2}$: $R = {}^{n}Bu$, X = I; $L^{6}H_{2}$: R = PyCH₂, X = Br and $L^{7}H_{2}$: R = PhCH₂, X = Br), as well as their eight NHC silver(I), palladium(II) and mercury(II) complexes, $[(L^1Ag)_2Ag_2Cl_4]$ (1), $[L^{1}(PdCl_{2}CH_{3}CN)_{2}]$ (2), $[(L^{2}Ag)_{2}AgCl_{2}][AgCl_{2}]$ (3), $[(L^{3}Ag_{2}Cl_{2})_{n}]$ (4), $[(L^{4}Ag_{2}Cl_{2})_{n}]$ (5), $[L^{5}HgI][HgI_{4}]_{0.5}$ (6), $[L^{6}Hg][HgBr_{4}]$ (7) and $[L^{7}Ag][(NO_{3})_{0.76}Br_{0.24}]$ (8) have been prepared and characterized. The complexes 1-8 adopt four different structures: (1) the bis-macrometallocycles connected via Ag_2Cl_4 unit for 1 and via $AgCl_2$ unit for 3, (2) the open structure formed via one ligand and two metal atoms for 2, (3) 1D polymeric chains formed by the monomers of cage-like cavity via weak Ag...Cl bonds (monomer: $L^{3}Ag_{2}Cl_{2}$ for **4** and $L^{4}Ag_{2}Cl_{2}$ for **5**) and (4) the macrocyclic structure formed by one ligand and one metal for 6-8. In the crystal packings of these complexes, 1D supramolecular chains, 2D supramolecular layers and 3D supramolecular architectures are formed via intermolecular weak interactions, including π - π interactions, hydrogen bonds, C-H··· π contacts and weak Hg···Br bonds. Particularly, the catalytic activity of the NHC palladium(II) complex 2 in

Suzuki-Miyaura cross-coupling reaction was studied.

Keywords: Carbene; Silver; Palladium; Mercury; Catalysis

Introduction

The metal complexes of N-heterocyclic carbene (NHC) have been known since 1968.¹ After the isolation of the first stable free N-heterocyclic carbene by Arduengo et al. in 1991,² metal complexes based on imidazol-2-ylidene (imy) or benzimidazol-2-ylidene (bimy) have received considerable attention in organometallic chemistry.³ The transition metal complexes of N-heterocyclic carbenes are frequently prepared through deprotonation of N, N'-disubstituted imidazolium (or benzimidazolium) salts.⁴ And another widely employed synthetic strategy is the use of NHC silver complexes as carbene transfer agents to the preparation of some other metal NHC complexes such as Ni, Pd, Pt, Cu, Au, Rh, Ir and Ru carbene complexes.⁵ The relatively easy preparation of the NHC metal complexes with monodentate, bidentate and polydentate ligands allowed that they were studied systematically.⁶ One of main applications of NHC transition metal complexes is used as catalyst in some organic reactions.⁷ In particular, the palladium(II) complexes containing the NHC ligands have been demonstrated to be excellent catalysts for some organic reactions, such as Suzuki-Miyaura and Heck cross-couplings.⁸ The valuable properties of the NHC metal complexes are relevant to their higher thermal stability and lower sensitivity toward oxygen and moisture.

In the family of N-heterocyclic carbenes, NHC metal complexes from bis-imidazolium (or bis-benzimidazolium) salts with bridging linkers (such as phenelene,⁹ pyridyl and lutidinyl,¹⁰ ether chain¹¹ and alkyl¹²) are an attractive field of research, because different bridging linkers can generate different coordination possibilities. We are interested in bis-NHC ligands and their metal complexes. Recently, some silver(I) and mercury(II) complexes based on bidentate bis-NHC ligands with alkyl, oligoether and phenylene linkers have been reported by us.¹³ In this paper, we report the synthesis of a group of new bis-benzimidazolium salts,

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1,2-bis[2-(N-R-benzimidazolemethyl)phenoxy]ethane chloride ($L^{1}H_{2}$: R = Et, $L^{2}H_{2}$: R = ⁿBu), 1,3-bis[2-(N-R-benzimidazolemethyl)phenoxy]propane chloride ($L^{3}H_{2}$: R = ⁿPr, $L^{4}H_{2}$: R = ⁿBu) and bis[N-R-benzimidazolemethyl]mesitylene 2X ($L^{5}H_{2}$: R = ⁿBu, X = I; $L^{6}H_{2}$: R = PyCH₂, X = Br and $L^{7}H_{2}$: R = PhCH₂, X = Br), as well as the synthesis and structures of eight NHC silver(I), palladium(II) and mercury(II) complexes, [($L^{1}Ag$)₂Ag₂Cl₄] (1), [L^{1} (PdCl₂CH₃CN)₂] (2), [($L^{2}Ag$)₂AgCl₂][AgCl₂] (3), [($L^{3}Ag_{2}Cl_{2}$)_n] (4), [($L^{4}Ag_{2}Cl_{2}$)_n] (5), [$L^{5}HgI$][HgI₄]_{0.5} (6), [$L^{6}Hg$][HgBr₄] (7) and [$L^{7}Ag$][(NO₃)_{0.76}Br_{0.24}] (8). Moreover, the catalytic activity of NHC palladium(II) complex 2 in Suzuki-Miyaura cross-coupling reaction was investigated.

Result and discussions

Synthesis and general characterization of bis-benzimidazolium salts L¹H₂-L⁷H₂

The salicylic aldehyde as starting material was etherificated with 1,2-dibromoethane, then the aldehyde groups were reduced by sodium borohydride to form 1,2-bis(2-hydroxymethylphenoxy)ethane. The hydroxyl groups of 1,2-bis(2-hydroxymethylphenoxy)ethane were substituted by chlorine atoms through using thionyl chloride to give 1,2-bis(2-(chloromethyl)phenoxy)ethane. Finally, the reaction of 1,2-bis(2-(chloromethyl)phenoxy)ethane with N-alkyl-benzimidazole afforded bis-benzimidazolium salts. the 1,2-bis[2-(N-R-benzimidazolemethyl)phenoxy]ethane chloride ($L^{1}H_{2}$: R = Et, $L^{2}H_{2}$: $R = {}^{n}Bu$) (Scheme 1). 1,3-bis[2-(N-R-benzimidazolemethyl)phenoxy]propane chloride ($L^{3}H_{2}$: R = ⁿPr, $L^{4}H_{2}$: R = ⁿBu) were prepared in a manner analogous to that for $L^{1}H_{2}$ (Scheme 1). Bis[N-R-benzimidazolemethyl]mesitylene bromide ($L^{6}H_{2}$: R = $PyCH_2$ and L^7H_2 : R = PhCH₂) was prepared via the reaction of N-alkyl-benzimidazole with 1,3-bis(bromomethyl)mesitylene (method 1 of Scheme 2). Bis[N-butyl-benzimidazolemethyl]mesitylene iodide ($L^{5}H_{2}$) was obtained via two steps, and first step is in a manner analogous to that of $L^{6}H_{2}$ and section step is the anion exchange with sodium iodide in acetone (method 2 of Scheme 2). Precursors $L^{1}H_{2}-L^{7}H_{2}$ are stable toward air and moisture, soluble in polar organic solvents such

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as dichloromethane, acetonitrile and methanol, and almost insoluble in benzene, diethyl ether and petroleum ether. In the ¹H NMR spectra of $L^{1}H_{2}-L^{7}H_{2}$, the benzimidazolium proton signals (NC*H*N) appear at $\delta = 9.47$ -10.03 ppm, which are consistent with the chemical shifts of reported imidazolium (or benzimidazolium) salts.³



Scheme 1 Preparation of precursors $L^{1}H_{2}-L^{4}H_{2}$



Reagents: method 1 for $L^{6}H_{2}$ and $L^{7}H_{2}$, THF, reflux. method 2 for $L^{5}H_{2}$, (i) THF, reflux; (ii) anionic exchange with NaI in acetone.

Scheme 2 Preparation of precursors $L^{5}H_{2}-L^{7}H_{2}$

Synthesis and general characterization of complexes 1-8

Published on 16 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CE25365H

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Synthetic methods of complexes **1-5** are shown in Scheme 3. The reaction of precursor L^1H_2 with silver(I) oxide in dichloromethane afforded tetranuclear complex $[(L^1Ag)_2Ag_2Cl_4]$ (1) containing two 15-membered macrometallocycles and one bridging Ag_2Cl_4 unit. Then complex 1 was treated by $[PdCl_2(CH_3CN)_2]$ in dichloromethane to give an open structural complex $[L^1(PdCl_2CH_3CN)_2]$ (2) (Scheme

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3(1)). The precursor L^2H_2 was treated with anhydrous silver(I) acetate in dichloromethane to afford complex [(L^2Ag)₂AgCl₂][AgCl₂] (**3**) (Scheme 3(2)). The precursors L^3H_2 and L^4H_2 were treated with silver(I) oxide in dichloromethane to afford complexes [($L^3Ag_2Cl_2$)_n] (**4**) and [($L^4Ag_2Cl_2$)_n] (**5**), respectively (Scheme 3(3)).

Synthetic methods of complexes 6-8 are shown in Scheme 4. The precursor $L^{5}H_{2}$ was treated with anhydrous mercury(II) iodide in the presence of KO^tBu in CH₂Cl₂ to afford complex $[L^{5}HgI][HgI_{4}]_{0.5}$ (6) (Scheme 4(1)). Complex $[L^{6}Hg][HgBr_{4}]$ (7) was prepared by the reaction of $L^{6}H_{2}$ with anhydrous mercury (II) bromide in the presence of KO^tBu in CH₂Cl₂ (Scheme 4(2)). Treatment of the precursor $L^{7}H_{2}$ with silver(I) nitrate in the presence of KO^tBu in CH₂Cl₂ yields complex $[L^7Ag][(NO_3)_{0.76}Br_{0.24}]$ (8) (Scheme 4 (3)). The complexes 1-8 are stable toward air and moisture, soluble in DMSO and insoluble in diethyl ether and hydrocarbon solvents. In the ¹H NMR spectra of 1-8, the resonances for the benzimidazolium protons (NCHN) have disappeared, and the chemical shifts of other protons are similar to those of the corresponding precursors. For ¹³C NMR spectra, the signals of the carbon in complexes 1-8 appear at 156.0-188.0 ppm, which are similar to the reported carbene metal complexes.^{5, 6} The NHC silver(I) complexes 1, 3-5 and 8 are stable in the solid state and slightly light sensitive in solution. In the IR spectra of complex 2, the characteristic band of the cvano group appears at 2221 cm^{-1} , and this value is comparable to those of reported complexes containing cyano groups.¹⁴

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Scheme 4 Preparation of complexes 6-8

Structures of complexes 1-8

The complexes **1-8** were characterized by ¹H NMR and ¹³C NMR spectra, and X-ray analysis. The crystals of **1-8** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into their DMSO/CH₂Cl₂ (or DMSO/CH₃CN) solution. The internal ring angles (N-C-N) at the carbene centers in complexes **1-8** are in the range of 105.4-108.3°, which are comparable to those of the known NHC-metal complexes.⁵ In complexes **1-5**, two benzimidazole rings on the same ligand form the dihedral angles of 2.2-14.1° (Table S1 in Supplementary material), the dihedral angles between benzimidazole ring and adjacent benzene ring are 76.7-88.5°, and two benzene rings on the same ligand form the dihedral angles of 49.5-88.1°. In complexes **6-8**, two benzimidazole rings on the same ligand form the dihedral angles of 6.6-86.7° (Table S2). The mesitylene plane and two benzimidazole rings on the same ligand form the dihedral angles of 71.1-89.0°. The dihedral angles between benzimidazole ring and adjacent pyridine ring for **7** (or benzene ring of benzyl group for **8**) are 67.7-78.3°.

