# Synthesis and Structural Characterization of Metal Complexes with Macrocyclic Tetracarbene Ligands

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#### Abstract

Fourteen Ag(I), Au(I), Ni(II), Pd(II), and Pt(II) complexes with macrocyclic tetradentate N-heterocyclic carbene (NHC) ligands were prepared *via* reactions between three macrocyclic tetrabenzimidazolium salts and metal precursors. All except two Au complexes were characterized using single-crystal X-ray diffraction. Three different structures, including a trinuclear one containing a NHC–Ag–(H<sub>2</sub>O) moiety and a hexanuclear propeller-like supramolecular assembly, are found for Ag–NHC complexes. Nine complexes of group 10 metal ions adopt square-planar geometry, in which the different ring-sizes of the macrocyclic tetracarbene ligands lead to a variation of metal–carbene bond lengths.  $\pi$ - $\pi$  stackings are observed between the rigid aromatic benzimidazole rings in the nickel group complexes.

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#### Introduction

Since the first stable N-heterocyclic carbene (NHC) was isolated by Arduengo in 1991,<sup>1</sup> NHCs have been employed as a class of fascinating ligands in organometallic chemistry due to their strong sigma-electron-donating ability and tunable steric effects, that make their metal complexes with applications in transition metal catalysed reactions,<sup>2</sup> medicine<sup>3</sup> and luminescent materials.<sup>4</sup> The steric and electronic properties of NHC ligands can be fine-tuned by introduction of a variety of substituents on the nitrogen atoms of heterocyclic rings via simple synthetic protocols.<sup>5</sup>

N-Heterocyclic carbene ligands are usually known to be incorporated into various bidentate, tridentate, or polydentate open chain ligands,<sup>6</sup> but in recent years there has been particular interest in marcocyclic NHC ligands<sup>7-13</sup> in view of the applications of the derived metal complexes in electron transfer reagents,<sup>8a-8b</sup> aziridination and epoxidation catalysts.<sup>9a,10b</sup> Besides, marcocyclic NHC ligands can stabilize some active intermediates such as Fe(IV)-oxo<sup>9b</sup> and Fe(IV)-tetrazene<sup>9c</sup> species due to the macrocyclic effect.<sup>14</sup>

In the past decade, tetradentate macrocyclic tetra(NHC) ligands, which are constructed by four NHC units, are the most important macrocyclic NHC ligands and have received considerable attention<sup>8-12</sup> since the report of macrocyclic tetra(NHC)-Pt complex synthesized via template controlled reaction by Hahn et al.<sup>13</sup> In 2007, Murphy et al. developed a more convenient route to obtain macrocyclic tetra(NHC) metal complexes by *in situ* deprotonation of macrocyclic imidazolium salts.<sup>8c</sup> Subsequently, various metal complexes with several macrocyclic tetra(NHC) ligands

(Chart 1) have been reported.<sup>8-12</sup> The macrocyclic tetra(NHC) Ni, Pd and Pt complexes usually exhibit a square-planar configuration irrespective of the lengths of the linker between the NHC units (A, B, C, E, Chart 1),<sup>8a,8c,9d,9e,10c,12</sup> while the structure of the tetra(NHC)-Co(II) complex depends on the linker lengths. The Co(II) complex with ligand C exhibit a tetrahedral geometry<sup>8b</sup> while that of ligand **B** is a five-coordinate complex with square pyramidal configuration.<sup>9d</sup> The structures of macrocyclic tetraNHC Ag(I) complexes have more intricate structures, in which three coordination modes have been revealed. The first structural type is the dinuclear unit containing two silver ions encapsulated by one tetracarbene molecule, which is found for ligand C (see F, Chart 2).<sup>8c</sup> The box- or cage-like complexes were formed by the four silver ions and two tetraNHC ligands, where two silver ions act as a bridge between both NHC units, while the other two silver ions connect the intramolecular carbenes (G, Chart 2). This second type of the twisted structure is found with ligand **B**.<sup>9d</sup> The last structural type has sandwich-like construction (**H**, **I**, Chart 2), which was found in the silver complexes bearing ligand A or E.<sup>10c,12</sup>

In addition to tetra(NHC) complexes, other bidentate and polydentate NHC-containing macrocyclic complexes have also be studied.<sup>15</sup> All these previously reported examples contain imidazolylidene as the NHC unit with the exception of one macrocyclic tetra(benzimidazolylidene)–Pt complex (**J**, Chart 2) synthesized via template reaction by Hahn et al.<sup>13</sup> Beer et al.<sup>16</sup> reported a series of macrocyclic tetrabenzimidazolium salts (H4L<sup>1</sup>)(PF6)4, (H4L<sup>2</sup>)(PF6)4 and (H4L<sup>3</sup>)(PF6)4 featuring different length of flexible linkers (Chart 1) as the supramolecular receptors for the

anions, but no report has published for coordination chemistry of the tetraNHC ligands derived from these salts. In this contribution, we describe the synthesis and structural characterizations of twelve new metal (Ni, Pd, Pt and Ag) complexes with the macrocyclic tetra-NHC ligands  $L^1-L^3$  with different linker lengths.



