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N-Hetercocyclic carbene metallacrown ethers based on 1,8-dihydroxy-9,10-anthraquinone: Synthesis, structures and application in situ palladium-catalyzed Suzuki–Miyaura reaction

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ABSTRACT

N-Hetercocyclic carbene precursors containing 1,8-dihydroxy-9,10-anthraquinone derivative: 1,8-bis(3-(N-R-imidazole)propoxy)-9,10-anthraquinone 2X (**$L1H_2$**: R = $PhCH_2$, X = Br, **$L3H_2$**: R = ^{n}Bu, X = PF_6, **$L4H_2$**: R = $PhCH_2$, X = PF_6, **$L5H_2$**: R = $PyCH_2$, X = PF_6), 1,8-bis(2-(N-R-imidazole)ethoxy)-9,10-anthraquinone 2X (**$L2H_2$**: R = $PhCH_2$, X = PF_6) and 1,8-bis(3-(N-R-imidazole)propoxy)anthracene 2X (**$L6H_2$**: R = $PhCH_2$, X = PF_6) were synthesized. N-Heterocyclic carbene metallacrown ethers: L1AgBr (**1**), $L2AgPF_6$ (**2**), $L3AgPF_6$ (**3**), $L4AgPF_6$ (**4**), $L6AgPF_6$ (**5**), $L4AuPF_6$ (**6**), $L5Hg(PF_6)_2$ (**7**) have been prepared. Complexes **1**–**7** were characterized by elemental analysis, NMR spectroscopy and single crystal X-ray diffraction. Particularly, complex **4** and $PdCl_2(CH_3CN)_2$ synergetically and efficiently catalyzed in situ Suzuki–Miyaura cross-coupling reaction in 100% aqua-phase.

1. Introduction

Since first stable imidazol-2-ylidene was isolated by Arduengo in 1991 [1], N-heterocyclic carbenes (NHCs) have been proved to be efficient ancillary ligands and alternative ligands of typical phosphines [2]. The properties of N-heterocyclic carbenes resemble those of electron-donating phosphines as robust σ-donors with negligible π-accepting ability [3]. NHCs have become widespread ligands in coordination chemistry [4–7]. Metal-NHC complexes have been found ubiquitous applications in homogeneous and asymmetric catalysis [8–12], pharmaceutical science [13–15] and photoelectric material [16,17]. Organic crown ethers have been used as multifunctional ligands in many aspects because of their remarkable size selectivity for some small molecules and metal ions [18]. Therefore, the metal ions centered into crown to form metallacrown ether. Metallacrown ether is a kind of chemical structure which is significantly different from that of either the metal center or the crown ether [19,20]. So far, there are some reports concerning N-heterocyclic carbene metallacrown ethers have been described in the published work. Cavell et al. prepared oxoether-bridged bis-(imidazolium) ligand [21]. Chen et al. reported bidentate NHC-bridged polynuclear silver metallacrown ethers [22]. N-Heterocyclic carbene complexes exhibiting fluorescent may be good candidates for fluorescent switch [23–25]. Anthracene and anthraquinone derivative as fluorescence group were applied to molecular recognition [26]. To the best of our knowledge, few N-Heterocyclic carbene metallacrown ethers involving 1,8-dihydroxy-9,10-anthraquinone derivative have been reported.

Our group is interested in the metallacrown ether and catalytic performance of N-heterocyclic carbene metal complexes. In this paper, we reported the synthesis, structural characterization of seven new silver(I), gold(I) and mercury(II) NHC metallacrown ethers complexes involving 1,8-dihydroxy-9,10-anthraquinone derivative. Moreover, catalytic performance of silver NHC complex **4** and $PdCl_2(CH_3CN)_2$ in Suzuki–Miyaura reactions in pure water was studied.

2. Results and discussion

2.1. Synthesis and structures of silver-NHC complexes 1–5

1,8-Dihydroxy-9,10-anthraquinone underwent alkylation with 1,2-dibromoethane or 1,3-dibromopropane to provide

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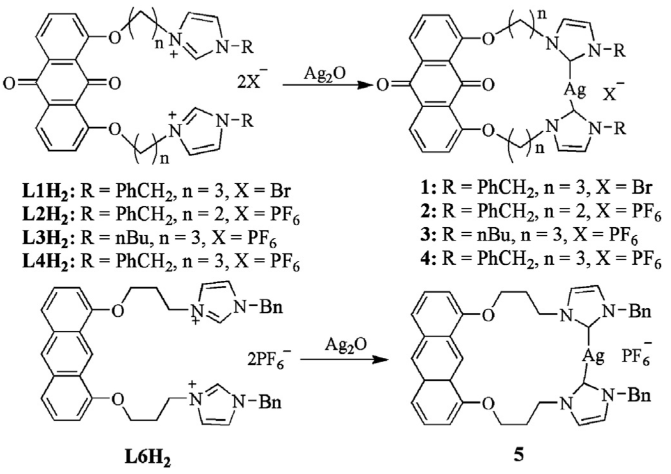
1,8-bis(2-bromoethoxy)-9,10-anthraquinone (**a**) or 1,8-bis(3-bromopropoxy)-9,10-anthraquinone (**b**) [27,28]. Compound **c** was obtained by reduction of the 1,8-dihydroxy-9,10-anthraquinone at first and underwent alkylation with 1,3-dibromopropane [29]. The NHCs bis-(imidazolium) salts **L1H$_2$** were prepared from imidazole by stepwise alkylation with benzyl bromide in the presence of NaH in THF at 70 °C for 48 h, followed by quarterization with 1,8-bis(3-bromopropoxy)-9,10-anthraquinone in sequence (method 1, Scheme 1). Precursors of **L2H$_2$**–**L5H$_2$** were obtained by two steps. The first step is in a manner similar to that for **L1H$_2$**, and the second step is through an anionic exchange with ammonium hexafluorophosphate in methanol (method 2, Scheme 1). Precursors of **L2H$_2$**–**L5H$_2$** are stable towards air and moisture, soluble in organic solvents such as acetonitrile and dimethyl sulfoxide, and insoluble in diethyl ether and petroleum ether.