The complexes 1 and 3 have similar molecular structure (Fig. 1(a) and Fig. 3(a)),

in which each molecule contains two 15-membered macrometallocycles, and each macrometallocycle is formed by one bidentate carbene ligand and one silver(I) atom. The difference is that two 15-membered macrometallocycles are connected together by Ag₂Cl₄ unit for **1** and by AgCl₂ unit for **3** via Ag-Ag bonds (Ag-Ag distance = 2.993(6) Å for **1** and 3.077(6) Å for **3**). In each 15-membered macrometallocycle of **1** and **3**, the silver atom is tricoordinated with two carbene carbon atoms and another silver(I) atom. The C-Ag-C arrangement is approximately linear with the bond angles of 171.6(1)° for **1** and 171.4(3)° for **3**. The bond distances of Ag-C are 2.107(4) Å and 2.112(3) Å for **1** and 2.104(8) Å and 2.110(7) Å for **3**, respectively. The X-ray crystal structural analysis of **1** and **3** shows that there exist inversion centers in these complexes.

Additionally, the anionic unit Ag₂Cl₄ in complex **1** is formed by two silver(I) atoms and four chlorine atoms (two bridging chlorines Cl(2) and Cl(2A), and two non-bridging chlorines Cl(1) and Cl(1A)). The coplanar four atoms Ag(2), Cl(2), Ag(2A) and Cl(2A) form a quadrangle Ag₂Cl₂ arrangement (Cl(2)-Ag(2)-Cl(2A) = 94.8(5)° and Ag(2)-Cl(2)-Ag(2A) = 85.2(2)°. The two non-bridging chlorine atoms Cl(1) and Cl(1A) lie in both sides of the quadrangle plane (Cl(1)-Ag(2)-Cl(2) = 136.4(6)°). Each silver(I) atom in Ag₂Cl₄ unit is tetracoordinated with three chlorine atoms and another silver(I) atom. The distances of non-bridging chlorine and silver(I) (Ag(2)-Cl(1) = 2.392(1) Å) are slightly shorter than those of bridging chlorine and silver(I) (Ag(2)-Cl(2) = 2.522(1) Å). The Ag(2)-··Ag(2A) separation of 3.505(2) Å shows no metal-metal interactions (the van der Waals radii of silver = 1.7 Å). The Ag₂Cl₂ plane and two benzimidazole rings on the same ligand form the dihedral angles are 17.4° and 18.7°.

Published on 16 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CE25365H

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In complex **3**, five atoms of Ag_3Cl_2 unit are coplanar. The Ag(2)-Ag(1)-Ag(2A) and Cl(1)-Ag(1)-Cl(1A) are all linear with bond angle of $180.0(1)^\circ$, moreover, they are perpendicular to each other. Two Ag-Cl bonds are equal in length with the value of 2.390(1) Å.

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Fig. 1 (a) Perspective view of 1 and anisotropic displacement parameters depicting 50% probability. All hydrogen atoms were omitted for clarity. Symmetry code: i: 1-x, -y, 1-z. Selected bond lengths (Å) and angles (°): Ag(1)-C(7) 2.107(4), 2.993(6), Ag(2)-Cl(1) 2.392(1), Ag(2)-Cl(2) 2.522(1), Ag(1)-Ag(2)Ag(2)-Cl(2A) 2.653(1); C(7)-Ag(1)-C(26) 171.6(1), C(7)-Ag(1)-Ag(2)73.7(1), C(26)-Ag(1)-Ag(2)Cl(2)-Ag(2)-Cl(2A)114.4(1),94.8(5), Cl(1)-Ag(2)-Cl(2) 136.4(6), Cl(2)-Ag(2)-Ag(1) 117.6(4), Cl(2A)-Ag(2)-Ag(1) 75.2(4), N(1)-C(7)-N(2) 105.7(3). (b) The 2D supramolecular layer via two

types of π - π interactions. All hydrogen atoms and ethyl groups on nitrogen atoms were omitted for clarity in **1**. (c) 3D supramolecular network of **1** via π - π interactions and C-H··· π interactions. All hydrogen atoms except those participating in the C-H··· π hydrogen bonds and ethyl groups on nitrogen atoms were omitted for clarity.



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Fig. 3(b)



Fig. 3(c)

Fig. 3 (a) Perspective view of 3 and anisotropic displacement parameters depicting 50% probability. All hydrogen atoms were omitted for clarity. Symmetry code: i: 1-x, 2-y, 1-z. Selected bond lengths (Å) and angles (°): Ag(1)-Cl(1) 2.390(1), Ag(1)-Ag(2) 3.077(6), Ag(2)-C(7) 2.104(8); Cl(1)-Ag(1)-Cl(1A) 180.0(1), 180.0, Ag(2)-Ag(1)-Ag(2A)C(7)-Ag(2)-C(34) 171.4(3), C(7)-Ag(2)-Ag(1) 100.0(2), Cl(1)-Ag(1)-Ag(2) 88.6(5), Cl(1A)-Ag(1)-Ag(2) 91.4(5), N(1)-C(7)-N(2) 105.4(6). (b) The 2D supramolecular layer of 3 via two types of π - π interactions. All hydrogen atoms and n-butyl groups on nitrogen atoms were omitted for clarity. (c) 3D supramolecular network of 3 via π - π interactions and C-H··· π interactions. All hydrogen atoms and n-butyl groups on nitrogen atoms except those participating in the C-H $\cdots\pi$ hydrogen bonds were omitted for clarity.

As shown in Fig. 2(a), each palladium atom in complex **2** is surrounded by one carbene carbon atom, one nitrogen atom from acetonitrile and two chlorine atoms to adopt a square *trans* conformation. The C(7)-Pd(1)-N(5) and Cl(1)-Pd(1)-Cl(2) arrays are almost linear with the bond angles of $178.2(1)^{\circ}$ and $175.8(3)^{\circ}$, respectively. The bond distances of Pd(1)-C(7), Pd(1)-Cl(1) and Pd(1)-N(5) are 1.935(3) Å, 2.302(1) Å and 2.090(4) Å, respectively. Two PdCl₂(NCCH₃) arms in the same molecule point to opposite directions.



Fig. 2(a)



Fig. 2 (a) Perspective view of 2 and anisotropic displacement parameters depicting 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-C(7) 1.935(3), Pd(1)-N(5) 2.090(4), Pd(1)-Cl(1) 2.302(1), Pd(1)-Cl(2) 2.288(1), N(5)-C(35) 1.118(5), C(35)-C(36) 1.454(6); C(7)-Pd(1)-N(5) 178.2(1), C(7)-Pd(1)-Cl(2) 87.4(1), C(7)-Pd(1)-Cl(1) 89.1(1), N(1)-C(7)-N(2) 107.0(3). (b) 2D supramolecular layer of 2 via C-H…Cl hydrogen bonds. All hydrogen atoms except those participating in the C-H…Cl hydrogen bonds and ethyl groups on nitrogen atoms were omitted for clarity.

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Complexes 4 and 5 have similar 1D polymeric chains, and only alkyl groups on nitrogen atoms are different as shown in Fig. 4(a) and Fig. 5(a) (ⁿPr for 4 and ⁿBu for 5). Each 1D polymeric chain in 4 and 5 is formed by the monomers ($L^{3}Ag_{2}Cl_{2}$ for 4 $L^{4}Ag_{2}Cl_{2}$ for 5) via weak Ag…Cl bonds (Ag…Cl separation = 3.167(1) Å for 4 and 3.404(1) Å for 5, and the van der Waals radii of chlorine = 1.8 Å). In each monomer of 4 and 5, the bond distances of Ag-C and Ag-Cl are 2.087(5) Å and 2.344(2) Å for 4 and 2.100(7) Å and 2.419(1) Å for 5, respectively. In parallelogram Ag₂Cl₂ units of 4 and 5, the bond angles of Ag-Cl-Ag and Cl-Ag-Cl are 101.7(3)° and 78.3(2)° for 4, and 89.8(5)° and 90.2(5)° for 5, respectively. All interval Ag₂Cl₂ units in 4 and 5 are parallel, however, two adjacent Ag₂Cl₂ units form the dihedral angles of 49.8(1)° for 4 and 35.9(6)° for 5, respectively. An interesting feature is that each monomer in polymers 4 and 5 (Fig. 4(b) and Fig. 5(b)).

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Fig. 4 (a) 1D polymeric chain of of 4. All hydrogen atoms were omitted for clarity. Symmetry code: i: 3-x, -y, 1-z. Selected bond lengths (Å) and angles (°): Ag(2)-C(34) 2.087(5), Ag(2)-Cl(2) 2.344(2); C(34)-Ag(2)-Cl(2) 173.7(1), N(3)-C(34)-N(4) 105.7(4). (b) Perspective view of the cage-like cavity in the monomer of 4. All hydrogen atoms were omitted for clarity. (c) 2D supramolecular layer of 4 via π-π interactions. All hydrogen atoms and n-propyl groups were omitted for clarity.

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Fig. 5 (a) 1D polymeric chain of of 5. All hydrogen atoms were omitted for clarity. Symmetry code: i: 2-x, y, 0.5-z; ii: 1+x, -y, 0.5+z. Selected bond lengths (Å) and angles (°): Ag(1A)-C(7A) 2.100(7), Ag(1A)-Cl(1A) 2.419(1); C(7A)-Ag(1A)-Cl(1A) 167.9(2), N(1A)-C(7A)-N(2A) 105.5(6). (b) Perspective view of the cage-like cavity in the monomer of 5. All hydrogen atoms were omitted for clarity. (c) 2D supramolecular layer of 5 via π-π

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interactions. All hydrogen atoms and n-butyl groups were omitted for clarity.

Each cation in **6** contains a 10-membered macrometallocycle formed by one bidentate chelate carbene ligand and one metal atom (Fig. 6(a)). The mercury(II) atom in the cation of **6** is tricoordinated with two carbene carbon atoms and one iodine atom. The angles of C-Hg-C and C-Hg-I are $166.5(4)^{\circ}$ and $96.3(3)^{\circ}$. The distances of Hg-C and Hg-I are 2.110(1) Å and 3.034(1) Å. These data are analogous to those of some known NHC mercury(II) complexes.¹⁵ In the anionic unit $[HgI_4]^{2-}$ of **6**, the mercury(II) atom is surrounded by four iodine atoms affording a slightly distorted tetrahedral arrangement, in which the bond angles of four I-Hg-I are in the range of $103.7(3)-115.1(3)^{\circ}$, and the distance of Hg-I vary from 2.779(1) Å to 2.819(1) Å.