Chart 1 Selected examples of tetra-NHC Ligands











Chart 2 Selected examples of tetra-NHC metal complexes

## **Results and discussion**

To study the coordination behaviour of macrocyclic tetraNHC ligands  $L^1$ , (H<sub>4</sub> $L^1$ )(PF<sub>6</sub>)<sub>4</sub> was employed to react with Ag<sub>2</sub>O in DMF at ambient temperature, which yielded an Ag(I) complex [Ag<sub>2</sub>( $L^1$ )](PF<sub>6</sub>)<sub>2</sub> (1) as a white solid in 85% yield

(Scheme 1). Its <sup>1</sup>H NMR spectrum shows no resonance at 9.15-9.52 ppm for 2*H*-benzimidazole protons of  $(H_4L^1)(PF_6)_4$ . The resonances of benzimidazole backbone protons appear at 7.59-8.02 ppm. Two sets of carbon atom resonances at  $\delta =$  $187.76 ({}^{1}J_{Ag(109),C} = 197 \text{ H}, {}^{1}J_{Ag(107),C} = 174 \text{ Hz})$  were found at the  ${}^{13}C$  NMR spectrum, showing the typical characteristic coupling to the silver isotopes.<sup>17</sup> Single crystals of 1.2DMF were obtained by slow diffusion of diethyl ether into a DMF solution. The solid-state structure of 1.2DMF was confirmed by X-ray crystallography (Figure 1, Table S1) to contain two Ag(I) ions coordinated by one macrocyclie ligand, which was found in the tetra(imidazolylidene) analog<sup>8c</sup> (F, Chart 2). Two Ag<sup>I</sup> ions reside in the center of the folded macrocycle  $L^1$  due to the flexibility of  $L^1$  ligand. Each Ag(I) is coordinated with two opposite carbene donors in a linear fashion with C-Ag-C angles (171.7°, 179.2°). The two C-Ag-C groups cross in a approximate orthogonal mode with the C-Ag-Ag-C torsion angles in the range of 87.68° to 92.54°. The Ag-Ag distance is 2.7826(6) Å, which is shorter than the sum of the van der Waals radii of Ag (ca. 3.44 Å), indicating the argentophilic interaction.<sup>18</sup> This distance is shorter than those of dinuclear silver(I) complexes with the tetra(imidazolylidene) analog J  $(2.8349(6) \text{ Å})^{8c}$  and acyclic NHC ligands (3.025(1) Å).<sup>19,20a</sup> It is noted that such dinuclear Ag<sub>2</sub> units with various C-Ag-Ag-C torsion angles are commonly found for Ag complexes with acyclic NHC ligands with Ag-Ag distances in the range from 2.9712 to 3.1514 Å.<sup>20</sup> The shorter Ag-Ag distance in 1 and the tetra(imidazolylidene) analog could be due to the constraint imposed by the macrocyclic NHC ligands.



Scheme 1 Synthesis of  $[Ag_2(L^1)](PF_6)_2(1)$ 



**Figure 1** Structure of [Ag<sub>2</sub>(L<sup>1</sup>)](PF<sub>6</sub>)<sub>2</sub>·2DMF (1·2DMF) showing 30% probability ellipsoids. Hydrogen atoms, the hexafluorophosphate anions and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C11 2.117(5), Ag1-C31 2.113(5), Ag2-C1 2.123(5), Ag2-C21 2.121(6), Ag1-Ag2 2.7826(6); C31-Ag1-C11 179.3(2), C1-Ag2-C21 178.30(18), C31-Ag1-Ag2-C21 90.95(19), C11-Ag1-Ag2-C21 89.76(19), C31-Ag1-Ag2-C1 89.1(2), C11-Ag1-Ag2-C1 90.23(19).

To investigate the effect of different ring size on the coordination properties,

 $(H_4L^2)(PF_6)_4$  and  $(H_4L^3)(PF_6)_4$  were also reacted with Ag<sub>2</sub>O under the same condition to give  $[Ag_3(L^2)(H_2O)_2](PF_6)_3(2)$  and  $[Ag_6(L^3)_3](PF_6)_6(3)$  as off-white solids in 66% and 76% yields, respectively (Schemes 2 and 3). The <sup>1</sup>H NMR spectrum of **2** shows two sets of resonances for magnetically unequal benzimidazole backbone protons at 7.55-7.86 ppm and four resonances for each of four alkyl bridges at 4.18-4.64 ppm. The resonances of carbon carbon atom were observed at 185.80 ppm in the <sup>13</sup>C NMR spectrum, which was similar to those reported for the complexes with linear C<sub>NHC</sub>-Ag-C<sub>NHC</sub> moiety. Single crystals of 2.2DMF were obtained by slow diffusion of diethyl ether into a DMF solution. A novel trinuclear fashion  $[Ag_3(L^2)(H_2O)_2]^{3+}$  was revealed by single crystal X-ray diffraction (Figure 2 and Table S1). One silver(I) ion Ag2 occupies the center of the molecule to connect two opposite carbene donors in a linear fashion while each of the other two silver(I) ions Ag1 or Ag3 coordinates one carbene donor and one H<sub>2</sub>O molecule. The distances of Ag2-C12 and Ag2-C33 are 2.124(7) and 2.130(11) Å, respectively, which are longer than those of Ag1-C1 (2.074(10) Å) and Ag3-C22 (2.046(11) Å). The Ag-O(H<sub>2</sub>O) distances are 2.089(12) and 2.130(11) Å which are comparable with those in compounds with linear L-Ag-H<sub>2</sub>O moiety.<sup>21</sup> To the best of our knowledge, 2 is the first example of Ag(I) compound with the simultaneous coordination of NHC and H<sub>2</sub>O at the Ag(I) ion.