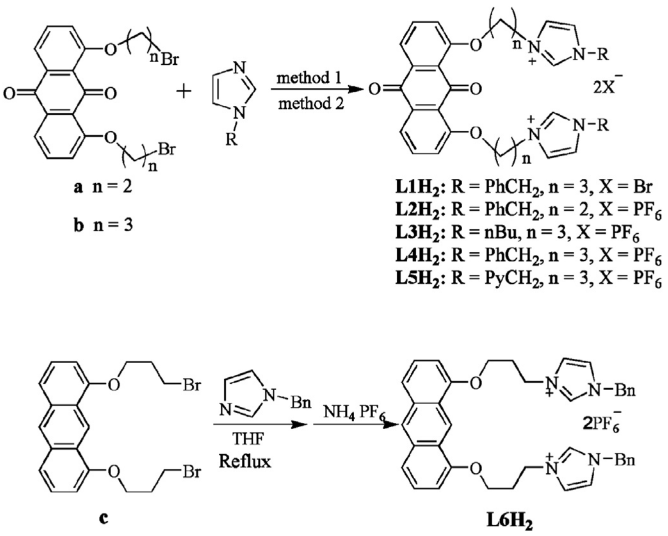
Synthetic methods of complexes **1**–**5** were shown in Scheme 2. Treatment of the bis-(imidazolium) salts **L1H$_2$**–**L4H$_2$** and **L6H$_2$** with Ag$_2$O in DMSO for 2 days in the dark under nitrogen atmosphere obtained silver-NHC complexes **1**–**5**. The structures of complexes **1**–**5** were confirmed by elemental analysis, ^{1}H NMR, ^{13}C NMR spectroscopy and X-ray crystallography. In the ^{1}H NMR spectra of **L1H$_2$**–**L4H$_2$** and **L6H$_2$**, the imidazolium protons signal (NCHN) appear at δ = 9.10–9.40 ppm, which are consistent with the chemical shifts of reported imidazolium salts [30–32]. In the ^{1}H NMR spectra of **1**–**5**, the disappearance of the resonances for the imidazolium protons (NCHN) show the formation of the expected metal carbene complexes, and the chemical shifts of other hydrogens are similar to their corresponding precursors.

Complexes **1**–**5** suitable for single crystal X-ray diffraction were obtained by slow diffusion of diethyl ether into CH$_3$OH/CH$_3$CN solution at room temperature. In NHC metal complexes **1**–**5** (Figs. 1–5), each complex contains a macrometallocycle (16-membered ring for **2**, 18-membered ring for **1**, **3**–**5**) constructed by one silver atom and bidentate chelate biscarbene ligand containing two flexible ether chains and one rigid anthraquinone or one anthracene ring. The coordination environment of silver atoms in these complexes markedly depends on carbene carbons. As shown in Fig. 1, complex **1** is mononuclear and crystallized as triclinic, *P*–1 space group. The crystallographic parameters are listed in Table 1. The coordination geometry around the silver atom is nearly linear of complex **1**. The angle of C(10)–Ag–C(33) is 171.65(13)°. The Ag–C(10) and Ag–C(33) bond lengths are 2.075(4) and 2.078(3) Å, respectively. Complex **4** is mononuclear and crystallized as triclinic, *P*–1 space group (Fig. 4), compared with the complex **1**, which has a different anion (Fig. 4), the angle of C(8)–Ag(1)–C(33) is 174.69(12)° which is little larger than the value of complex **1**. The bond lengths of C(8)–Ag(1) and C(33)–Ag(1) are 2.075(4) and 2.083(4) Å. In the complexes **1** and **4** of dihedral angles which are formed by two imidazole rings are 39.90(3) and 45.64(3)°, respectively. Moreover, the dihedral angles which are formed by two benzene rings are 9.10(1) and 41.03(6)°, probably due to the different anion of complexes **1** and **4**.

In complex **2**, two benzyl groups point to the opposite directions. However, two alkyl chains of complexes **3** and **5** point to the same direction (butyl chains for **3** and benzyl groups for **5**). The molecular structure of complex **2** is shown in Fig. 2 and crystallographic data are listed in Table 1. The complex **2** which the silver atom is coordinated with two carbene carbon atoms a linear arrangement [C(10)–Ag(1)–C(33) = 173.47(14)°] is mononuclear and crystallized as triclinic, *P*–1 space group. The C(10)–Ag(1) and C(31)–Ag(1) distances are 2.105(3) and 2.092(4) Å of the metal NHC complex **2**. The two imidazole rings have a dihedral angle of



Scheme 2. Synthesis of silver NHC complexes **1**–**5**.



Scheme 1. Synthesis of bis(imidazolium) precursors **L1H$_2$**–**L6H$_2$**.

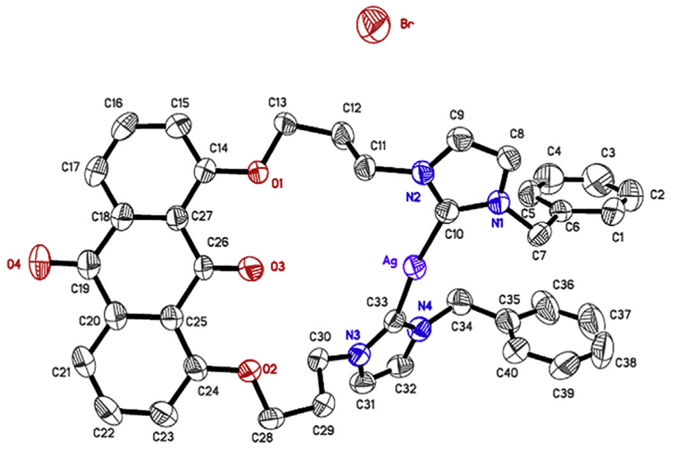


Fig. 1. The molecular structure of **1**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms of NHC were omitted for clarity. Selected bond distances (Å) and angles (°): Ag–C(10) 2.075(4), Ag–C(33) 2.078(3) Å; C(10)–Ag–C(33) 171.65(13)°.

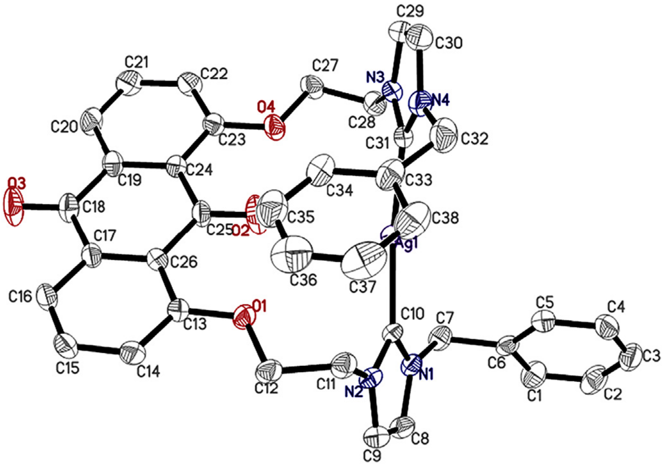


Fig. 2. The molecular structure of **2**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms of NHC and PF_6^- anion were omitted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–C(31) 2.092(4), Ag(1)–C(10) 2.105(3) Å; C(31)–Ag(1)–C(10) 173.47(14)°.

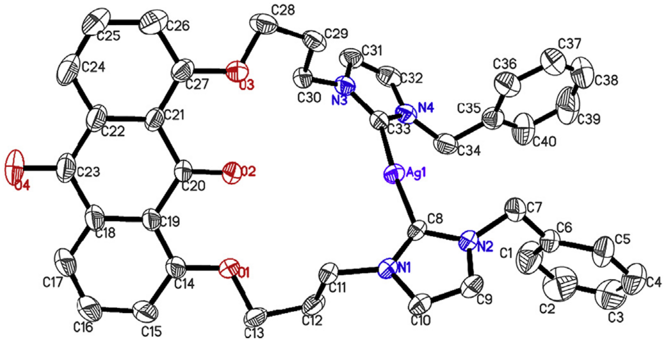


Fig. 4. The molecular structure of **4**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms of NHC and PF_6^- anion were omitted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–C(8) 2.075(4), Ag(1)–C(33) 2.083(4) Å; C(31)–Ag(1)–C(10) 174.69(4)°.