Compared to complex **6**, each cation in complexes **7** and **8** also contains a 10-membered macrometallocycle formed by one bidentate chelate carbene ligand and one metal atom (Fig. 7(a) and Fig. 8(a)). In complex **7**, the mercury(II) atom is tetracoordinated with two carbene carbon atoms, one nitrogen atom of pyridine ring and one bromine atom to adopt a distorted tetrahedral geometry. The C(13)-Hg(1)-C(25) array is approximately linear with the bond angles of 173.3(3)°. The bond angles of N(1)-Hg(1)-C(13) and N(1)-Hg(1)-C(25) are 76.3(2)° and 104.1(3)°, respectively. The bond distances of Hg(1)-C(13) (2.093(6) Å) in **7** is similar to that of Hg-C bond (2.110(1) Å) in **6**. The distance of Hg(1)-N(1) is 2.785(2) Å. In the anionic unit $[HgBr_4]^{2-}$ of **7**, the mercury(II) atom is surrounded by four bromine atoms to afford a slightly distorted tetrahedral arrangement, in which the bond angles of four Br-Hg-Br are in the range of 103.4(3)-119.6(4)°, and the distance of Hg-Br vary from 2.561(1) Å to 2.752(8) Å. Besides, the cation and anion are connected together via weak Hg-Br bond (Hg-Br distance = 3.011(9) Å).

In complex **8**, the silver(I) atom has a linear dicoordinated structure with a C(14)-Ag(1)-C(32) bond angles of 178.5(1)°. The distance of C-Ag bond (2.105(3) Å) is similar to that of C-Ag bond (2.087(5)-2.107(4) Å) in **1** and **3-5**.

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Fig. 6(a)



Fig. 6(b)

Fig. 6 (a) Perspective view of 6 and anisotropic displacement parameters depicting 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)-C(7) 2.110(1), Hg(1)-I(1) 3.0345(1); C(7)-Hg(1)-C(29) 166.5(4), C(7)-Hg(1)-I(1) 96.3(3), C(29)-Hg(1)-I(1) 97.2(3), N(1)-C(2)-N(2) 108.3(1). (b) 1D double strand supramolecular chain of 6 via C-H…π contacts and C-H…I hydrogen bonds. All hydrogen atoms except those participating in the C-H…π contacts and C-H…I hydrogen bonds, and irrelevant methyl groups on mesitylene and irrelevant butyl groups were omitted for clarity.

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Fig. 7(a)



Fig. 7(b)



Fig. 7(c)

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Fig. 7 (a) Perspective view of 7 and anisotropic displacement parameters depicting 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)-C(13) 2.108(7), Hg(1)-N(1) 2.785(2), Hg(1)-Br(1) 3.001(9), Hg(2)-Br(1) 2.752(8); C(25)-Hg(1)-C(13) 173.3(3), C(13)-Hg(1)-N(1) 76.3(2), C(25)-Hg(1)-N(1) 104.1(3), N(2)-C(13)-N(3) 107.7(6). (b) 2D supramolecular layer of 7 by π-π interactions, weak Hg…Br bonds and C-H…Br hydrogen bonds. All hydrogen atoms except those participating in the C-H…Br hydrogen bonds and the methyl groups on mesitylene were omitted for clarity. (c) 3D supramolecular architecture of 7 via π-π interactions, weak Hg…Br bonds and C-H…Br hydrogen bonds and the methyl groups on mesitylene were omitted for clarity.



Fig. 8(a)



Fig. 8(b)

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Fig. 8(c)

Fig. 8 (a) Perspective view of 8 and anisotropic displacement parameters depicting 50% probability. All hydrogen atoms, NO₃⁻ and Br⁻ were omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)-C(14)2.105(3);C(14)-Ag(1)-C(32)178.5(1), N(1)-C(14)-N(2)2D 105.7(3). (b) supramolecular layer of 8 via three types of π - π interactions. All hydrogen atoms were omitted for clarity. (c) 3D supramolecular architecture of 8 by three types of π - π interactions and C-H···O hydrogen bonds. All hydrogen atoms except those participating in the C-H--O hydrogen bonds were omitted for clarity.

The crystal packings of complexes 1-8

Complexes **1** and **3** have similar crystal packings, and their 2D supramolecular layers are formed by two types of π - π interactions (Fig. 1(b) and Fig. 3(b)).¹⁶ One is from intermolecular benzene rings, and another is from the intermolecular benzimidazole rings (Table S3). Additionally, their 2D supramolecular layers are further extended into 3D architecture through C-H… π contacts (Fig. 1(c) and Fig. 3(c)).¹⁷ In the C-H… π contacts (Table S3), the hydrogen atoms are from CH₂ of ether chains for **1**, and from CH₃ of butyl group for **3**, and π systems are from benzene rings for **1** and **3**.

An interesting feature in the crystal packing of 2 is that 2D supramolecular layer is formed through C-H···Cl hydrogen bonds as shown in Fig. 2(b).¹⁸ The hydrogen

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atoms in the hydrogen bonds are from methyl of acetonitrile (Table S4).

Complexes 4 and 5 have also similar crystal packings, and their 2D supramolecular layers are formed via intermolecular π - π interactions from benzimidazole (Fig. 4(c) and Fig. 5(c)).

Double strand 1D supramolecular chain of **6** is formed by C-H··· π contacts and C-H···I hydrogen bonds (Fig. 6(b)).¹⁹ In C-H··· π contacts, the hydrogen atoms are from CH₂ of propyl groups and benzimidazole rings, respectively, and π systems are from benzene rings of mesitylenes. In C-H···I hydrogen bonds, the iodine atoms are from the anionic unit [HgI₄]²⁻, and the hydrogen atoms are from CH₂ of propyl groups and benzimidazole rings, respectively.

An interesting feature in the crystal packing of **7** (Fig. 7(b)) is that 2D supramolecular layers are formed via three types of weak interactions, including π - π interactions from the benzimidazole rings, C-H···Br hydrogen bonds²⁰ and weak Hg···Br bonds (Hg···Br distance = 3.011(2) Å; the sum of van der Waals Radii of mercury and bromine = 3.65 Å). In C-H···Br hydrogen bonds, the hydrogen atoms are from pyridine rings and bromine atoms are from [HgBr₄]²⁻ units. Additionally, 2D layers are further extended into 3D supramolecular architectures (Fig. 7(c)) via new C-H···Br hydrogen bonds. In new C-H···Br hydrogen bonds, the hydrogen atoms are from CH₂ and bromine atoms from [HgBr₄]²⁻ units.

Compared to the crystal packing of 7, 2D supramolecular layer in 8 is formed two types of π - π interactions (Fig. 8(b)). One is from intermolecular benzimidazole rings, and another is from intermolecular benzene rings of mesitylenes. Additionally, anionic unit NO₃⁻ are packed between successive layers and hold the layers together via C-H···O hydrogen bonds,²¹ which extends the above 2D layers into 3D supramolecular architectures (Fig. 8(c)). In the C-H···O hydrogen bonds, the hydrogen atoms are from benzimidazole rings and oxygen atoms are from nitryl groups.

The effects of some experimental conditions on N-heterocyclic silver complexes

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The effects of various experimental conditions, such as different silver base (Ag₂O, Ag_2CO_3 or Ag(OAc), the radio between ligand and silver base, the solvents used in crystallization, the anion and the structures of ligands, on N-heterocyclic silver complexes have been reviewed in detail by Lin et al in 2007.²² Additionally, the different structures of N-heterocyclic silver complexes formed via the reaction of benzimidazolium (or imidazolium) salts of chloride with silver bases have also been reported, ^{5a, 5d, 6c, 13b} in which the by-products bearing silver(I) are mainly AgCl, AgCl₂ or $Ag_2Cl_4^{2-}$, and they can transform to each other under appropriate conditions. Under a certain condition, one of them may be predominant. These anions may be dissociative or form N-heterocyclic silver complexes along with ligands. Therefore, the components of crude product and single crystal in N-heterocyclic silver complexes may be same or different under different conditions. However, there are not clear rules to be found between the structures of N-heterocyclic silver complexes and experimental conditions. The single crystal structure of N-heterocyclic silver complex is mainly relevant to the crystallization condition, especially the solvent used in crystallization.²³ Besides, the structure of complex itself (such as size of N-side arms, imidazole ring and benimidazole ring etc) could also have some effects on single crystal structure. The effect of solvent on single crystal structure displays mainly in two aspects. Firstly, the cation and anion in complex can conduct different association in different solvent, which may lead to different components contained in crude product and single crystal. Secondly, the solvent molecule can fill in the gaps of crystal packing, and thus different solvent molecules contained in crystals can lead to the different crystal shape. By contrast, the temperature in crystallization may have small effect on single crystal structure, and it influences mainly both the speed of crystallization and the size of single crystal particle.

In order to explore further the relations between N-heterocyclic silver complexes and experimental conditions, we chose the reaction of bis-benzimidazolium salt ligands (L^1H_2 and L^2H_2) with Ag bases (Ag₂O and Ag(OAc)) to test the effects of

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some experimental conditions on the products, yields and reproducibility. In the reaction of ligand $L^{1}H_{2}$ with Ag₂O (Table 1), when the radio between $L^{1}H_{2}$ and Ag₂O (equiv/equiv) is equal to 1:1 in 40°C in 6 h, the crude product $[(L^1Ag)_2Ag_2Cl_4]$ (I) was obtained with yield of 49% (entry 1). The crude product I was characterized by 1 H NMR, element analysis and melting point, and its components are the same as those of single crystal structure 1 obtained by X-ray analysis. When time was prolonged to 8 h and 10 h under same radio and temperature, the same crude product I was obtained with yields of 63% and 62% (entries 2 and 3). When temperature was dropped to 25°C and time is 10 h under same radio, only the yield of 46% was obtained (entry 4). Thus, when $L^{1}H_{2}/Ag_{2}O$ (equiv/equiv) is equal to 1:1, 8 h and 40 °C are found to be the optimal time and temperature. Two times repeating tests in 8 h and in 40 °C were carried out when $L^{1}H_{2}/Ag_{2}O$ (equiv/equiv) is equal to 1:2 and 1:3, and the yields of 61-63% were obtained (entries 5-8). The results show that excess Ag₂O has not obvious effect on the crude products and yields. Furthermore, this type of reaction has good reproducibility. Similarly, the reaction of ligand $L^{1}H_{2}$ with Ag(OAc) was also carried out (Table S5). The results obtained were similar to the case of Ag₂O, and only optimal time rose up to 16 h, which shows that different Ag bases have not obvious effect on the crude products, yields and reproducibility.