Scheme 2 Synthesis of  $[Ag_3(L^2)(H_2O)_2](PF_6)_3(2)$ 



**Figure 2** Structure of [Ag<sub>3</sub>(L<sup>2</sup>)(H<sub>2</sub>O)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>·2DMF (**2**·2DMF) showing 30% probability ellipsoids. Hydrogen atoms, the hexafluorophosphate anions and solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C1 2.074(10), Ag2-C12 2.129(9), Ag2-C33 2.124(7), Ag3-C22 2.046(11), Ag1-O1 2.130(11), Ag3-O2 2.089(12); C1-Ag1-O1 174.0(5), C33-Ag2-C12 172.1(4), O2-Ag3-C22 174.0(4).

The <sup>1</sup>H NMR spectrum of **3** shows the resonances of benzimidazole backbone

protons at 7.21-7.94 ppm and the resonances of alky bridges detected at 3.96-4.18 ppm and 1.58-2.30 ppm. In <sup>13</sup>C NMR spectrum, the carbon resonances are found at 186.84 ppm along with the coupling of Ag-C<sub>carbene</sub> ( ${}^{1}J_{Ag(109),C} = 215$  Hz,  ${}^{1}J_{Ag(107),C} = 203$  Hz). In order to clarify the structure of **3**, single crystals were obtained by slow diffusion of diethyl ether into a solution in acetonitrile. The molecular structural analysis reveals a novel hexanuclear supramolecular turbo-like structure consisting of three tetraNHC molecules (Figure 3). One silver ion (Ag1, Ag3, or Ag3\*) connects the opposite two carbene donors from each tetraNHC macrocycle  $L^3$ , where the other two carbene donors rotates out of the ring due to the flexibility of L<sup>3</sup>. The other three Ag ions (Ag2, Ag2\*, Ag4) are each ligated to two NHC donors from two adjacent tetraNHC macrocycles to form a closed loop, creating a turbo-like supramolecular structure. The Ag-Ccarbene distances in 3 are 2.056-2.127 Å, which are in the range of related box-like Ag-NHC complexes reported by Hahn.<sup>11,12,20</sup> The C-Ag-C angles are in the range of 171.7°-179.2°. Ag-Ag distances amount to 5.760 Å to 6.243 Å, which are far more than the sum of the respective van der Waals radii.<sup>18</sup> Six silver ions are co-planar and formed a hexagonal cavity with the diagonal distances from 11.171 to 12.684 Å.

Recently poly(N-heterocyclic carbene) ligands have been used to construct discrete metallosupramolecular assemblies such as molecular squares and rectangles,<sup>22</sup> and cylinder or box-like structures.<sup>23</sup> As described in Introduction, Ag(I) ions can be held by some macrocyclic tetra-NHC ligands to give tetranuclear box-like structures such as **H** and **I** (Chart 2). There are two hexanuclear cylinder-like Ag-NHC assemblies reported.<sup>15,23a</sup> It should be noted that **3** is an unprecedented cage-like supramocular structure formed from macrocyclic tetraNHC ligands and  $Ag^+$  ion via the Ag-NHC bonds.

The different structures of **1-3** clearly demonstrate that the coordination properties of the macrocyclic tetraNHC ligands depend on the linker lengths. Furthermore, as a host molecule, **3** includes the hexafluorophosphate ion in its cavity (Figure 4), implying that PF<sub>6</sub><sup>-</sup> anion could play a template in the formation of **3**. In order to justify the role of PF<sub>6</sub><sup>-</sup> anion, we have attempted to prepare the Ag-NHC using (H<sub>4</sub>L<sup>3</sup>)(X)<sub>4</sub> (X = BPh<sub>4</sub><sup>-</sup>) in the similar reaction conditions. No complexes were isolated even after many attempts, implying the unique role of PF<sub>6</sub><sup>-</sup> anion in the formation of **3**.



**3**, 76%

Scheme 3. Synthesis of  $[Ag_6(L^3)_3](PF_6)_6(3)$ 



**Figure 3** Structure of  $[Ag_6(L^3)_3](PF_6)_6(3)$  in two directions, showing 30% probability ellipsoids. Hydrogen atoms and the hexafluorophosphate anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C1 2.104(8), Ag2-C2 2.126(9), Ag2-C3 2.127(9), Ag3-C4 2.056(16), Ag3-C6 2.112(15), Ag4-C5 2.114(16); C1-Ag1-C1 174.6(5), C2-Ag2-C3 171.7(4), C4-Ag3-C6 172.1(6), C5-Ag4-C5 179.2(8).



Figure 4 Structure of [Ag<sub>6</sub>(L<sup>3</sup>)<sub>3</sub>](PF<sub>6</sub>)<sub>6</sub> (**3**) including a hexafluorophosphate anion in its cavity. Selected bond lengths (Å): F1-H1B 2.530, F2-H2A 2.362, F2-H3A 2.202, F3-H1A 2.635, F3-H2B 2.616, F3-H3A 2.728, F3-H3B 2.989.