39.95(9)°. Complex **3** crystallized in the monoclinic space group *P*2/*c*, and complex **5** crystallized in the triclinic space group *P*–1. The C(16)–Ag(1)–C(16A) bond angle in complex **3** is 176.5(2)°, and the C(16)–Ag(1) and C(16A)–Ag(1) bond lengths are the same (2.092(5) Å) (Fig. 3). The imidazole rings of complex **3** form the dihedral angle which is 37.69(5)°. There is some difference from the complex **5** when is compared with the complex **3** (Figs. 3 and 5). The crystal data are found in Table 1. Coordination geometry on the silver of complex **5** is also linear conformation, with a C(10)–Ag(1)–C(31) angle of 174.7(3)°. This value is little larger than 171.65(13)° in **1** and 173.47(14)° in **2**. The bond distances of Ag(1)–C(10) = 2.083(10) and Ag(1)–C(31) = 2.088(11) Å are slightly different from **2** due to the variation of coordination environment. The dihedral angle of two imidazole rings is 41.21(2)°. When complex has a longer ether chain linkage, the coordination geometry at the silver atom tends to be linear probably due to the flexibility of the long oxoether bridge.

2.2. *Synthesis and structures of gold-NHC complexes* **6**

Transmetalation reaction has proved to be a promising procedure to obtain NHC–metal complexes [33,34]. The gold-NHC complex **6** was formed by a transmetalation reaction between $[Au(Me_2S)Cl]$ and the Ag-containing carbene **4** at room temperature (Scheme 3). The ^1H NMR spectrum of complex **6** in DMSO-d_6 is similar to complex **4**. As shown in Fig. 6, the gold-NHC complex **6** is mononuclear and crystallized as triclinic, *P*–1 space group. The crystallographic parameters are listed in Table 2. The central gold atom is biscoordinated by two carbene carbons in a linear fashion [bond angle C(14)–Au(1)–C(33) = 176.43(19)°]. The C(14)–Au(1) and C(33)–Au(1) bond lengths are 2.043(3) and 1.995(3) Å, respectively. The average Au–C (carbene) bond length is in the expected range reported for other related two-coordinate gold carbene complex [35]. The dihedral angle of the two imidazole rings is 46.21(2)°.

2.3. *Synthesis and structures of mercury-NHC complexes* **7**

Mercury (II) complex **7** was prepared by reaction of the imidazolium salts $\mathbf{L5H_2}$ with excess mercury (II) acetate in acetonitrile at 90 °C for 2 days under nitrogen atmosphere (Scheme 3). After recrystallization with acetonitrile, complex **7** was obtained as yellow solid. Single crystal X-ray diffraction was obtained by slow diffusion of diethyl ether into CH_3CN solution at room temperature. The ^1H NMR spectrum of complex **7** in DMSO-d_6 shows the obvious disappearance of acidic 2H-imidazolium protons, which is diagnostic for the loss of the carbonium protons and the formation for metal carbene complex, and the ^{13}C NMR spectrum of the carbene carbon for complex **7** is at 174.4 ppm within the range reported in the literature for other mercury–carbene carbon signals (δ 170–185 ppm) [36,37].

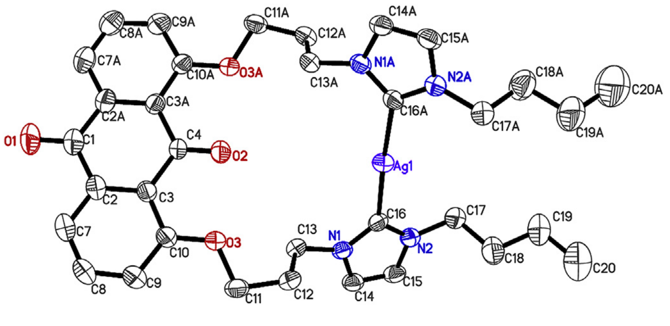


Fig. 3. The molecular structure of **3**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms of NHC and PF_6^- anion were omitted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–C(16) 2.092(5), Ag(1)–C(16A) 2.092(5) Å; C(31)–Ag(1)–C(10) 176.5(2)°.

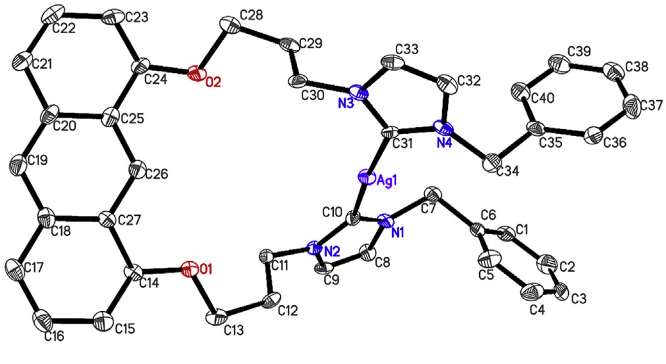


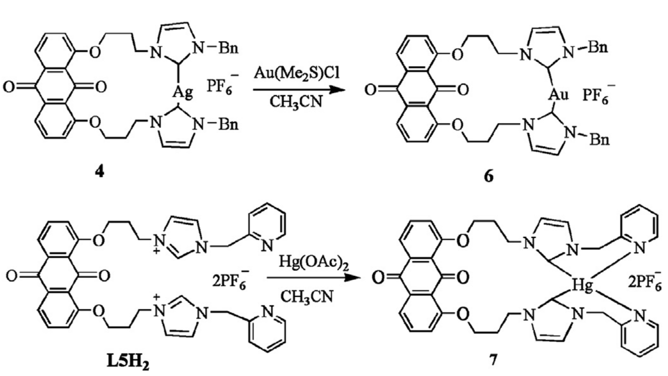
Fig. 5. The molecular structure of **5**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms of NHC and PF_6^- anion were omitted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–C(10) 2.083(10), Ag(1)–C(31) 2.088(11) Å; C(10)–Ag(1)–C(31) 174.7(3)°.

Table 1
Crystal data and refinement parameters for complexes **1**–**5**.