As a comparison, the reaction of L^2H_2 with Ag₂O (or Ag(OAc)) were also carried out (Tables S6 and S7) under the similar experimental condition. Using Ag₂O or Ag(OAc) as silver base, the same crude product $[(L^2Ag)_2AgCl_2][AgCl_2]$ (II) was obtained, and other results are similar to those from $L^{1}H_{2}$. The product II was characterized by ¹H NMR, element analysis and melting point, and its components are the same as those of single crystal structure **3** obtained by X-ray analysis. Notably, the $[(L^1Ag)_2Ag_2Cl_4]$ L^1H_2 and structures of product **(I**) from product $[(L^2Ag)_2AgCl_2][AgCl_2]$ (II) from L^2H_2 are different, and they contain similar NHC-Ag unit (L¹Ag and L²Ag) and different anionic units ([Ag₂Cl₄] for $L^{1}H_{2}$ and $[AgCl_2]$ for L^2H_2). This may be attributed to the difference of ligands (N-side arms being ethyl group for L^1 and n-butyl group for L^2).

Summary, the different Ag base and excess Ag base have not obvious effect on

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the crude products and yields in the preparation of N-heterocyclic silver complexes. But use of Ag(OAc) need longer reaction time than use of Ag₂O, and this may be reason why Ag₂O was used in the overwhelming majority of preparation of NHC-Ag complexes. Temperature and time in the reactions have not obvious effect on the crude product, however, have large effect on yields. Additionally, these reactions have all good reproducibility as shown in Table 1 and Tables S5-S7.

$L^{1}H_{2} \xrightarrow{Ag_{2}O} \left[(L^{1}Ag)_{2}Ag_{2}Cl_{4} \right] $ (I)						
L ¹ H ₂ /Ag ₂ O	Entry	Time (h)	Temp. (°C)	Crude	Ag ₂ O	
(equiv/equiv)				product ^[b]	yield (%)	
1:1	1	6	40	Ι	49	
	2	8	40	Ι	63	
	3	10	40	Ι	62	
	4	10	25	Ι	46	
1:2	5	8	40	Ι	63	
	6	8	40	Ι	61	
1:3	7	8	40	Ι	61	
	8	8	40	Ι	62	

Table 1 The reaction of ligand L^1H_2 with $Ag_2O^{[a]}$

[a] Reaction conditions: the solvent CH₂Cl₂ in N₂.

[b] Crude product was characterized by ¹H NMR, element analysis and melting point.

Catalytic activity of NHC palladium(II) complex 2

The Suzuki-Miyaura cross-coupling reaction of aryl halides and arylboronic acids is of general interest to organic synthesis. The Suzuki-Miyaura reaction catalyzed by Pd-NHC complexes has provided an efficient and powerful method for the formation of carbon-carbon and carbon-heteroatom bonds.²⁴ We choose the cross-coupling reaction of 4-bromotoluene with phenylboronic acid as a model reaction to test the solvent and base effects (Table 2). Use of absolute MeOH as solvent and K₃PO₄·3H₂O as base gives 69% coupling yield at 50 °C in 24 h in air (entry 1). Use of pure water as solvent and K₃PO₄·3H₂O as base gives 25% coupling yield at 50 °C in 24 h in air (entry 2). Use of MeOH/H₂O (1:1) as mixed solvent and K₃PO₄·3H₂O as base gives the yield of 90% in 5 h in air (entry 3) and the yield of 98% in 22 h in air (entry 4).

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The higher activity is attributed to the better solubility of catalyst and $K_3PO_4 \cdot 3H_2O$ in the aqueous MeOH mixture and rapid reduction of Pd(II) to Pd(0).²⁵ Up on using MeOH/H₂O (1:1) as mixed solvent and using other bases (such as KOH, K₂CO₃ and NaHCO₃), the yields of 73-95% are obtained (entries 5-7). Based on the extensive screen, MeOH/H₂O (1:1) and $K_3PO_4 \cdot 3H_2O$ are found to be the most efficient solvent and base with a catalyst loading of 0.1 mol % complex **2** at 50 °C in air, thus giving the optimal coupling result. The reactions were monitored by GC analysis after the appropriate intervals. In order to further study the influence of ligand on catalysis, the control experiment was performed, in which PdCl₂(CH₃CN)₂ were added in the absence of ligand with the optimized conditions, and only 18% coupling product was obtained (entry 8). This result shows that the ligand has the preponderant function in the catalytic reaction.

Published on 16 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CE25365H

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We attempted the cross-coupling reaction of various aryl halides with phenylboronic acid under the optimal reaction condition (Table 3). In general, complex 2 can catalyze the cross-coupling of various aryl halides with phenylboronic acid to give different yields. The catalyst is high efficiency toward the coupling of aryl bromides with phenylboronic acid to give 83-95% yields (entries 1-7). The aryl chlorides could be also coupled with phenylboronic acid, in which 4-chloroaniline, 2-chlorotoluene and 2,4-dinitrochlorobenzene are coupled with phenylboronic acid to lead to medium yields of 56-78% (entries 8-10), and 2-nitrochlorobenzene and 2-chlorobenzaldehyde lead to poor yields of 10% and 14% (entries 11 and 12). Notably, the cross-coupling reaction of some aryl halides with phenylboronic acid under the optimal reaction condition is difficult, but when 0.1 mol% tetrabutylamonium bromide (TBAB) or 0.1 mol% PPh₃ is added, the coupling reactions can be smoothly carried out (entries 5-8). This result shows that the cross-coupling reactions could be dramatically improved in the presence of TBAB²⁶ or PPh₃.²⁷ It has been known that the addition of TBAB as a cocatalyst can enhance the activity of many catalystic systems. And TBAB is able to activate and stabilize the palladium(0) species in situ generated, which is believed to be the real catalytically active species. Above results show that this catalyst has high stability to air and water,

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and good tolerance toward various functional groups, to make it into a valuable precatalyst for thermally sensitive substrates. Therefore, this catalytic system provides an effective method for facile coupling of aryl halides under mild and aerobic conditions.

 Table 2 Suzuki-Miyaura Coupling Reaction of 4-bromotoluene with phenylboronic acid catalyzed by complex 2^[a]

[a] Reaction conditions: 4-bromotoluene 0.50 mmol, phenylboronic acid 0.60 mmol, base 1.2 mmol, complex 2 0.1 mol %, solvent 3 mL, 50 °C in air.

- [b] Reactions were monitored by TLC.
- [c] Determined by GC.
- [d] Reaction conditions are the same as [a], and only PdCl₂(CH₃CN)₂ was added in the absence of ligand.

Table 3 Suzuki-Miyaura coupling reaction of aryl halides with phenylboronic acid

catalyzed by complex **2**^[a]

R	× +	$ B(OH)_2 = \frac{0.1 \text{ m}}{\text{MeOH}} $	ol % cat, base → H ₂ O, 50□, air	R R
	Entry	Aryl halide	Time (h) ^[b]	Yield (%)
	1	4-bromoanisole	7	91 ^[c]
	2	4-bromoanisole	26	95 ^[c]
	3	3-bromoanisole	6	95 ^[d]
	4	1-bromonaphthaline	28	90 ^[d]
	5 ^[e]	4-bromoaniline	40	94 ^[d]

$6^{\left[f ight]}$	4-bromoacetophenone	40	86 ^[d]
7 ^[f]	4-nitrobromobenzene	40	83 ^[d]
8 ^[e]	4-chloroaniline	40	78 ^[d]
9	2-bromotoluene	36	56 ^[d]
10 ^[f]	2,4-dinitrochlorobenzene	40	72 ^[d]
11 ^[f]	2-nitrochlorobenzene	40	$10^{\left[d ight]}$
12 ^[f]	2-chlorobenzaldehyde	40	14 ^[d]

[a] Reaction conditions: aryl halide 0.50 mmol, phenylboronic acid 0.60 mmol, K₃PO₄·3H₂O 1.2 mmol, complex 2 0.1 mol %, MeOH/H₂O (1:1) mixed solvent 3 mL, 50°C in air.

- [b] Reactions were monitored by TLC.
- [c] Determined by GC.
- [d] Isolated yield.
- [e] TBAB 0.1 mol % was added, complex 2 0.3 mol %, 70 °C.
- [f] PPh₃0.1 mol % was added, complex 20.3 mol %, 70 °C.

Conclusions

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In summary, a series of NHC silver(I), palladium(II) and mercury(II) complexes have been synthesized and characterized. The complexes 1-8 adopt four different structures: (1) the bis-macrometallocycles connected via Ag_2Cl_4 unit for 1 and via $AgCl_2$ unit for **3**, (2) the open structure formed via one ligand and two metal atoms for **2**, (3) 1D polymeric chains formed by the monomers of cage-like cavity via weak Ag...Cl bonds (monomer: $L^{3}Ag_{2}Cl_{2}$ for **4** and $L^{4}Ag_{2}Cl_{2}$ for **5**) and (4) the macrocyclic structure formed by one ligand and one metal for 6-8. In crystal packings, 1D supramolecular chain of 6, 2D supramolecular layers of 2, 4 and 5 and 3D supramolecular architectures of 1, 3, 7 and 8 are formed via intermolecular weak interactions, including π - π interactions, hydrogen bonds, C-H··· π contacts and weak Hg···Br bonds. The resultant structures of these complexes will provide valuable experimental data engineering and supramolecular chemistry. Additionally, for crystal the macrometallocycles of 1, 3 and 6-8 and the structures of cage-like cavity of 4 and 5 suggest that they may have potential applications in the host-guest chemistry. The study of catalytic activity of NHC Pd(II) complex 2 in Suzuki-Miyaura cross-coupling

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reaction shows that this complex can catalyze the coupling reaction of aryl halides (iodide, bromide and chloride) with phenylboronic acid in MeOH/H₂O as solvent and K_3PO_4 ·3H₂O as base in air. Therefore, this catalytic system provides an effective phosphine-free catalyst for facile coupling of aryl halides under mild and aerobic conditions. Further studies on new organometallic compounds from precursors L^1H_2 - L^7H_2 and analogous ligands are underway.

Experimental Section

General procedures

All manipulations were performed using Schlenk techniques, and solvents were purified by standard procedures. All the reagents for synthesis and analyses are of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. IR spectra were measured with a Bruker IR Equinox-55 infrared spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts, δ , are reported in ppm relative to the internal standard TMS for both ¹H and ¹³C NMR. *J* values are given in Hz. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. GC analysis was carried out using a Focus DSQI GC-MS equipped with an integrator (C-R8A) with a capillary column (CBP-1 or CBP-5, 0.25 mm i.d. × 40 m).

Synthesis of 1,2-bis(2-(chloromethyl)phenoxy)ethane. Salicylic aldehyde (15.601 g, 127.7 mmol) and 1,2-dibromoethane (10.000 g, 53.2 mmol) were added to DMF (80 mL) containing potassium carbonate (17.656 g, 127.7 mmol), and the mixture solution was stirred for 24 hours at 50°C in nitrogen protection. The colorless solution became yellow, and finally the dark brown solution was obtained. The resulting solution was poured into a beaker of 500 mL containing water (200 mL) with stirring, and a brown powder of 1,2-bis(2-formylphenoxy)ethane by filtration was obtained. Yield: 12.196 g (85%). M.p.: 146-148 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 4.44 (s,

4H, CH₂), 7.01-7.08 (m, 4H, Ph*H*), 7.53 (t, *J* = 8.8, 2H, Ph*H*), 7.80 (d, *J* = 8.0, 2H, Ph*H*), 10.53 (s, 2H, CHO).