To further study their coordination chemistry,  $(H_4L^1)(PF_6)_4$ ,  $(H_4L^2)(PF_6)_4$  and  $(H_4L^3)(PF_6)_4$  were reacted with d<sup>8</sup> transition metal (Ni, Pd, Pt) precursors Ni(OAc)<sub>2</sub>, Pd(OAc)<sub>2</sub>, or Pt(acac)<sub>2</sub> in presence of sodium acetate in DMSO to give nine complexes **4-12** (Scheme 4). It was found that the three different size macrocycles have various reactivities with metal precursors. The largest macrocycle  $(H_4L^3)(PF_6)_4$  gave the highest yield to obtain  $[M(L^3)](PF_6)_2$  (M = Ni, Pd, Pt) after reaction for one day.  $[M(L^1)](PF_6)_2$  and  $[M(L^2)](PF_6)_2$  can be obtained in good yields by extending the reaction time to three days. Compared to Ni(OAc)<sub>2</sub> and Pd(OAc)<sub>2</sub>, Pt(acac)<sub>2</sub> has the lowest reactivity with the three marocyclic NHC ligands. It is found that at least 4 equivalents of sodium acetate were required for the formation of nickel complexes in

a high yield.



Scheme 4 Synthesis of complexes 4-12

**Complexes 4-12** are stable in air- and moisture-stable in both solution and solid state. They were characterized by NMR spectroscopy and ESI-MS. The <sup>1</sup>H NMR spectra of Ni(II) complexes do not exhibit the *2H*-benzimidazolium proton signal at 9.15-9.52 ppm, indicating the coordination of the carbene carbon to the Ni(II) ion. The chemically different alkyl bridges show various signals in high field, compared to those of NHC precuors  $(H_4L^1)(PF_6)_4$ ,  $(H_4L^2)(PF_6)_4$  and  $(H_4L^3)(PF_6)_4$ , which have only one broad singlet signal detected. [Ni(L<sup>2</sup>)](PF\_6)<sub>2</sub> (**5**) has four <sup>1</sup>H NMR signals of alkyl bridges while [Ni(L<sup>1</sup>)](PF\_6)<sub>2</sub> (**4**) or [Ni(L<sup>3</sup>)](PF\_6)<sub>2</sub> (**6**) has only two <sup>1</sup>H NMR signals. These is consistent with the lower symmetry of **5** compared to **4** and **6**. The <sup>13</sup>C NMR spectra show only one signal for all four carbene carbon atoms at 184.4 (**4**), 180.2 (**5**), 176.2 (**6**), which shift upfield compared to the *2C*-benzimidazolium signal at 141.5, 142.7, and 141.2 ppm for  $(H_4L^1)(PF_6)_4$ ,  $(H_4L^2)(PF_6)_4$  and  $(H_4L^3)(PF_6)_4$ , respectively. For **5**, the aryl carbons have two sets of signals because of the low symmetric structure.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of Pd(II) complexes **7-9** are similar to those of the Ni<sup>II</sup> analogs **4-6** with only slight differences. It is worth mentioning that the resonances of four carbene carbon atoms of **7-9** are very close (181.3 (7), 177.3 (**8**), 176.2 (**9**) ppm). The <sup>1</sup>H NMR spectra of Pt(II) complexes **10-12** are very similar to those of the Pd(II) analogs. The <sup>13</sup>C NMR spectra show that the resonances of the carbene carbon atoms were obviously upfield shifted in respective to those of Ni<sup>II</sup> or Pd<sup>II</sup> complexes.

Formation of complexes 4-12 were also confirmed by ESI-MS spectrometry with strong peaks for the cations  $[M(L)(PF_6)]^+$  and  $[M(L)]^{2+}$ .

The structures of metal complexes have been determined by X-ray diffraction analyses. Crystals of **4-12** suitable for an X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a solution of each in acetonitrile. As expected, **4-12** have similar square-planar configuration, in which the central metal center is wrapped by a marcocyclic tetracarbene ligand (Figures 5 and S1-S3). The macrocycle is so flexible to adjust to fit the square-planar geometry.



Figure 5 Structure of  $[Ni(L1)](PF_6)_2(4)$  showing 30% probability ellipsoids. Hydrogen atoms and the hexafluorophosphate anions are omitted for clarity.

The metal-C<sub>carbene</sub> bond distances are in the range of 1.900 Å-1.956 Å for Ni complexes **4-6**, 2.025 Å-2.072 Å for Pd complexes **7-9**, and 2.019 Å2.081 Å for Pt complexes **10-12** (Table 1), which are comparable to those of previously reported similar metal tetra-NHC compounds.<sup>8a,8c,9d,9e,10c,12</sup> The larger the size of the marcocycle ligand is, the longer metal-C<sub>carbene</sub> distances are, which could be due to the additional tension provided by the more distorted longer alkyl bridge. The geometry index  $\tau_4$  values,<sup>24</sup> which were suggested to reveal the four-coordinate coordination geometry, were calculated for **4-12** and listed in Table 2. The largest  $\tau_4$  value of 0.105 was found for **5**, while those of other eight complexes are in the range of 0.025-0.055, which is consistent with their square planar configuration.