Compound	1	2	3	4	5
Formula	$C_{40}H_{36}AgBrN_4O_4$	$C_{38}H_{32}AgF_6N_4O_4P$	$C_{38}H_{50}AgF_6N_4O_5P$	$C_{44}H_{46}AgF_6N_4O_5P$	$C_{44}H_{48}AgF_6N_4O_3P$
Formula weight	824.51	861.52	895.66	963.69	933.70
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Crystal size (mm)	0.33 × 0.20 × 0.08	0.20 × 0.14 × 0.10	0.29 × 0.24 × 0.18	0.23 × 0.21 × 0.18	0.20 × 0.18 × 0.10
Space group	*P*−1	*P*−1	*P*2/*c*	*P*−1	*P*−1
a (Å)	9.0056(2)	11.4224(19)	9.126(6)	9.459(7)	9.365(9)
b (Å)	12.0808(2)	11.762(2)	18.424(12)	13.162(9)	13.149(12)
c (Å)	17.6199(3)	15.083(2)	12.506(9)	19.000(13)	18.451(15)
α (°)	71.827(1)	106.247(3)	90.00	106.616(11)	75.012(11)
β (°)	88.126(1)	101.587(3)	100.807(12)	93.489(11)	88.16(2)
γ (°)	74.954(1)	105.817(3)	90.00	103.822(11)	75.63(3)
V (Å^3)	1756.46(6)	1785.6(5)	2065(2)	2180(3)	2125(3)
Z	2	2	2	2	2
D_c (g/cm^3)	1.559	1.602	1.440	1.468	1.459
Abs. coeff.	1.759 mm^{-1}	0.688 mm^{-1}	0.599 mm^{-1}	0.574 mm^{-1}	0.583 mm^{-1}
F(000)	836	872	924	988	960
θ_{min}, θ_{max}, deg	3.04, 27.48	2.21, 26.34	2.76, 24.07	2.29, 27.07	1.66, 25.02
No. of data collected	14,501	8878	11,026	11,829	14,687
No. of unique data	6520	6153	4067	8374	7316
No. of refined params.	452	523	252	538	534
Goodness-of-fit on F^2	1.004	1.077	1.037	1.045	1.095
R indices (*all*)					
R_1[a]	0.0436	0.0705	0.0778	0.0589	0.1311
wR_2[b]	0.1238	0.1275	0.1488	0.1266	0.3192
Final R indices [$I > 2sigma(I)$]					
R_1[a]	0.0394	0.0524	0.0514	0.0463	0.1176
wR_2[b]	0.1202	0.1145	0.1330	0.1170	0.3085

[a] $R_1 = |\sum F_o - |.F_c|.|/|\sum|F_o||$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Since the first report, the majority of the mercury-NHC complexes are mononuclear containing linear $Hg(NHC)_2$ units [38–41], although in some cases association with the counter ions distorts the mercury environment toward tetrahedral geometry [36]. Complex **7** exhibits special conformations (Fig. 7), the mercury atom is coordinated with two carbene carbons and two picolyl nitrogen atoms adopting tetrahedral geometry. The Hg(1)–C(20) and Hg(1)–C(32) bond distances are 2.068(5) and 2.066(5) Å, which are a little shorter when compared to those of known mercury-NHC complexes [42,43]. The distances of Hg(1)–N(6) and Hg(1)–N(3) are 2.651(5) and 2.699(5) Å, respectively. The C(20)–Hg(1)–C(32) is nearly linear with the bond angle of 175.15(19)°. The bond angle of N(3)–Hg(1)–N(6) is 82.46(18)°. In the structure of **7**, one NHC ligand and one pyridine ring are linked by central mercury atom forming a six-membered metallacycle which adopts a distorted boat conformation. The dihedral angle between the coordinated pyridine rings is 35.88° and the two imidazole rings on either side of the mercury atom are not coplanar with angle of 28.26(6)°.



Scheme 3. Synthesis of gold and mercury NHC complexes **6**–**7**.

2.4. *Catalytic activity of the NHC silver complex* **4** *with* $PdCl_2(CH_3CN)_2$ *in situ aqua-phase*

The Suzuki–Miyaura cross-coupling reaction of aryl halides and arylboronic acids is of general interest in organic synthesis and meanwhile one of the most important methods for C–C coupling in organic synthesis [44]. 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 [45–49]. We chose the cross-coupling reaction of bromobenzene with 4-methylphenylboronic acid as a model reaction to test the solvent, base and catalyst activity (Table 3). No product was observed when used H_2O as solvent, $K_3PO_4 \cdot 3H_2O$ as base and silver NHC complex **4** as catalyst was used, while added 1 mol% tetrabutyl ammonium bromide (TBAB) as phase transfer catalyst at 50 °C in 24 h in air (entry 1). Coupling

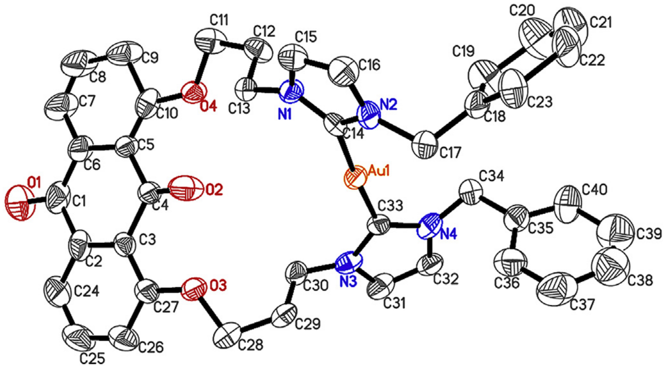


Fig. 6. The molecular structure of **6**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms of NHC and PF_6^- anion were omitted for clarity. Selected bond distances (Å) and angles (°): Au(1)–C(14) 2.043(4), Ag(1)–C(33) 2.083(4) Å; C(31)–Ag(1)–C(10) 174.69(4)°.

Table 2
Crystal data and refinement parameters for complexes **6** and **7**.

Compound	6	7
Formula	$C_{40}H_{38}AuF_6N_4O_5P$	$C_{38}H_{34}F_{12}HgN_6O_4P_2$
Formula weight	996.66	1129.24
Crystal size (mm^3)	0.23 × 0.18 × 0.14	0.60 × 0.44 × 0.22
Crystal system	Triclinic	Monoclinic
Space group	*P*−1	*P*2(1)/*c*
a (Å)	9.535(6)	18.164(5)
b (Å)	13.125(6)	11.863(2)
c (Å)	19.087(12)	20.333(4)
α (°)	106.953(10)	90.00
β (°)	93.315(12)	109.05(2)
γ (°)	105.027(7)	90.00
V ($Å^3$)	2184(2)	4141.4(16)
Z	2	4
D_c (g/cm^3)	1.513	1.811
Abs. coeff.	3.475 mm^{-1}	3.897 mm^{-1}
F(000)	984	2216
θ_{min}, θ_{max}, deg	2.35, 19.26	2.50, 14.68
No. of data collected	12,098	8732
No. of unique data	8471	7708
No. of refined params.	433	619
Goodness-of-fit on F^2	1.012	0.885
Final R indices (all)		
R_1[a]	0.1091	0.0789
wR_2[b]	0.1722	0.0599
Final R indices [I > 2sigma(I)]		
R_1[a]	0.0652	0.0360
wR_2[b]	0.1477	0.0560

[a] $R_1 = |\sum F_o - |.F_c|.|/|\sum|F_o||$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

yield exceeded 99%, when catalyst was changed to $PdCl_2(CH_3CN)_2$ and silver NHC complex **4** (entry 2). However, using acetonitrile as solvent, coupling yield dropped to 77% (entry 3). The common bases, such as K_2CO_3, Na_2CO_3, and $NaHCO_3$ gave medium yield in pure water (entries 4, 5, 7). Poor yield was obtained using KOH as base (entry 6). In order to further study the catalytic activity of $PdCl_2(CH_3CN)_2$ and complex **4**, the control experiment was performed, in which $PdCl_2(CH_3CN)_2$ was added in the absence of complex **4** with the optimized conditions, and only 26% coupling yield was observed (entry 8).