The sodium borohydride (3.359 g, 88.8 mmol) was slowly added to the solution of 1,2-bis(2-formylphenoxy)ethane (10.000 g, 37.0 mmol) in tetrahydrofuran and ethanol (100 mL, v/v = 1:1) in ice water bath for 1 hour, and the solution was stirred continuously for 2 hours at room temperature, and then was refluxed for 10 hours. The solvent was removed with a rotary evaporator and H₂O (100 mL) was added to the residue, and acetic acid was added dropwise to the solution until pH = 7. The solution was extracted with CH₂Cl₂ (30 mL × 3) and washed with sodium chloride solution, and the extracting solution was dried over anhydrous MgSO₄. After removing CH₂Cl₂, a white solid 1,2-bis(2-hydroxymethylphenoxy)ethane was obtained. Yield: 9.192 g (91%). M.p.: 122-124°C. ¹H NMR (400 MHz, DMSO-d₆): δ 4.31 (s, 4H, CH₂), 4.49 (s, 4H, CH₂), 6.95-7.00 (m, 4H, PhH), 7.18 (t, *J* = 7.5, 2H, PhH).

Thionyl chloride (17.348 g, 145.8 mmol) was added dropwise to the chloroform (100 mL) solution of 1,2-bis(2-hydroxymethylphenoxy)ethane (10.000 g, 36.5 mmol) and pyridine (11.534 g, 145.8 mmol). The mixture solution was stirred for 12 hours at 70°C. The resulting mixture was poured into a beaker of 500 mL, and water of 300 mL was added. The chloroform layer was separated and dried over anhydrous MgSO₄. After removing CHCl₃, a white solid 1,2-bis(2-(chloromethyl)phenoxy)ethane was obtained. Yield: 8.475 g (75%). M.p.: 96-98°C. ¹H NMR (400 MHz, DMSO-d₆): δ 4.43 (s, 4H, CH₂O), 4.70 (s, 4H, CH₂Cl), 6.96 (d, *J* = 7.2, 2H, Ph*H*), 7.14 (d, *J* = 8.4, 2H, Ph*H*), 7.34-7.41 (m, 4H, Ph*H*).

Synthesis of 1,3-bis(2-(chloromethyl)phenoxy)propane. This compound was prepared in a manner analogous to that of 1,2-bis(2-(chloromethyl)phenoxy)ethane. Yield: 8.165 g (72.4%). M.p.: 97°C. ¹H NMR (400 MHz, DMSO-d₆): δ 2.26-2.29 (m, 2H, CCH₂C), 4.31 (t, *J* = 6.0, 4H, CH₂O), 4.72 (s, 4H, CH₂Cl), 6.93 (t, *J* = 7.2, 2H, Ph*H*), 7.05 (d, *J* = 8.0, 2H, Ph*H*), 7.35-7.38 (m, 4H, Ph*H*).

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Synthesis of 1,2-bis[2-(N-ethylbenzimidazolemethyl)phenoxy]ethane chloride ($L^{1}H_{2}$). A solution of 1-ethylbenzimidazole (2.066 g, 14.1 mmol) and 1,2-bis(2-(chloromethyl)phenoxy)ethane (3.409 g, 6.4 mmol) in acetone (100 mL) was stirred for 5 days under refluxing, and a white precipitate was formed. The product was filtered and washed with acetone. The white powder of dibenzimidazolium salt $L^{1}H_{2}$ was obtained by recrystallization from methanol/ether. Yield: 3.127 g (81%). M.p.: 154-156°C. ¹H NMR (400 MHz, DMSO-d₆): δ 1.35 (t, J = 6.9, 6H, CH₃), 4.13 (q, J = 6.9, 4H, CH₂), 4.35 (s, 4H, CH₂), 5.50 (s, 4H, CH₂), 7.05-7.09 (m, 4H, PhH), 7.34-7.38 (m, 4H, PhH), 7.52-7.56 (m, 4H, PhH), 7.75 (d, J = 8.4, 2H, PhH), 7.93 (d, J = 8.4, 2H, PhH), 9.65 (s, 2H, 2-bimiH) (bimi = benzimidazole).

The following bis-benzimidazolium salts $L^2H_2-L^4H_2$ were prepared in a manner analogous to that of L^1H_2 .

Synthesis of 1,2-bis[2-(N-ⁿbutyl-benzimidazolemethyl)phenoxy]ethane chloride (L²H₂). Yield: 3.279 g (77%). M.p.: 273-276°C. ¹H NMR (400 MHz, DMSO-d₆): δ 0.83 (t, J = 7.2, 6H, CH_3), 1.19-1.26 (m, 4H, CH_2), 1.72-1.80 (m, 4H, CH_2), 4.30 (s, 4H, CH_2), 4.35 (t, J = 7.2, 4H, CH_2), 5.58 (s, 4H, CH_2), 7.05-7.10 (m, 4H, Ph*H*), 7.12-7.41 (m, 4H, Ph*H*), 7.53-7.60 (m, 4H, Ph*H*), 7.78 (d, J = 8.4, 2H, Ph*H*), 9.70 (s, 2H, 2-bimi*H*).

Synthesis of 1,3-bis[2-(N-ⁿpropyl-benzimidazolemethyl)phenoxy]propane chloride (L³H₂). Yield: 3.223 g (81%). M.p.: 232-234°C. ¹H NMR (400 MHz, DMSO-d₆): δ 0.86 (t, J = 7.2, 6H, CH₃), 1.81-1.83 (m, 4H, CH₂), 1.86-1.88 (m, 4H, CH₂), 3.97 (t, J = 6.0, 4H, CH₂), 4.52 (t, J = 8.0, 4H, CH₂), 5.68 (s, 4H, CH₂), 7.00 (t, J = 8.0, 4H, PhH), 7.03 (d, J = 8.0, 2H, PhH), 7.37 (t, J = 7.8, 2H, PhH), 7.57 (m, 4H, PhH), 7.94 (d, J = 8.0, 2H, PhH), 8.10 (d, J = 8.0, 2H, PhH), 10.01 (s, 2H, 2-bimiH). Synthesis of 1,3-bis[2-(N-ⁿbutyl-benzimidazolemethyl)phenoxy]propane chloride (L⁴H₂). Yield: 3.371 g (81%). M.p.: 202-204°C. ¹H NMR (400 MHz, DMSO-d₆): δ 0.84 (t, *J* = 7.4, 6H, *CH*₃), 1.24-1.30 (m, 4H, *CH*₂), 1.81-1.85 (m, 4H, *CH*₂), 2.09 (m, 2H, *CH*₂), 3.99 (t, *J* = 6.0, 4H, *CH*₂), 4.50 (t, *J* = 7.0, 4H, *CH*₂), 5.70 (s, 4H, *CH*₂), 6.94 (d, *J* = 8.4, 2H, Ph*H*), 6.99 (t, *J* = 7.4, 2H, Ph*H*), 7.35 (t, *J* = 7.8, 2H, Ph*H*), 7.55-7.66 (m, 6H, Ph*H*), 7.96 (d, *J* = 8.4, 2H, Ph*H*), 8.09 (d, *J* = 8.4, 2H, Ph*H*), 10.03 (s, 2H, 2-bimiH).

Synthesis of 1,3-bis[1-ⁿbutyl-benzimidazolemethyl]mesitylene iodide ($L^{5}H_{2}$). A solution of 1-ⁿbutylbenzimidazole (2.509)14.4mmol) and g, 1,3-dibromomethylmesitylene (2.000 g, 6.5 mmol) in THF (100 mL) was stirred for five days under refluxing, and a white precipitate was formed. The product was filtred THF. and washed with The white powder of 1,3-bis[1-ⁿbutyl-benzimidazolemethyl]mesitylene bromide was obtained by recrystallization from methanol/ether. Yield: 3.978 g (93%).

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NaI (1.319 g, 8.8 mmol) was added to a acetone solution of 1,3-bis[1-ⁿbutyl-benzimidazolemethyl]mesitylene bromide (2.618 g, 4.0 mmol) with stirring and a white precipitate is formed immediately. The product was collected by filtration, washed with small portions of acetone, and dried in vacuum to give a white powder of 1,3-bis[1-ⁿbutyl-benzimidazolemethyl]mesitylene iodide (L^5H_2). Yield: 2.455 g (82%). M.p.: 220-222°C. Anal. Calcd for C₃₃H₄₂N₄I₂: C, 52.95; H, 5.65; N, 7.48%. Found: C, 52.63; H, 5.89; N, 7.81%. ¹H NMR (400 MH_Z, DMSO-d₆): δ 1.22 (t, *J* = 6.0, 6H, CH₃), 1.38 (m, 4H, CH₂), 1.89 (m, 4H, CH₂), 2.08 (s, 6H, CH₃), 2.33 (s, 3H, CH₃), 4.27 (t, *J* = 5.4, 4H, CH₂), 5.79 (s, 4H, CH₂), 7.30 (s, 1H, PhH), 7.52 (m, 4H, PhH), 7.86 (d, *J* = 7.2, 2H, PhH), 8.20 (d, *J* = 7.2, 2H, PhH), 9.58 (s, 2H, 2-bimiH).

Synthesis of 1,3-bis[1-pycolylbenzimidazolemethyl]mesitylene bromide (L⁶H₂).

A THF solution (40 mL) of benzimidazole (2.457 g, 20.8 mmol) was added to a suspension of oil-free sodium hydride (0.500 g, 20.8 mmol) in THF (40 mL) and

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stirred for 1 h at 60°C. Then pycolyl bromide (3.268 g, 19.0 mmol) was added dropwise to the above solution. The mixture was stirred for 22 h at 60°C, and a brown solution was obtained. The solvent was removed with a rotary evaporator and H₂O (50 mL) was added to the residue. Then the solution was extracted with CH₂Cl₂ (3 × 30 mL), and the extracting solution was dried with anhydrous MgSO₄. After removing CH₂Cl₂, a pale yellow solid was obtained.