The  $\pi$ - $\pi$  stacking interactions of benzimidazole rings are observed in the crystal

packing of **4-12** (Figure 5). **4** has the strongest  $\pi$ - $\pi$  interactions in nine complexes with a face-to-face distance between the two benzimidazole rings of 3.477 Å (centroid-to-centroid 3.589 Å). The molecules are connected and extended into a 1-D chain. **5-8** and **10-12** form a 2-D supramolecular layer by two kinds of  $\pi$ - $\pi$ interactions (T-shaped and parallel displaced).<sup>25</sup> The expanding of ligand ring size leads to the weaker  $\pi$ - $\pi$  interactions, indicated by the distance between the two benzimidazole rings (Table 3). There was no  $\pi$ - $\pi$  stacking interaction was observed in **9**.

| Table 1 Selected bond lengths of Ni, Pd and Pt complexes |          |          |          |          |  |  |
|--|----------|----------|----------|----------|--|--|
|  | M-C [Å]  |          |          |          |  |  |
|  | M-C1     | M-C2     | M-C3     | M-C4     |  |  |
| 4  | 1.911(5) | 1.911(5) | 1.908(5) | 1.900(5) |  |  |
| 5  | 1.952(5) | 1.931(6) | 1.953(5) | 1.954(6) |  |  |
| 6  | 1.914(7) | 1.956(7) | 1.954(7) | 1.951(7) |  |  |
| 7  | 2.044(4) | 2.033(5) | 2.042(4) | 2.025(5) |  |  |
| 8  | 2.032(8) | 2.048(8) | 2.056(8) | 2.036(9) |  |  |
| 9  | 2.072(9) | 2.054(8) | 2.059(8) | 2.042(8) |  |  |
| 10   | 2.019(8) | 2.043(9) | 2.021(9) | 2.042(9) |  |  |
| 11   | 2.053(4) | 2.035(5) | 2.039(5) | 2.037(5) |  |  |
| 12   | 2.069(7) | 2.053(6) | 2.081(7) | 2.055(7) |  |  |

| Table 2 Selected angles of Ni, Pd and Pt complexes |            |            |                         |  |  |
|--|------------|------------|-------------------------|--|--|
|  | А          | В          | τ4 value <sup>[a]</sup> |  |  |
| 4  | 178.3(2)   | 177.5(2)   | 0.029                   |  |  |
| 5  | 172.9(2)   | 172.2(2)   | 0.105                   |  |  |
| 6  | 177.4(3)   | 175.9(3)   | 0.047                   |  |  |
| 7  | 178.72(16) | 176.27(18) | 0.035                   |  |  |
| 8  | 176.5(4)   | 175.6(4)   | 0.055                   |  |  |
| 9  | 180.0      | 176.4(5)   | 0.025                   |  |  |
| 10   | 178.8(4)   | 176.6(4)   | 0.032                   |  |  |
| 11   | 177.4(2)   | 176.8(2)   | 0.041                   |  |  |
| 12   | 177.7(4)   | 177.2(3)   | 0.036                   |  |  |

[a]  $\tau_4 = [360-(\alpha+\beta)]/141$ ,  $\alpha$  and  $\beta$  are the two largest  $\theta$  angles in the four-coordinate species.<sup>23</sup>

| Table 3 $\pi$ - $\pi$ stacking interaction distances of 4-12 |                          |                  |  |  |
|--|--------------------------|------------------|--|--|
|  | Centroid to centroid [Å] | Face to face [Å] |  |  |
| 4  | 3.589                    | 3.477            |  |  |
| 5  | 3.607                    | 3.372            |  |  |
| 6  | 3.989                    | 3.464            |  |  |
| 7  | 3.761                    | 3.414            |  |  |

| 8  | 3.712 | 3.470 |
|----|-------|-------|
| 9  | null  | null  |
| 10 | 3.759 | 3.418 |
| 11 | 3.617 | 3.386 |
| 12 | 4.151 | 3.485 |

#### Conclusions

In this work, three macrocyclic tetraNHC ligand precursors (H<sub>4</sub>L<sup>1</sup>)(PF<sub>6</sub>)<sub>4</sub>-(H<sub>4</sub>L<sup>3</sup>)(PF<sub>6</sub>)<sub>4</sub> were used to react with metal precursors to form macrocyclic tetraNHC Ag, Ni, Pd and Pt complexes **1-12**. Three different structures, which contain binuclear, trinuclear and hexanuclear silver units, respectively, were found for Ag complexes **1-3**. A novel trinulear Ag structure, containing a rare NHC-Ag-(OH<sub>2</sub>) moiety, was observed with the tetraNHC from (H<sub>4</sub>L<sup>2</sup>)(PF<sub>6</sub>)<sub>4</sub>. An unprecedented hexanuclear turbo-like complex [Ag<sub>6</sub>(L<sup>3</sup>)<sub>3</sub>](PF<sub>6</sub>)<sub>6</sub> (**3**) was obtained for the metal-NHC supramolcules. For the group 10 metals (Ni, Pd and Pt), the highly flexible tetra-NHC ligand wraps around the metal ion to form a square-planar structure. The metal-C<sub>carbene</sub> distance increases with the increase in the ligand ring size. The  $\pi$ - $\pi$  stacking interactions, which is provided by benzimidazole rings, determine the mode of packing in the crystal lattice. The distinction of ligand ring sizes also influences the strength of  $\pi$ - $\pi$  interactions.