Various aryl halides and arylboronic acids were chosen to explore the catalytic activity of silver NHC complex **4** and $PdCl_2(CH_3CN)_2$, with $K_3PO_4{\cdot}3H_2O$ as base at 50 °C in pure water. The results are summarized in Table 4. Aryl bromides containing electron-donating groups ($-OCH_3$, $-NH_2$, $-CH_3$, entries 1–3) were obtained yield above 99%. Aryl bromides containing electron-withdrawing groups ($-CHO$, $-COCH_3$, $-NO_2$) gave high yield over 90%, except the slightly decreased yield with nitro substitution, probably due to the steric hindrance effect (entries 4–7). Then the cross-coupling reaction of 3-bromopyridine with 4-methylphenylboronic acid was tested to obtain the good yield 95% (entry 8). The catalysts were highly efficient toward the coupling of iodobenzene with 4-methylphenylboronic acid to give a near theory yield above 99% (entry 9). The coupling reaction of chlorobenzene with 4-methylphenylboronic acid gave a yield of 85% (entry 10), while *p*-chloroacetophenone or *p*-chloroaniline gave moderate yield of 82% and 88%, respectively (entries 11 and 12). Additionally, the coupling reactions of other arylboronic acids bearing electron-withdrawing in the para-position with bromobenzene proceeded with good to excellent yields (entries 14–16). The coupling of bromobenzene with phenylboronic acid gave a good yield of 95% (entry 13). Though various catalysts have been developed for the Suzuki–Miyaura reactions [50–53], a few catalysts can have a good yield both in aryl bromide and aryl chloride [54–56]. The above results show that complex **4** and $PdCl_2(CH_3CN)_2$ have high catalytic activity for aryl bromide and aryl chloride in pure water.

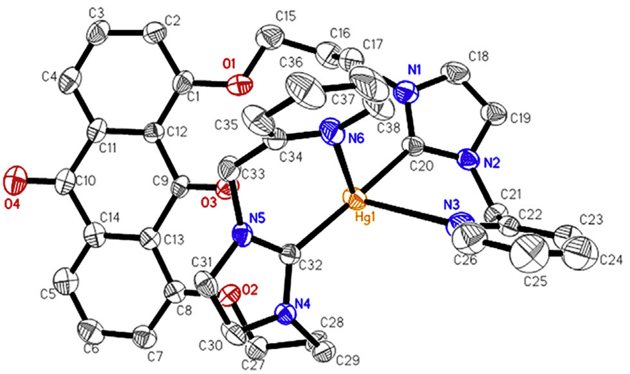


Fig. 7. The molecular structure of **7**. The thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms of NHC and PF_6^- anions were omitted for clarity. Selected bond distances (Å) and angles (°): Hg(1)–C(32) 2.066(5), Hg(1)–C(20) 2.068(5), Hg(1)–N(6) 2.651(5), Hg(1)–N(3) 2.699(5) Å; C(32)–Hg(1)–C(20) 175.15(19), C(32)–Hg(1)–N(6) 82.46(18), C(20)–Hg(1)–N(6) 100.71(18), C(32)–Hg(1)–N(3) 105.96(16), C(20)–Hg(1)–N(3) 78.19(17), N(6)–Hg(1)–N(3) 82.96(15)°.

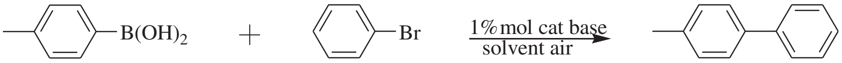
2.5. *Fluorescent emission spectra of precursors **L4H₂** and complexes **4** and **6***

The fluorescent emission spectra of precursors **L4H$_2$** and complexes **4** and **6** in acetonitrile (1×10^{-6} mol/L) at room temperature are obtained upon excitation at 295 nm (Fig. S27). Precursor **L4H$_2$** exhibits intense emission band in the region of 360–380 nm, which can be attributed to intraligand $n-\pi^*$ and $\pi-\pi^*$ transitions. Complexes **L4H$_2$** and **6** exhibit a broad emission band in the region of 455–475 nm. Complexes **4** and **6** show emission band in the region of 345–355 nm, the fluorescent emission of complexes **4** and **6** are weaker than their precursor **L4H$_2$**, which may be assigned to the incorporation of metal–ligand coordination interaction [57,58].

3. Conclusions

In summary, we have synthesized and characterized the first N-hetercocyclic carbene metallacrown ether containing 1,8-dihydroxy-9,10-anthraquinone derivative of silver, gold and mercury complexes. Each of complexes **1**–**6** possesses a macrometallocycle, complex **2** contain a 16-membered macrometallocycle and complexes **1**, **3**–**6** possess an 18-membered macrometallocycle, which is formed by a one metal atom and one bidentate chelate carbene ligand. Complex **7** exhibits flexibility conformations, the mercury atom is coordinated with two carbene carbons and two pyridine nitrogen atoms adopting tetrahedral geometry. In the structure of **7**, one NHC ligand and one pyridine ring are linked by central mercury forming a six-membered metallacycle which adopts a distorted boat conformation. Above of the study in the catalytic activity of NHC silver complex **4** and $PdCl_2(CH_3CN)_2$ in Suzuki–Miyaura cross-coupling reactions show that they can catalyze the coupling reaction of aryl halides (iodide, bromide, chloride) with arylboronic acids in pure water as solvent and $K_3PO_4{\cdot}3H_2O$ as base in air. The macrocyclic structures of NHC metal complex suggest that they have potential applications in the organic chemistry.

Table 3
Optimization of the Suzuki–Miyaura coupling reaction in pure water.[a]



Entry	Solvent	Base	Yield[b] (%)
1[c]	H_2O	$K_3PO_4\cdot 3H_2O$	Trace
2[d]	H_2O	$K_3PO_4\cdot 3H_2O$	>99
3	CH_3CN	$K_3PO_4\cdot 3H_2O$	77
4	H_2O	Na_2CO_3	81
5	H_2O	K_2CO_3	82
6	H_2O	KOH	34
7	H_2O	$NaHCO_3$	60
8[e]	H_2O	$K_3PO_4\cdot 3H_2O$	26

[a] Reaction conditions: 4-bromotoluene 0.20 mmol, 4-methylphenylboronic acid 0.22 mmol, base 0.44 mmol, solvent 2 mL, 50 °C, 24 h.
[b] Isolated yield.
[c] Reaction conditions are the same as [a], 1 mol% TBAB and 1 mol% **4** was added.
[d] Reaction conditions are the same as [a], 1 mol% $PdCl_2(CH_3CN)_2$, 1 mol% TBAB and 1 mol% **4** were added in the reaction.
[e] Reaction conditions are the same as [a], only $PdCl_2(CH_3CN)_2$ and 1 mol% TBAB were added in the absence of complex **4**.