(3.013 А solution of 1-pycolylbenzimidazole 14.4 mmol) and g, 1,3-dibromomethylmesitylene (2.000 g, 6.5 mmol) in acetone (100 mL) was stirred for five days under refluxing, and a white precipitate was formed. The product was filtred and washed with acetone. The white powder of 1,3-bis[1-pycolylbenzimidazolemethyl]mesitylene bromide ($L^{6}H_{2}$) was obtained by recrystallization from methanol/ether. Yield: 4.176 g (88%). M.p.: 300-302 °C. Anal. Calcd for C₃₇H₃₆N₆Br₂: C, 61.34; H, 5.01; N, 11.60%. Found: C, 61.62; H, 5.42; N, 11.35%. ¹H NMR (400 MH_Z, DMSO-d₆): δ 2.09 (s, 6H, CH₃), 2.43 (s, 3H, CH₃), 5.78 $(s, 4H, CH_2), 5.85 (s, 4H, CH_2), 7.25 (d, J = 6.8, 2H, PyH or PhH), 7.37 (s, 1H, PhH),$ 7.62-7.67 (m, 6H, PyH or PhH), 7.85 (t, J = 8.0, 2H, PyH or PhH), 7.93 (d, J = 8.2H, PyH or PhH), 8.21 (m, 4H, PyH or PhH), 9.47 (s, 2H, 2-bimiH).

Synthesis of 1,3-bis[1-benzylbenzimidazolemethyl]mesitylene bromide ($L^{7}H_{2}$). The compound was prepared in a manner analogous to that for $L^{6}H_{2}$, only instead of 1-pycolylbenzimidazole with 1-benzylbenzimidazole. Yield: 4.253 g (90%). M.p.: 280-282 °C. Anal. Calcd for C₃₉H₃₈N₄Br₂: C, 64.83; H, 5.30; N, 7.75%. Found: C, 64.52; H, 5.64; N, 7.91%. ¹H NMR (400 MH_Z, DMSO-d₆): δ 2.08 (s, 6H, CH₃), 2.34 (s, 3H, CH₃), 5.79 (s, 4H, CH₂), 5.81 (s, 4H, CH₂), 7.34 (m, 9H, PhH), 7.46 (d, *J* = 7.2, 2H, PhH), 7.67 (t, *J* = 6.8, 2H, PhH), 7.74 (t, *J* = 6.8, 2H, PhH), 7.90 (d, *J* = 8.0, 2H, PhH), 8.23 (d, *J* = 8.0, 2H, PhH), 9.80 (s, 2H, 2-bimiH).

Synthesis of complex $[(L^1Ag)_2Ag_2Cl_4]$ (1). Silver oxide (0.077 g, 0.3 mmol) was added to a solution of precursor L^1H_2 (0.164 g, 0.3 mmol) in dichloromethane (30 mL)

in N₂, and the suspension solution was stirred for 8 hours under refluxing. The resulting solution was filtered and concentrated to 5 mL, and Et₂O (5 mL) was added to precipitate a white powder. Isolation by filtration yields complex **1**. Yield: 0.169 g (63%). M.p.: 210-212°C. Anal. Calcd for C₃₄H₃₄Ag₂Cl₂N₄O₂: C, 49.96; H, 4.19; N, 6.86%. Found: C, 49.58; H, 3.85; N, 6.42%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.38 (t, *J* = 7.2, 6H, CH₃), 4.23 (s, 4H, CH₂), 4.54 (q, *J* = 7.2, 4H, CH₂), 5.72 (s, 4H, CH₂), 6.99-7.06 (m, 4H, PhH), 7.34-7.42 (m, 6H, PhH), 7.58 (d, *J* = 2.8, 2H, PhH), 7.70 (d, *J* = 6.8, 2H, PhH), 7.83 (d, *J* = 6.0, 2H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 156.7 (*C*_{carbene}), 134.0, 133.4, 131.5, 130.4, 124.4, 124.1, 121.2, 113.2, 112.7, 112.6 (PhC or imiC), 67.0 (NCH₂Ph), 50.5 (OCH₂C), 45.1 (CH₂), 17.7 (CH₃).

Synthesis of $[L^{1}(PdCl_{2}CH_{3}CN)_{2}]$ (2). The suspension solution of complex 1 (0.245 g, 0.3 mmol) and Pd(CH₃CN)₂Cl₂ (0.172 g, 0.7 mmol) in dichloromethane (30 mL) was stirred for 24 hours under refluxing in N₂ protection. The resulting solution was filtered and concentrated to 5 mL, and Et₂O (5 mL) was added to precipitate a pale yellow powder. Isolation by filtration yields complex 2. Yield: 0.191 g (55%). M.p.: 250-252°C. Anal. Calcd for C₃₈H₄₀Cl₄N₆O₂Pd₂: C, 47.18; H, 4.17; N, 8.69%. Found: C, 46.86; H, 3.93; N, 8.36%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.12 (t, *J* = 8.4, 6H, CH₃), 1.61 (s, 6H, CH₃), 4.28 (s, 4H, CH₂), 4.61 (q, *J* = 8.4, 4H, CH₂), 6.06 (s, 4H, CH₂), 6.90-7.05 (m, 4H, PhH), 7.36-7.45 (m, 6H, PhH), 7.66 (d, *J* = 8.4, 2H, PhH). 7.72 (d, *J* = 7.6, 2H, PhH), 7.80 (d, *J* = 8.4, 2H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 155.9 (*C*_{carbene}), 134.3, 133.8, 130.3, 129.5, 127.5, 124.2, 123.7, 121.5, 113.1, 112.6, 111.4 (PhC or imiC), 67.9 (NCH₂Ph), 47.4 (OCH₂C), 44.9 (NCH₂C), 44.2 (CH₂), 16.7 (CH₃), 16.1 (CH₃). IR (KBr): *v* CN, 2221 cm⁻¹.

Published on 16 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CE25365H

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Synthesis of complex $[(L^2Ag)_2AgCl_2][AgCl_2][3]$. Silver acetate (0.101 g, 0.6 mmol) was added to a solution of precursor L^2H_2 (0.181 g, 0.3 mmol) in dichloromethane (30 mL) in N₂, and the suspension solution was stirred for 18 hours under refluxing. The resulting solution was filtered and concentrated to 5 mL, and Et₂O (5 mL) was added to precipitate a white powder. Isolation by filtration yields complex **3**. Yield:

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0.174 g (66%). M.p.: 230-232°C. Anal. Calcd for $C_{38}H_{42}Ag_2Cl_2N_4O_2$: C, 52.26; H, 4.85; N, 6.41%. Found: C, 51.86; H, 4.43; N, 6.12%. ¹H NMR (400 MHz, DMSO-d₆): δ 0.86 (t, J = 7.2, 6H, CH₃), 1.30-1.36 (m, 4H, CH₂), 1.84-1.87 (m, 4H, CH₂), 4.27 (s, 4H, CH₂), 4.48 (t, J = 6.8, 4H, CH₂), 5.74 (s, 4H, CH₂), 6.97 (t, J = 7.2, 2H, PhH), 7.04 (d, J = 8.4, 2H, PhH), 7.30-7.44 (m, 6H, PhH), 7.58 (d, J = 6.8, 2H, PhH), 7.72 (d, J = 8.0, 2H, PhH), 7.84 (d, J = 8.0, 2H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 156.6 ($C_{carbene}$), 133.9, 131.6, 130.5, 124.4, 121.2, 113.2, 112.8 (PhC or imiC), 66.8 (NCH₂Ph), 50.6 (OCH₂C), 49.8 (NCH₂C), 33.7 (CH₂), 21.2 (CH₂), 15.2 (CH₃).

The following complexes **4** and **5** were prepared in a manner analogous to that of **1**, and only precurors are different from that of **1**.

Synthesis of complex $[(L^3Ag_2Cl_2)_n]$ (4). Yield: 0.185 g (70.0%). M.p.: 176-178°C. Anal. Calcd for C₃₇H₄₀Ag₂Cl₂N₄O₂: C, 51.71; H, 4.69; N, 6.52%. Found: C, 52.18; H, 4.67; N, 6.61%. ¹H NMR (400 MHz, DMSO-d₆): δ 0.81 (t, J = 7.4, 6H, CH₃), 1.79 (m, 4H, CH₂), 2.07 (m, 4H, CH₂), 4.03 (t, J = 2.4, 2H, CH₂), 4.30 (t, J = 7.0, 2H, CH₂), 5.63 (s, 4H, CH₂), 6.93-7.00 (m, 4H, PhH), 7.37-7.42 (m, 6H, PhH), 7.76-7.82 (m, 6H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 156.5 ($C_{carbene}$), 134.2, 133.6, 130.3, 124.4, 121.2, 113.0, 112.8 (PhC or imiC), 65.2 (NCH₂Ph), 51.5 (OCH₂C), 49.0 (NCH₂C), 29.7 (CH₂), 24.8 (CH₂), 12.7 (CH₃).

Synthesis of complex $[(L^4Ag_2Cl_2)_n]$ (5). Yield: 0.212 g (73.0%). M.p.: 174-176°C. Anal. Calcd for C_{19.50}H₂₂AgClN₂O: C, 52.78; H, 5.00; N, 6.31%. Found: C, 52.36; H, 4.76; N, 6.12%. ¹H NMR (400 MHz, DMSO-d₆): δ 0.78 (t, J = 7.2, 6H, CH₃), 1.21-1.27 (m, 4H, CH₂), 1.72-1.77 (m, 4H, CH₂), 2.09 (m, 2H, CH₂), 4.02 (t, J = 4.8, 4H, CH₂), 4.31 (t, J = 7.0, 4H, CH₂), 5.64 (s, 4H, CH₂), 6.93-6.99 (m, 4H, PhH), 7.27-7.43 (m, 8H, PhH), 7.77-7.84 (m, 4H, PhH). ¹³C NMR (100 MHz, DMSO-d₆): δ 156.6 ($C_{carbene}$), 134.2, 133.6, 130.7, 130.4, 124.5, 124.3, 121.2, 113.0, 112.9, 112.7 (PhC or imiC), 65.0 (NCH₂Ph), 49.8 (OCH₂C), 49.0 (NCH₂CH₂), 33.4 (CH₂), 29.5 (CH₂), 21.0 (CH₂), 15.0 (CH₃).

and

Synthesis of [L⁵HgI][HgI₄]_{0.5} (6). A suspension of KO^tBu (0.112 g, 1.0 mmol), (0.319)0.7 mercury iodide mmol) g, 1,3-bis[1-ⁿbutyl-benzimidazolemethyl]mesitylene hexafluorophosphate ($L^{5}H_{2}$) (0.200 g, 0.3 mmol) in dichloromethane (30 mL) was stirred for 18 h under refluxing in N_2 protection. The resulting solution was filtered and concentrated to 5 mL, and Et₂O (10 mL) was added to precipitate a pale yellow powder. Isolation by filtration yields complex 6. Yield: 0.156 g (52%); M.p.: 266-268 °C. Anal. Calcd for C₃₃H₄₀Hg_{1.5}I₃N₄: C, 33.75; H, 3.43; N, 4.77%. Found: C, 33.52; H, 3.65; N, 4.53%. ¹H NMR (400 MH_z, DMSO-d₆): δ 0.93 (t, J = 3.6, 6H, CH₃), 1.39 (m, 4H, CH₂), 2.00 (m, 4H, CH₂), 2.17 $(s, 6H, CH_3), 2.61$ $(s, 3H, CH_3), 4.45$ $(m, 2H, CH_2), 4.58$ $(m, 2H, CH_2), 5.74$ $(d, J = 10^{-10})$ 7.2, 2H, CH_2), 6.05 (d, J = 7.2, 2H, CH_2), 7.32 (s, 1H, PhH), 7.67-7.76 (m, 4H, PhH), 8.04 (d, J = 4.0, 2H, PhH), 8.28 (d, J = 4.0, 2H, PhH). ¹³C NMR (100 MH₇) DMSO-d₆): δ 184.3 (C_{carbene}), 141.1, 137.9, 134.9, 134.5, 133.6, 129.0, 126.5, 126.2 and 113.4 (PhC), 49.8 (NCH₂Ph), 45.7 (NCH₂CH₂), 31.6 and 20.1 (PhCH₃), 19.9 and 17.2 (CCH₂C), 13.9 (CH₂CH₃).