#### EXPERIMENTAL

General Procedures. Unless otherwise noted, all reactions and manipulations were

performed under a dry nitrogen atmosphere using the standard Schlenk techniques. Solvents were dried using conventional methods and freshly distilled before use. NMR spectra were obtained on a Bruker AM-400 spectrometer. ESI-MS were recorded on a Bruker MaXis mass spectrometer. Elemental analysis was performed in a Perkin-Elmer 240C analytic instrument. Macrocyclic tetraNHC ligand precursors (H4L<sup>1</sup>)(PF<sub>6</sub>)4, (HL<sup>2</sup>)(PF<sub>6</sub>)4 and (H4L<sup>3</sup>)(PF<sub>6</sub>)4 were prepared following the reported procedures.<sup>16</sup>

Synthesis of  $[Ag_2(L^1)](PF_6)_2(1)$ 

(H<sub>4</sub>L<sup>1</sup>)(PF<sub>6</sub>)<sub>4</sub> (304 mg, 0.25 mmol) and Ag<sub>2</sub>O (144 mg, 0.625 mmol) were added to a 100 mL Schlenk flask. Then 5 mL acetonitrile was added into the mixture and stirred for overnight at room temperature. The solution was filtered through Celite. The filtrate was poured into 100 mL ethyl ether to precipitate a pale solid, which was collected by filtration and dried under vacuum to give complex **1** as a brown solid (241.4 mg, yield 85.2 %). Slow evaporation of the solvent from DMF solution of **1** gave colorless prism crystals of **1**·2DMF suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  8.00-8.02 (m, 8H, Ph-*H*), 7.59-7.62 (m, 8H, Ph-*H*), 4.62-4.67 (m, 8H, N-C*H*<sub>2</sub>), 4.27-4.35 (m, 8H, N-C*H*<sub>2</sub>), 2.56-2.65 (br, 8H, C*H*<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C):  $\delta$  187.76 (d + d, <sup>1</sup>J<sub>Ag(109),C</sub> = 197 Hz, <sup>1</sup>J<sub>Ag(107),C</sub> = 174 Hz, carbene-C), 134.11 (imidazole-ring-C), 124.85 (PhC), 113.73 (PhC), 45.43 (N-CH<sub>2</sub>), 27.61 (CH<sub>2</sub>). Anal. Calcd for C<sub>40</sub>H<sub>40</sub>N<sub>8</sub>F<sub>12</sub>Ag<sub>2</sub>P<sub>2</sub>·2C<sub>3</sub>H<sub>7</sub>NO (1284.67 g mol<sup>-1</sup>): C, 43.01; H, 4.24; N, 10.90. Found: C, 43.00; H, 4.25; N, 10.86. Synthesis of  $[Ag_3(L^2)(H_2O)_2](PF_6)_3(2)$ 

(H4L<sup>2</sup>)(PF<sub>6</sub>)<sub>4</sub> (311 mg, 0.25 mmol) and Ag<sub>2</sub>O (144 mg, 0.625 mmol) were added to a 100 mL Schlenk flask. Then 5 mL acetonitrile was added into the mixture and stirred overnight at room temperature. The solution was filtered through Celite. The filtrate was poured into 100 mL ethyl ether and a pale solid precipitated, which was collected by filtration and dried under vacuum to give **2** as a brown solid (248 mg, yield 66.3%). Slow evaporation of the solvent from DMF solution of **2** gave colorless prism crystals of **2**·2DMF suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  7.71-7.86 (m, 8H, Ph-*H*), 7.55-7.61 (m, 8H, Ph-*H*), 4.48-4.64 (m, 8H, N-CH<sub>2</sub>), 4.16-4.38 (m, 8H, N-CH<sub>2</sub>), 2.83-2.86 (m, 4H, CH<sub>2</sub>), 2.19-2.23 (m, 4H, CH<sub>2</sub>), 1.76-1.82 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C):  $\delta$  185.80 (carbene-*C*), 131.71 (imidazole-ring-*C*), 122.72 (PhC), 110.42 (PhC), 46.47 (N-CH<sub>2</sub>), 44.01 (N-CH<sub>2</sub>), 34.13 (CH<sub>2</sub>), 29.12 (CH<sub>2</sub>), 22.16 (CH<sub>2</sub>). Anal. Calcd for C<sub>42</sub>H<sub>48</sub>N<sub>8</sub>F<sub>18</sub>O<sub>2</sub>Ag<sub>3</sub>P<sub>3</sub>·2C<sub>3</sub>H<sub>7</sub>NO (1601.60 g mol<sup>-1</sup>): C, 36.00; H, 3.90; N, 8.75. Found: C, 36.02; H, 3.87; N, 8.76.