4. Experimental

4.1. General comments

All manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. And solvents were purified by standard procedures. Other reagents used for the synthesis were commercially available and were used without further purification. N-Substituted imidazoles were prepared according to reported procedures [59,60]. NMR spectra were recorded on an advance Ⅲ 400 Brucker (^1H NMR, 400 MHz; ^{13}C NMR, 100 MHz, respectively). Chemical shifts (δ) were expressed in ppm downfield to TMS at $\delta = 0$ ppm and coupling constants (J) were expressed in Hz. Elemental analysis were measured using a Perkin–Elmer 2400C Elemental Analyzer. The luminescent spectra were conducted on a Cary Eclipse fluorescence spectrophotometer.

*4.2. Synthesis of 1,8-bis(3-(3-benzyl-imidazole-2-ylidene) propoxy)-9,10-anthraquinone dibromide (**L1H$_2$**)*

To a solution of 3-(benzyl)-1*H*-imidazole (1.58 g, 10 mmol) in THF (50 mL) was added 1,8-bis(3-bromopropoxy)-9,10-anthraquinone (2.35 g, 5 mmol). The mixture was refluxed for 2 days. The orange precipitate was isolated and washed with THF (20 mL), and dried in vacuo. Yield: 3.00 g (75%). Anal. Calcd for $C_{40}H_{38}Br_2N_4O_4$: C, 60.16; H, 4.80; N, 7.02%. Found: C, 60.05; H, 4.81; N, 6.98%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 9.18 (s, 2H), 7.78–7.80 (m, 2H), 7.75–7.76 (m, 6H), 7.50–7.53 (m, 2H), 7.26–7.31 (m, 10H), 5.34 (s, 4H), 4.52 (t, $J = 6.6$ Hz, 4H), 4.10 (t, $J = 5.8$ Hz, 4H), 2.32–2.37 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.53, 182.37, 157.99, 136.64, 134.99, 134.92, 134.85, 134.51, 129.27, 129.04, 128.46, 123.71, 123.33, 123.10, 120.57, 119.17, 65.44, 52.32, 46.44, 28.91 ppm.

*4.3. Synthesis of 1,8-bis(2-(3-benzyl-imidazole-2-ylidene)ethoxy)-9,10-anthraquinone dihexafluorophosphate (**L2H$_2$**)*

This compound was prepared via two steps. The first step is mixture of 3-(benzyl)-1*H*-imidazole (1.58 g, 10 mmol) and 1,8-bis(2-bromoethoxy)-9,10-anthraquinone (2.23 g, 5 mmol) in THF (50 mL) was stirred and refluxed for 2 days. A yellow precipitate was isolated and washed with THF (20 mL) and dried in vacuo. The second step is an anionic exchange with ammonium hexafluorophosphate. The product was collected by filtration and washed with methanol. Yield: 3.42 g (75%). Anal. Calcd for $C_{38}H_{34}F_{12}N_4O_4P_2$: C, 50.68; H, 3.81; N, 6.22%. Found: C, 50.59; H, 3.79; N, 6.27%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 9.37 (s, 2H), 8.35–8.37 (m, 2H), 8.07 (t, $J = 2$ Hz, 2H), 7.74–7.80 (m, 10H), 7.50–7.53 (m, 2H), 7.41 (t, $J = 4$ Hz, 2H), 7.26–7.28 (m, 2H), 5.53 (s, 4H), 4.72 (t, $J = 4.6$ Hz, 4H), 4.52 (t, $J = 4.6$ Hz, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.23, 182.24, 157.62 153.70, 149.78, 137.80, 135.22, 134.44, 123.94, 123.63, 123.33, 123.24, 122.77, 120.61, 119.64, 67.93, 53.52, 48.93, 31.34 ppm.

The following di-imidazolium salts **L3H$_2$**–**L5H$_2$** were prepared in analogous to that for **L2H$_2$**.

*4.4. Synthesis of 1,8-bis(3-(3-(n-butyl)-imidazole-2-ylidene) propoxy)-9,10-anthraquinone dihexafluorophosphate(**L3H$_2$**)*

Yield: 3.09 g (72%). Anal. Calcd for $C_{34}H_{42}F_{12}N_4O_4P_2$: C, 47.45; H, 4.92; N, 6.51%. Found: C, 47.48; H, 4.87; N, 6.53%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 9.12 (s, 2H), 7.76–7.81 (m, 8H), 7.54–7.56 (m, 2H), 4.54 (t, $J = 6.6$ Hz, 4H), 4.09–4.16 (m, 8H), 3.35–3.41 (m, 4H), 2.38 (t, $J = 6.2$ Hz, 4H), 1.66–1.69 (m, 4H), 0.81 (t, $J = 7.5$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.59, 182.39, 158.14, 136.57, 135.06, 134.60, 123.85, 123.09, 123.03, 120.69, 119.23, 65.62, 49.05, 46.44, 31.71, 29.13, 19.18, 13.67 ppm.

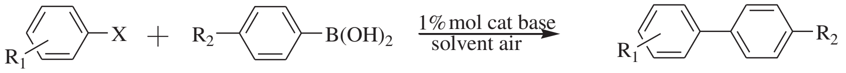
*4.5. Synthesis of 1,8-bis(3-(3-benzyl-imidazole-2-ylidene) propoxy)-9,10-anthraquinone dihexafluorophosphate (**L4H$_2$**)*

Yield: 3.38 g (73%). Anal. Calcd for $C_{40}H_{38}F_{12}N_4O_4P_2$: C, 51.73; H, 4.12; N, 6.03%. Found: C, 51.77; H, 4.08; N, 6.12%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 9.24 (s, 2H), 7.80–7.83 (m, 4H), 7.77–7.79 (m, 4H), 7.74–7.76 (m, 2H), 7.54–7.56 (m, 6H), 7.31–7.40 (m, 4H), 5.50 (s, 4H), 4.58 (t, $J = 6.4$ Hz, 4H), 4.14 (t, $J = 5.8$ Hz, 4H), 2.35–2.41 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 180.20, 154.52, 137.57, 132.83, 129.17, 129.12, 129.09, 128.32, 127.78, 126.50, 124.12, 122.52, 120.54, 114.99, 103.56, 65.90, 54.31, 49.70, 31.00 ppm.