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The following complexes 7 and 8 were prepared in a manner analogous to that of 6, and only ligands and metal salts are different from those of 6.

Synthesis of [L⁶Hg][HgBr₄] (7). Yield: 0.235 g (63%). M.p.: 220-222°C. Anal. Calcd for C₃₇H₃₄Br₄Hg₂N₆: C, 34.62; H, 2.67; N, 6.55%. Found: C, 34.41; H, 2.33; N, 6.32%. ¹H NMR (400 MH₇, DMSO-d₆): δ 1.69 (s, 6H, CH₃), 2.66 (s, 3H, CH₃), 5.79 $(d, J = 15.2, 2H, CH_2), 6.02-6.13 (m, 6H, CH_2), 7.12 (m, 2H, PhH or PyH), 7.29 (s, CH_2), 7.12 (m, 2H, PhH or PyH), 7.29 (s, CH_2), 7.12 (m, CH_2), 7.12 ($ 1H, Ph*H*), 7.39 (d, *J* = 8.0, 2H, Ph*H* or Py*H*), 7.59-7.73 (m, 6H, Ph*H* or Py*H*), 7.87 (d, J = 8.4, 2H, PhH or PyH), 8.05 (d, J = 4.8, 2H, PhH or PyH), 8.28 (d, J = 8.4, 2H, PhH or PyH), 8.28 (d, J =PhH or PyH). ¹³C NMR (100 MH_Z, DMSO-d₆): δ 182.4 (C_{carbene}), 153.9, 149.4, 140.5, 137.9, 134.5, 133.9, 133.5, 129.2, 126.6, 126.3, 123.9 and 123.1 (PhC or PyC), 53.4 and 46.9 (NCH₂Ph), 24.5, 20.6 and 18.2 (PhCH₃).

Synthesis of $[L^7Ag][(NO_3)_{0.76}Br_{0.24}]$ (8). Yield: 0.158 g (74%). M.p.: 290-292°C.

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Anal. Calcd for $C_{39}H_{36}AgBr_{0.24}N_{4.76}O_{2.28}$: C, 63.68; H, 4.93; N, 9.06%. Found: C, 63.32; H, 5.11; N, 9.52%. ¹H NMR (400 MH_Z, DMSO-d₆): δ 2.08 (s, 6H, CH₃), 2.75 (s, 3H, CH₃), 5.64 (s, 4H, CH₂), 5.76 (s, 4H, CH₂), 7.12-7.19 (m, 11H, PhH), 7.44 (t, J = 8.0, 2H, PhH), 7.54 (t, J = 8.0, 2H, PhH), 7.67 (t, J = 8.0, 2H, PhH), 8.12 (t, J = 8.0, 2H, PhH). ¹³C NMR (100 MH_Z, DMSO-d₆): δ 187.7 (C_{carbene}), 138.8, 137.9, 136.6, 135.3, 133.4, 132.5, 131.0, 129.2, 127.5, 125.0 and 124.8 (PhC), 54.3 and 46.5 (NCH₂Ph), 20.7 and 18.9 (PhCH₃).

General Procedure for the Suzuki-Miyaura Cross-Coupling Reaction. In a typical reaction, aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), base (1.2 mmol) and NHC-Pd complex 2 (0.1 mol %) in organic solvent (2.5 mL) and water (0.5 mL if needed) were stirred at 50 °C in air. After the desired reaction time, the reaction was stopped, and water (20 mL) was added to the reaction mixture. The mixture was extracted by n-hexane (10 mL × 3), and the organic layer was washed with water (10 mL × 3) and dried over anhydrous MgSO₄. Then the solution was filtered and concentrated to 5 mL. The solution was analyzed by GC or separated by a column to get the products.

X-ray data collection and structure determinations

X-ray single-crystal diffraction data for complexes **1-8** were collected by using a Bruker Apex II CCD diffractometer at 296(2) K with Mo-Ka radiation ($\lambda = 0.71073$ M) by ω scan mode. There was no evidence of crystal decay during data collection in all cases. Semiempirical absorption corrections were applied by using SADABS and the program SAINT was used for integration of the diffraction profiles.²⁸ All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL²⁹ by the full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . Hydrogen atoms bonded to C atoms were placed geometrically and presumably solvent H atoms were first located in difference Fourier maps and then fixed in the

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calculated sites. Further details for crystallographic data and structural analysis are listed in Table 4-Table 6. Figures were generated by using Crystal-Maker.³⁰

	1	2	3
chemical formula	$C_{34}H_{34}Ag_2Cl_2N_4O_2$	$\begin{array}{c} C_{38}H_{40}Cl_4N_6O_2Pd_2\\ \cdot (C_2H_5)_2O \end{array}$	$C_{38}H_{42}Ag_2Cl_2N_4O_2$
fw	817.29	1041.48	873.40
Cryst syst	Triclinic	Monoclinic	Triclinic
space group	Pī	$P2_{1}/c$	Pī
a /Å	9.777(6)	18.824(1)	11.333(5)
b /Å	11.117(7)	20.219(1)	13.358(6)
c /Å	15.974(1)	12.437(6)	13.947(7)
<i>a</i> /deg	102.3(1)	90	67.4(1)
β /deg	91.0(1)	103.5(1)	76.8(1)
¥/deg	108.9(1)	90	71.0(1)
$V/\text{\AA}^3$	1597.4(1)	4602.6(4)	1832.2(1)
Ζ	2	4	2
$D_{\rm calcd}$, Mg/m ³	1.699	1.503	1.583
Abs coeff, mm ⁻¹	1.431	1.057	1.253
<i>F</i> (000)	820	2112	884
Cryst size, mm	$0.22\times0.20\times0.18$	$0.20\times0.18\times0.17$	$0.25 \times 0.23 \times 0.10$
$\theta_{\min}, \theta_{\max}, \deg$	1.99, 25.01	1.50, 25.01	1.59, 25.01
<i>T /</i> K	296(2)	296(2)	296(2)
no. of data collected	8201	23202	9196
no. of unique data	5615	8082	6401
no. of refined params	419	520	438
goodness-of-fit on F^{2a}	1.032	1.048	1.069
Final <i>R</i> indices ^b $[I > 2\sigma(I)]$			
R_1	0.0371	0.0312	0.0674
wR_2	0.0908	0.0953	0.1993
R indices (all data)			
R_1	0.0428	0.0419	0.0829
wR_2	0.0953	0.1035	0.2152

Table 4 Summary	of crystallographic data for 1	1-3
2		

^a Goof = $[\Sigma\omega(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where *n* is the number of reflection and *p* is the number of parameters refined.^b $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigmaw(F_o^2)^2]^{1/2}$.

Table 5 Summary of crystallographic data for 4-6

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	4	5	6
chemical formula	$C_{37}H_{40}Ag_2Cl_2N_4O_2$	C _{19.50} H ₂₂ AgClN ₂ O	$C_{33}H_{40}Hg_{1.5}I_3N_4$
fw	859.37	445.71	1174.28
Cryst syst	Monoclinic	Monoclinic	Triclinic
space group	$P2_{1}/n$	C2/c	$P\bar{1}$
a /Å	10.883(1)	10.938(5)	11.235(2)
b /Å	19.173(1)	21.646(1)	18.637(3)
c /Å	17.744(1)	16.736(7)	18.650(3)
<i>a</i> /deg	90	90	109.4(3)
β/deg	103.1(2)	105.3(1)	104.1(2)
¥/deg	90	90	92.3(2)
$V/\text{\AA}^3$	3605.5(6)	3821.8(3)	3537.6(1)
Ζ	4	8	4
D_{calcd} , Mg/m ³	1.583	1.203	2.205
Abs coeff, mm ⁻¹	1.272	3.176	9.156
<i>F</i> (000)	1736	1800	2180
Cryst size, mm	$0.32\times0.28\times0.26$	$0.23\times0.22\times0.18$	$0.12 \times 0.11 \times 0.10$
θ_{\min} , θ_{\max} , deg	1.59, 25.03	2.15, 25.01	1.17, 25.01
Т /К	296(2)	296(2)	296(2)
no. of data collected	18333	9526	12279
no. of unique data	6363	3348	12279
no. of refined params	453	223	758
goodness-of-fit on F^{2a}	1.013	1.042	1.057
Final <i>R</i> indices ^b $[I > 2\sigma(I)]$			
R_1	0.0357	0.0670	0.0420
wR_2	0.0818	0.2216	0.1386
R indices (all data)			
R_1	0.0564	0.0735	0.0503
wR_2	0.0945	0.2289	0.1755

^a Goof = $[\Sigma\omega(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where *n* is the number of reflection and *p* is the number of parameters refined. ^b $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigmaw(F_o^2)^2]^{1/2}$.

	7 ·1.5CH ₃ CN	8-CH ₃ CN
chemical formula	$C_{37}H_{34}Br_4Hg_2N_6$	C39H36AgBr0.24N4.76
	·1.5CH ₃ CN	O _{2.28} ·CH ₃ CN
fw	1345.10	776.59

Table 6 Summary of crystalographic data for 7 and 8

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Cryst syst	Monoclinic	Triclinic
space group	<i>C</i> 2/ <i>c</i>	Pī
a /Å	15.963(1)	10.192(1)
b /Å	15.487(1)	10.741(1)
c /Å	34.670(2)	18.241(1)
<i>a</i> /deg	90	75.6(2)
β /deg	99.6(1)	86.5(2)
¥/deg	90	64.2(2)
$V/\text{\AA}^3$	8451.0(1)	1739.6(3)
Ζ	8	2
D_{calcd} , Mg/m ³	2.114	1.483
Abs coeff, mm ⁻¹	11.079	0.902
<i>F</i> (000)	5048	799
Cryst size, mm	$0.28\times0.26\times0.22$	$0.20\times0.18\times0.16$
$ heta_{\min}, heta_{\max}, \deg$	1.84, 25.03	2.17, 25.03
Т /К	296(2)	296(2)
no. of data collected	21420	8888
no. of unique data	7461	6110
no. of refined params	497	468
goodness-of-fit on F^{2a}	1.024	1.044
Final <i>R</i> indices ^b $[I > 2\sigma(I)]$		
R_1	0.0361	0.0372
wR_2	0.0836	0.0827
R indices (all data)		
R_1	0.0535	0.0556
wR_2	0.0910	0.0925

^a Goof = $[\Sigma\omega(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where *n* is the number of reflection and *p* is the number of parameters refined. ^b $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigmaw(F_o^2)^2]^{1/2}$.