Synthesis of  $[Ag_6(L^3)_3](PF_6)_6(3)$ 

(H4L<sup>3</sup>)(PF<sub>6</sub>)<sub>4</sub> (318 mg, 0.25 mmol) and Ag<sub>2</sub>O (144 mg, 0.625 mmol) were added to a 100 mL Schlenk flask. The mixture was then treated with 5 mL of acetonitrile and stirred overnight at room temperature. The solution was filtered through Celite. The filtrate was poured into 100 mL of ethyl ether to give a pale solid precipitate, which

was collected by filtration and dried under vacuum to give **3** as a pale solid (224 mg, yield 76.1%). Slow diffusion of diethyl ether into a solution of acetonitrile gave colorless needle crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  7.21-7.94 (m, 48H, Ph-*H*), 3.96-4.68 (m, 48H, N-C*H*<sub>2</sub>), 1.58-2.30 (m, 48H, C*H*<sub>2</sub>). <sup>13</sup>C NMR(100 MHz, DMSO-*d*<sub>6</sub>, 25°C):  $\delta$  186.84 (d + d, <sup>1</sup>*J*<sub>Ag(109),C</sub> = 215 Hz, <sup>1</sup>*J*<sub>Ag(107),C</sub> = 203 Hz, carbene-*C*), 134.38 (imidazole-ring-*C*), 134.83 (Ph*C*), 114.15 (Ph*C*), 124.57 (Ph*C*), 112.25 (Ph*C*), 66.38 (N-CH<sub>2</sub>), 47.89 (N-CH<sub>2</sub>), 29.88 (CH<sub>2</sub>), 27.62 (CH<sub>2</sub>). Anal. Calcd for C<sub>132</sub>H<sub>144</sub>N<sub>24</sub>F<sub>36</sub>Ag<sub>6</sub>P<sub>6</sub> (3576.71 g mol<sup>-1</sup>): C, 44.24; H, 4.05; N, 9.38. Found: C, 44.21; H, 4.11; N, 9.37.

Synthesis of  $[Ni(L^1)](PF_6)_2$  (4)

(H<sub>4</sub>L<sup>1</sup>)(PF<sub>6</sub>)<sub>4</sub> (304 mg, 0.25 mmol), Ni(OAc)<sub>2</sub> (44 mg, 0.25 mmol) and sodium acetate (82 mg, 1.0 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 2 h.Then 5 mL of DMSO was added into the mixture and stirred for 2 days. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL of water to give a brown solid , which was collected by filtration and dried under vacuum to yield **4** as a orange solid (229 mg, yield 93.6%). Slow evaporation of the solvent from an acetonitrile solution of **4** gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  7.47-7.52 (m, 8H, Ph-*H*), 7.26-7.30 (m, 8H, Ph-*H*), 5.48-5.55 (m, 8H, N-C*H*<sub>2</sub>), 4.98-5.04 (dt, <sup>2</sup>*J*<sub>H,H</sub> = 8 Hz, 16 Hz, 8H, N-C*H*<sub>2</sub>), 2.85 (br, 2H, C*H*<sub>2</sub>), 2.01-2.03 (m, 4H, C*H*<sub>2</sub>), 1.53 (br, 2H, C*H*<sub>2</sub>) <sup>13</sup>C NMR(100 MHz, DMSO-*d*<sub>6</sub>, 25 °C):  $\delta$ 

184.45 (carbene-*C*), 135.09 (imidazole-ring-*C*), 123.61 (Ph*C*), 111.11 (Ph*C*), 50.23 (N-*C*H<sub>2</sub>), 30.06 (*C*H<sub>2</sub>), MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 835.37. Anal. Calcd for C<sub>40</sub>H<sub>40</sub>N<sub>8</sub>F<sub>12</sub>NiP<sub>2</sub> (981.45 g mol<sup>-1</sup>): C, 48.95; H, 4.11; N, 11.42. Found: C, 48.95; H, 4.11; N, 11.41.

Synthesis of  $[Ni(L^2)](PF_6)_2$  (5)

(H4L<sup>2</sup>)(PF<sub>6</sub>)<sub>4</sub> (311 mg, 0.25 mmol), Ni(OAc)<sub>2</sub> (44 mg, 0.25 mmol) and sodium acetate (82 mg, 1.0 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 2 h. Then 5 mL of DMSO was added into the mixture and stirred for 2 days. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL of water and a brown solid precipitated which was collected by filtration and dried under vacuum to give nickel complex 5 as a orange solid (228 mg, yield 90.8 %). Slow evaporation of the solvent from an acetonitrile solution of the compound gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 25 °C): δ 7.71-7.79 (m, 8H, Ph-*H*), 7.25-7.31 (m, 8H, Ph-*H*), 5.67-5.76 (m, 8H, N-CH<sub>2</sub>), 5.10-5.16 (dt,  ${}^{2}J_{H,H} = 8$  Hz, 4 Hz, 16 Hz, 12 Hz, 4H, N-CH<sub>2</sub>), 4.92-4.95 (m, 4H, N-CH<sub>2</sub>), 2.75-2.86 (m, 2H, CH<sub>2</sub>), 2.25-2.33 (br, 4H, CH<sub>2</sub>), 1.83-1.92 (m, 2H, CH<sub>2</sub>), 1.34-1.36 (br, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 179.21 (carbene-C), 133.12, 132.10 (imidazole-ring-C), 121.78, 121.62 (PhC), 109.65, 108.99 (PhC), 42.42(N-CH<sub>2</sub>), 20.41 (CH<sub>2</sub>), MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 863.14. Anal. Calcd for C<sub>42</sub>H<sub>44</sub>N<sub>8</sub>F<sub>12</sub>NiP<sub>2</sub> (1009.50 g mol<sup>-1</sup>): C, 49.97; H, 4.39; N, 11.10. Found: C, 49.95; H, 4.41; N, 11.07.