*4.6. Synthesis of 1,8-bis(3-(3-picolyl-imidazole-2-ylidene) propoxy)-9,10-anthraquinone dihexafluorophosphate (**L5H$_2$**)*

Yield: 2.55 g (55%). Anal. Calcd for $C_{38}H_{36}F_{12}N_6O_4P_2$: C, 49.04; H, 3.90; N, 9.03%. Found: C, 49.09; H, 4.05; N, 8.98%. ^1H NMR

Table 4
Suzuki–Miyaura coupling reactions with various substrates.[a]



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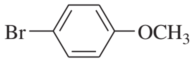
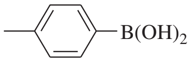
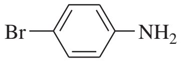
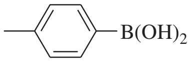
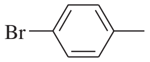
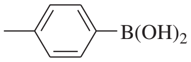
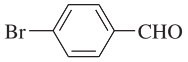
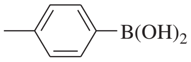
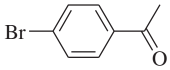
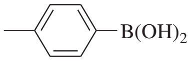
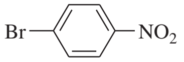
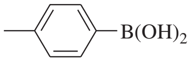
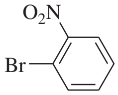
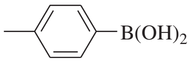
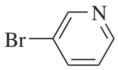
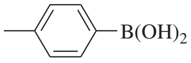
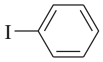
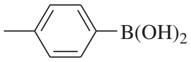
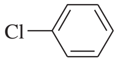
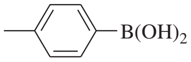
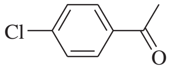
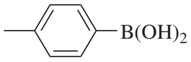
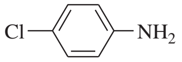
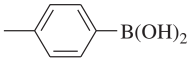
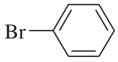
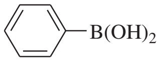
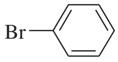
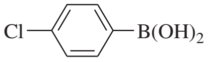
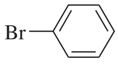
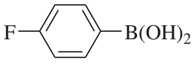
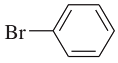
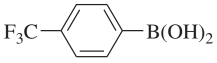
1			>99
2			>99
3			>99
4			93
5			95
6			92
7			90
8			95
9			>99
10			85
11			82
12			88
13			95
14			93
15			89
16			92

[a] Reaction conditions: aryl halide (0.2 mmol), arylboronic acids (0.22 mmol), $K_3PO_4 \cdot 3H_2O$ (0.44 mmol), 1 mol% $PdCl_2(CH_3CN)_2$, 1 mol% TBAB and 1 mol% complex **4** were added in the reaction, water (2 mL), 50 °C, 24 h.
[b] Isolated yield.

(400 MHz, DMSO-d_6, 25 °C): δ 9.22 (s, 2H), 7.77–7.82 (m, 6H), 7.52–7.55 (m, 2H), 7.28–7.33 (m, 10H), 5.36 (s, 4H), 4.53 (t, J = 6.6 Hz 4H), 4.12 (t, J = 6.0 Hz, 4H), 2.33–2.39 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.62, 182.45, 158.10, 136.76, 135.09, 135.06, 134.61, 129.37, 128.57, 123.81, 123.44, 123.20, 120.69, 119.26, 65.56, 52.40, 46.50, 29.03 ppm.

*4.7. Synthesis of 1,8-bis(3-(3-benzyl-imidazole-2-ylidene)propoxy) anthracene dihexafluorophosphate (**L6H₂**)*

A mixture of 3-(benzyl)-1*H*-imidazole (1.58 g, 10 mmol) and 1,8-bis(3-bromopropoxy)anthracene (2.26 g, 5 mmol) in THF (50 mL) was stirred and refluxed for 2 days. A tawny precipitate was isolated and washed with THF (20 mL) and dried in vacuo and through an anionic exchange with ammonium hexafluorophosphate. The product was collected by filtration and washed with methanol. Yield: 3.04 g (70%). Anal. Calcd for $C_{40}H_{40}F_{12}N_4O_2P_2$: C, 53.46; H, 4.49; N, 6.23%. Found: C, 53.37; H, 4.52; N, 6.18%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 9.18 (s, 2H), 7.78–7.80 (m, 2H), 7.75–7.76 (m, 6H), 7.50–7.53 (m, 2H), 7.41–7.45 (m, 2H), 7.26–7.31 (m, 10H), 5.33 (s, 4H), 4.52 (t, J = 6.6, 4H), 4.10 (t, J = 5.8 Hz, 4H), 2.32–2.37 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 158.58, 137.61, 134.80, 134.32, 128.98, 127.55, 125.84, 123.18, 122.52, 122.35, 120.43, 118.82, 66.83, 54.29, 52.30, 49.05, 30.45 ppm.

4.8. Synthesis of L1AgBr (*1*)

A mixture of Ag_2O (92.8 mg, 0.4 mmol) and **L1H₂** (159.6 mg, 0.2 mmol) in DMSO (10 mL) were stirred at 80 °C under nitrogen atmosphere for 2 days out of light. The resulting suspension was filtered, and water (50 mL) was added to obtain a yellow precipitate. The precipitate was filtered, washed with diethyl ether, and a pure product was obtained by recrystallization from CH_3OH and diethyl ether. Yield: 137 mg (83%). Anal. Calcd for $C_{40}H_{36}AgBr_2N_4O_4$: C, 58.29; H 4.40; N 6.80; found: C, 58.16; H, 4.49; N, 6.86%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.72–7.78 (m, 4H), 7.51–7.55 (m, 4H), 7.43 (d, J = 1.7 Hz 2H), 7.20 (t, J = 3.3 Hz, 6H), 7.10–7.13 (m, 4H), 5.20 (s. 4H), 4.52 (t, J = 7.0 Hz, 4H), 4.22 (t, J = 5.1 Hz, 4H), 2.33–2.39 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.65, 181.03, 158.68, 137.73, 134.90, 134.44, 129.09, 128.20, 127.67, 123.29, 122.64, 122.47, 120.53, 118.92, 66.93, 54.39, 49.15, 30.55 ppm.

The following NHC silver (I) complexes were prepared in the same procedure as that for **1**.

4.9. Synthesis of L2AgPF₆ (*2*)

A yellow powder. Yield: 103 mg (60%). Anal. Calcd for $C_{38}H_{32}AgF_6N_4O_4P$: C, 52.98; H, 3.74; N, 6.50; found: C, 52.93; H, 3.70; N, 6.47%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.71–7.78 (m, 4H), 7.53 (d, J = 13 Hz, 2H), 7.46 (d, J = 1.2 Hz, 2H), 7.44 (d, J = 1.6 Hz, 2H), 7.33–7.35 (m, 4H), 7.07–7.09 (m, 6H), 5.43 (s, 4H), 4.59 (t, J = 4.2 Hz, 4H), 4.33 (t, J = 4.2 Hz, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.23, 180.24, 157.62, 153.70, 149.78, 137.80, 135.22, 134.44, 123.94, 123.63, 123.24, 122.77, 120.61, 119.64, 67.93, 53.52, 48.93, 31.34 ppm.