Acknowledgments

This work was financially supported by the National Science Foundation of China (Project Grant No. 21172172) and the Natural Science Foundation of Tianjin (11JCZDJC22000).

References

1 H. W. Wanzlick, H. J. Schönherr, Angew. Chem. Int. Ed. Engl. 1968, 7, 141-142.

Downloaded by University of Sussex on 15 June 2012

CrystEngComm

View Online

- 2 A. J. Arduengo III, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361-363.
- 3 (a) S. P. Nolan, *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2006; (b) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* 2007, 251, 596-609; (c) J. A. Mata, M. Poyatos, E. Peris, *Coord. Chem. Rev.* 2007, 251, 841-859; (d) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* 2010, 110, 1746-1787; (e) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* 2009, 109, 3708-3742.
- 4 (a) P. L. Arnold, I. J. Casely, *Chem. Rev.* 2009, **109**, 3599-3611; (b) F. E. Hahn, M. C. Jahnke, Angew. Chem. Int. Ed. 2008, **47**, 3122-3172; (c) X. Wang, S. Liu, L. H. Weng, G. X. Jin, *Organometallics* 2004, **23**, 6002-6007.
- 5 (a) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz and G. Eastham, J. Chem. Soc., Dalton Trans., 2000, 4499; (b) J. J. Van Veldhuizen, J. E. Campbell, R. E. Giudici, A. H. Hoveyda, J. Am. Chem. Soc. 2005, 127, 6877-6882; (c) D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, Inorg. Chim. Acta 2003, 352, 143-150; (d) J. C. Garrison, W. J. Youngs, Chem. Rev. 2005, 105, 3978-4008.
- 6 (a) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* 2004, 248, 2247-2273; (b) L. H. Gade, S. Bellemin-Laponnaz, *Coord. Chem. Rev.* 2007, 251, 718-725; (c) J. C. Lin, Y. Huang, R. T. W. Lee, C. S. A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* 2009, 109, 3561-3598; (d) C. V. Georgios, H. G. Robert, *Chem. Rev.* 2010, 110, 1746-1787; (e) X. Wang, S. Liu, L. H. Weng, G. X. Jin, *Organometallics* 2006, 25, 3565-3569.
- 7 (a) F. W. Li, S. Q. Bai, T. S. A. Hor, Organometallics 2008, 27, 672-677; (b) H. L. Qiu, S. M. Sarkar, D. H. Lee, M. J. Jin, Green Chem. 2008, 10, 37-39; (c) F. Glorius, (Ed.), Topics in Organometallic Chemistry 21 (N-heterocyclic Carbenes in Transition Metal Catalysis), Springer, Berlin/Heidelberg, Germany, 2007; (d) S. K. Yen, L. L. Koh, F. E. Hahn, H. V. Huynh, T. S. A. Hor, Organometallics 2006, 25, 5105-5112.
- 8 (a) S. Ahrens, A. Zeller, M. Taige, T. Strassner, Organometallics 2006, 25, 5409-5415; (b) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, Angew. Chem. Int. Ed. 2007, 46, 2768-2813; (c) W. A. Herrmann, Angew. Chem. Int. Ed. 2002, 41,

View Online

1290-1309.

Published on 16 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CE25365H

Downloaded by University of Sussex on 15 June 2012

- 9 (a) E. Alcalde, R. M. Ceder, C. López, N. Mesquida, G. Muller, S. Rodríguez, Dalton Trans. 2007, 2696-2706; (b) M. Raynal, C. S. J. Cazin, C. Vallée, H. Olivier-Bourbigou, P. Braunstein, Dalton Trans. 2009, 3824-3832; (c) M. T. Zamora, M. J. Ferguson, R. McDonald, M. Cowie, Dalton Trans. 2009, 7269-7287; (d) M. Raynal, C. S. J. Cazin, C. Vallée, H. Oivier-Bourbigou, P. Braunstein, Organometallics 2009, 28, 2460-2470; (e) F. E. Hahn, M. C. Jahnke, T. Pape, Organometallics 2007, 26, 150-154.
- 10 (a) B. Liu, W. Chen, S. Jin, Organometallics 2007, 26, 3660-3667; (b) D. H. Brown, G. L. Nealon, P. V. Simpson, B. W. Skelton, Z. Wang, Organometallics 2009, 28, 1965-1968; (c) A. T. Normand, K. J. Cavell, Eur. J. Inorg. Chem. 2008, 6, 2781-2800; (d) F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, Organometallics 2005, 24, 6458-6463.
- 11 (a) D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, Organometallics 2006,
 25, 4850-4856; (b) A. A. D. Tulloch, A. A. Danopoulos, G. J. Tizzard, S. J. Coles,
 M. B. Hursthouse, R. S. H. Motherwell, W. B. Motherwell, Chem. Commun. 2001,
 1270-1271; (c) X. Q. Zhang, Y. P. Qiu, B. Rao, M. M. Luo, Organometallics
 2009, 28, 3093-3099.
- 12 (a) C. Marshall, M. F. Ward, W. T. A. Harrison, J. Organomet. Chem. 2005, 690, 3970-3975; (b) H. Clavier, J. C. Guillemin, M. Mauduit, Chirality 2007, 19, 471-476; (c) M. S. Jeletic, I. Ghiviriga, K. A. Abboud, A. S. Veige, Organometallics 2007, 26, 5267-5270; (d) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, Organometallics 2003, 22, 4384-4386; (e) F. E. Hahn, M. J. Foth, J. Organomet. Chem. 1999, 585, 241-245; (f) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, Angew. Chem. Int. Ed. 2000, 39, 541-544.
- 13 (a) Q. X. Liu, X. J. Zhao, X. M. Wu, J. H. Guo, X. G. Wang, J. Organomet. Chem.
 2007, 692, 5671-5679; (b) Q. X. Liu, X. Q. Yang, X. J. Zhao, S. S. Ge, S. W. Liu,
 Y. Zang, H. B. Song, J. H. Guo, X. G. Wang, CrystEngComm. 2010, 12,
 2245-2255; (c) Q. X. Liu, S. J. Li, X. J. Zhao, Y. Zang, H. B. Song, J. H. Guo, X.
 G. Wang, Eur. J. Inorg. Chem. 2010, 983-986; (d) Q. X. Liu, Z. Q. Yao, X. J. Zhao,

Downloaded by University of Sussex on 15 June 2012

CrystEngComm

View Online

A. H. Chen, X. Q. Yang, S. W. Liu, X. G. Wang, Organometallics 2011, 30, 3732-3739.

- 14 S. Otsuka, A. Nakamura and Y. Tatsuno, J. Am. Chem. Soc., 1969, 91, 6994-6999.
- 15 (a) U. J. Scheele, S. Dechert and F. Meyer, *Inorg. Chim. Acta.*, 2006, **359**, 4891-4900; (b) K. M. Lee, J. C. C. Chen, C. J. Huang and I. J. B. Lin, *CrystEngComm.*, 2007, **9**, 278-281; (c) Q. X. Liu, L. N. Yin and J. C. Feng, *J. Organomet. Chem.*, 2007, **692**, 3655-3663.
- 16 A. J. Black, G. Baum, N. R. Champness, S. S. M. Chung, P. A. Cooke, D. Fenske, A. N. Khlobystov, D. A. Lemenovskki, W. S. Li, M. Schröder, J. Chem. Soc., Dalton Trans. 2000, 4285-4291.
- 17 R. P. A. Bettens, D. D. Dakternieks, A. Duthie, F. S. Kuan, E. R. T. Tiekink, *CrystEngComm.* 2009, **11**, 1362-1372.
- 18 M. L. Cole, P. C. Junk, CrystEngComm. 2004, 6, 173-176.
- 19 F. Neve and A. Crispini, CrystEngComm., 2003, 5, 265-268.
- 20 L. Rajput and K. Biradha, CrystEngComm., 2009, 11, 1220-1222.
- 21 S. A. Baudron, D. Salazar-Mendoza and M. W. Hosseini, *CrystEngComm.*, 2009, 11, 1245-1254.
- 22 I. J. B. Lin, C. S. Vasam, Coord. Chem. Rev. 2007, 251, 642-670.
- 23 C. K. Lee, C. S. Vasam, T. W. Huang, H. M. J. Wang, R. Y. Yang, C. S. Lee and I. J. B. Lin. *Organometallics*. 2006, **25**, 3768-3775.
- 24 (a) N. Stylianides, A. A. Danopoulos, D. Pugh, F. Hancock, A. Zanotti-Gerosa, Organometallics 2007, 26, 5627-5635; (b) S. Ahrens, A. Zeller, M. Taige, T. Strassner, Organometallics 2006, 25, 5409-5415; (c) E. Negishi, Handbook of Organopalladium Chemistry for Organic Synthesis. John Wiley & Sons Inc, New York, 2002; (d) J. Tsuji, Palladium Reagents and Catalysts: New Perspectives for 21st Century, John Wiley & Sons Ltd, Chichester, 2004.
- 25 (a) F. Artuso, A. A. D'Archivio, S. Lora, K. Jerabek, M. Kràlik, B. Corain, *Chem. Eur. J.* 2003, 9, 5292-5296; (b) T. Teranishi, M. Miyake, *Chem. Mater.* 1998, 10, 594-600.
- 26 (a) K. Selvakumar, A. Zapf, M. Beller, Org. Lett. 2002, 4, 3031-3033; (b) R. B.

Bedford, M. E. Blake, C. P. Butts, D. Holder, *Chem. Commun.* 2003, 466-467; (c)
D. Yang, Y. C. Chen, N. Y. Zhu, *Org. Lett.* 2004, 6, 1557-1560; (d) H. V. Huynh, Y. Han, J. H. Ho, G. K. Tan, *Organometallics* 2006, 25, 3267-3274; (e) S. H. Li, Y. J. Lin, J. G. Cao, S. B. Zhang, *J. Org. Chem.* 2007, 72, 4067-4072.

27 (a) C. C. Lee, W. C. Ke, K. T. Chan, C. L. Lai, C. H. Hu, H. M. Lee, *Chem. Eur. J.* 2007, **13**, 582-591; (b) Z. X. Xi, X. M. Zhang, W. Z. Chen, S. Z. Fu, D. Q. Wang, *Organometallics* 2007, **26**, 6636-6642.

28 Bruker AXS, SAINT Software Reference Manual, Madison, WI, 1998.

29 G. M. Sheldrick, SHELXTL NT (Version 5.1), Program for Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), 1997.

30 D. C. Palmer, CrystalMaker 7.1.5, CrystalMaker Software, Yarnton, UK, 2006.

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Published on 16 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CE25365H

Downloaded by University of Sussex on 15 June 2012

A series of NHC silver(I), palladium(II) and mercury(II) complexes were prepared and characterized. The catalytic activity of the palladium complex was studied.



Software of Graphics:

Schemes 1-4: Chem Draw 8.0

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