4.10. Synthesis of L3AgPF₆ (*3*)

A yellow powder. Yield: 106 mg (65%). Anal. Calcd for $C_{34}H_{40}AgF_6N_4O_4P$: C, 49.71; H, 4.91; N, 6.82%; found: C, 49.76; H, 4.87; N, 6.79%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.70–7.77 (m, 4H), 7.50–7.53 (m, 4H), 7.42 (d, J = 1.7 Hz, 2H), 4.54 (t, J = 7.0 Hz, 4H), 4.23 (t, J = 5.1 Hz, 4H), 4.03 (t, J = 7.1 Hz, 4H), 2.38–2.45 (m, 4H), 1.64–1.72 (m, 4H), 1.12–1.18 (m, 4H), 0.77 (t, J = 5.1 Hz, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.58, 180.98, 158.73, 134.88, 134.38, 123.21, 122.13, 122.10, 120.45, 118.87, 66.85, 51.04, 49.04, 33.50, 30.54, 19.55, 15.62, 13.81 ppm.

4.11. Synthesis of L4AgPF₆ (*4*)

A yellow powder. Yield: 129 mg (73%). Anal. Calcd for $C_{40}H_{36}AgF_6N_4O_4P$: C, 54.01; H, 4.08; N, 6.30%; found: C, 54.08; H, 4.13; N, 6.25%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.74 (t, J = 4.8 Hz, 4H), 7.53–7.55 (m, 4H), 7.44 (d, J = 2 Hz, 2H), 7.20–7.21 (m, 6H), 7.13 (t, J = 3.0 Hz, 4H), 5.20 (s, 4H), 4.51 (t, J = 7.2 Hz, 4H), 4.22 (t, J = 5.2 Hz, 4H), 2.35–2.41 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.64, 181.03, 158.69, 137.72, 134.89, 134.45, 129.09, 128.20, 127.67, 123.33, 122.64, 122.47, 120.56, 118.93, 66.97, 65.30, 54.41, 49.17, 30.58 ppm.

4.12. Synthesis of L6Ag·PF₆ (*5*)

A brown powder. Yield: 132 mg (77%). Anal. Calcd for $C_{40}H_{38}AgF_6N_4O_2P$: C, 55.89; H, 4.46; N, 6.52%; found: C, 55.78; H, 4.52; N, 6.47%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.70–7.76 (m, 6H), 7.51–7.53 (m, 4H), 7.42 (d, J = 1.6 Hz, 2H), 7.17–7.19 (m, 6H), 7.08–7.10 (m, 4H), 5.17 (s, 4H), 4.49 (t, J = 7.0 Hz, 4H), 4.20 (t, J = 5.1 Hz, 4H), 2.31–2.37 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 158.56, 137.55, 134.84, 134.40, 128.98, 128.19, 127.52, 123.15, 122.49, 122.31, 120.43, 118.84, 66.82, 54.29, 49.03, 30.42 ppm.

4.13. Synthesis of L4AuPF₆ (*6*)

A mixture of Ag_2O (46.4 mg, 0.2 mmol) and **L4H₂** (185.6 mg, 0.2 mmol) in acetonitrile was stirred for 12 h at 50 °C in the dark, by that time almost all the Ag_2O dissolved. [Au(Me_2S)Cl] (63.6 mg, 0.2 mmol) was added and the mixture was stirred for 4 h at room temperature. Then the solvent was removed under vacuum. The residue was treated with diethyl ether, giving the desired product as a yellow solid, which was filtered, washed with diethyl ether and dried under vacuum. Yield: 127.1 mg (65%). Anal. Calcd for $C_{40}H_{36}F_6AuN_4O_4P$: C, 49.09, H, 3.71, N, 5.72%; found: C, 49.15; H, 3.63; N, 5.65%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.71–7.78 (m, 4H), 7.48–7.58 (m, 6H), 7.20–7.26 (m, 10H), 5.28 (s, 4H), 4.53 (t, J = 7.2 Hz, 4H), 4.26 (t, J = 5.1 Hz, 4H), 2.38–2.44 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.67, 183.65, 158.67, 137.39, 134.84, 134.45, 129.13, 128.39, 127.71, 123.42, 128.88, 122.63, 120.51, 118.91, 67.29, 53.83, 49.01, 30.93 ppm.

4.14. Synthesis of L5Hg(PF₆)₂ (*7*)

Mercury acetate (64 mg, 0.40 mmol) was added to a solution of **L5H₂** (154.8 mg, 0.2 mmol) in 40 mL of acetonitrile. The mixture was refluxed for 2 days under nitrogen atmosphere, after which the solvent was removed under reduced pressure. The yellow residue was washed with distilled water and recrystallization from acetonitrile to produce a yellow solid. Yield: 135.4 mg (60%). Anal. Calcd for $C_{38}H_{34}F_{12}HgN_6O_4P$: C, 40.42, H, 3.03, N, 7.44%. Found: C, 40.36; H, 3.10; N, 7.37%. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 8.07–8.09 (m, 2H), 7.98 (d, J = 1.8 Hz, 2H), 7.86 (d, J = 1.8 Hz, 2H), 7.69–7.86 (m, 6H), 7.47–7.50 (m, 2H), 7.42 (d, J = 7.7 Hz, 2H), 7.20–7.24 (m, 2H), 5.56 (s, 4H), 4.75 (t, J = 6.5 Hz, 4H), 4.19 (t, J = 5.2 Hz, 4H), 2.53–2.56 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.23, 182.24, 174.50, 158.49, 154.14, 149.58, 138.86, 135.30, 134.23, 125.13, 124.46, 123.92, 123.35, 122.53, 120.09, 118.91, 65.28, 54.60, 48.84, 28.19 ppm.

4.15. General procedure for the Suzuki–Miyaura cross-coupling reaction

In a typical reaction, aryl halide (0.2 mmol), phenylboronic acid (0.22 mmol), base (0.44 mmol), TBAB (tetrabutyl ammonium bromide 1 mol%), $PdCl_2(CH_3CN)_2$ (1 mol%) and complex **4** (1 mol%) and pure water (2 mL) were stirred at 50 °C in the dark for 24 h. The mixture was extracted by ethyl acetate (2 mL × 3). Then the solution concentrated to 1 mL. The solution was separated by column chromatography to get the pure products.

4.16. X-ray structure determinations

X-ray diffraction data for **1**–**7** were collected on a Bruker AMART APEX Π diffractometer with a Mo-Kα ($\lambda = 0.71073$ Å) by using ω scan mode. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares refinement on F^2 with SHELXL-97 [60]. All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Crystallographic data were summarized in Tables 1 and 2 for **1**–**7**.

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Appendix A. Supplementary material

CCDC 920160, 920156, 920159, 920158, 920157, 920161 and 920162 contain the supplementary crystallographic data for **1**–**7** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.001.

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