Synthesis of  $[Ni(L^3)](PF_6)_2$  (6)

(H4L<sup>3</sup>)(PF<sub>6</sub>)<sub>4</sub> (318 mg, 0.25 mmol), Ni(OAc)<sub>2</sub> (44 mg, 0.25 mmol) and sodium acetate (82 mg, 1 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 2 h. Then 5 mL of DMSO was added into the mixture and stirred for 2 days. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL water and a brown solid precipitated which was collected by filtration and dried under vacuum to give **6** as a orange solid (236 mg, yield 91.5%). Slow evaporation of the solvent from an acetonitrile solution of the compound gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  7.48-7.53 (m, 8H, Ph-*H*), 7.25-7.30 (m, 8H, Ph-*H*), 5.72-5.79 (m, 8H, N-C*H*<sub>2</sub>), 4.77-4.83 (m, 8H, N-C*H*<sub>2</sub>), 2.38-2.42 (m, 8H, C*H*<sub>2</sub>), 1.27-1.34 (m, 8H, C*H*<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C):  $\delta$  176.06 (carbene-*C*), 133.49 (imidazole -ring -*C*), 123.61 (PhC), 111.85 (PhC), 44.01 (N-CH<sub>2</sub>), 23.38 (CH<sub>2</sub>), MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 891.37. Anal. Calcd for C44H48N8F12NiP<sub>2</sub> (1037.55 g mol<sup>-1</sup>): C, 50.94; H, 4.66; N, 10.80. Found: C, 50.95; H, 4.66; N, 11.00.

Synthesis of  $[Pd(L^1)](PF_6)_2(7)$ 

(H<sub>4</sub>L<sup>1</sup>)(PF<sub>6</sub>)<sub>4</sub> (304 mg, 0.25 mmol), Pd(OAc)<sub>2</sub> (56 mg, 0.25 mmol) and sodium acetate (82 mg, 1.0 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 1 h, then 5 mL DMSO was added into the mixture and stirred for one day at 50 °C. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL water and a dark brown solid precipitated which was collected by filtration and dried under vacuum to give **7** as a brown solid (212 mg, yield 82.7 %). Slow evaporation of the solvent from an acetonitrile solution of the compound gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  7.52-7.57 (m, 8H, Ph-*H*), 7.30-7.35 (m, 8H, Ph-*H*), 5.09-5.15 (m, 8H, N-C*H*<sub>2</sub>), 4.91-4.96 (m, 8H, N-C*H*<sub>2</sub>), 2.79-2.87 (m, 4H, C*H*<sub>2</sub>), 2.04-2.12 (m, 4H, C*H*<sub>2</sub>) <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C):  $\delta$  181.32 (carbene-*C*), 134.59 (imidazole-ring -*C*), 123.95 (Ph*C*), 111.50 (Ph*C*), 50.49 (N-CH<sub>2</sub>), 30.70 (*C*H<sub>2</sub>), MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 883.24. Anal. Calcd for C4<sub>0</sub>H<sub>40</sub>N<sub>8</sub>F<sub>12</sub>PdP<sub>2</sub> (1029.14 g mol<sup>-1</sup>): C, 46.68; H, 3.92; N, 10.89. Found: C, 46.69; H, 3.94; N, 10.93.

Synthesis of  $[Pd(L^2)](PF_6)_2(8)$ 

(H<sub>4</sub>L<sup>2</sup>)(PF<sub>6</sub>)<sub>4</sub> (311 mg, 0.25 mmol), Pd(OAc)<sub>2</sub> (56 mg, 0.25 mmol) and sodium acetate (82 mg, 1 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 1 h. Then 5 mL of DMSO was added into the mixture and stirred for one day at 50 °C. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL of water and a dark brown solid precipitated which was collected by filtration and dry under vacuum to give **8** as a brown solid (207 mg, yield 78.5%). Slow evaporation of the solvent from an acetonitrile solution of the compound gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  7.52-7.58 (m, 8H, Ph-*H*),

7.30-7.34 (m, 8H, Ph-*H*), 5.67-5.76 (m, 8H, N-C*H*<sub>2</sub>), 5.21-5.39 (m, 4H, N-C*H*<sub>2</sub>), 4.91-4.96 (dt,  ${}^{2}J_{H,H} = 8$  Hz, 16 Hz, 4Hz, 4H, N-C*H*<sub>2</sub>), 4.70-4.76 (m, 4H, N-C*H*<sub>2</sub>), 2.75-2.82 (m, 2H, C*H*<sub>2</sub>), 2.16-2.27 (m, 4H, C*H*<sub>2</sub>), 2.09-2.12 (m, 2H, C*H*<sub>2</sub>), 1.46-1.51 (m, 2H, C*H*<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C):  $\delta$  177.32 (carbene-*C*), 132.59, 131.69 (imidazole-ring-*C*), 122.01, 121.90 (Ph*C*), 109.97, 109.40 (Ph*C*), 63.27 (N-CH<sub>2</sub>), 48.50 (N-CH<sub>2</sub>), 42.36 (CH<sub>2</sub>), 27.52 (CH<sub>2</sub>), 22.46 (CH<sub>2</sub>). MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 911.24. Anal. Calcd for C<sub>42</sub>H<sub>44</sub>N<sub>8</sub>F<sub>12</sub>PdP<sub>2</sub> (1057.19 g mol<sup>-1</sup>): C, 47.72; H, 4.19; N, 10.60. Found: C, 47.70; H, 4.18; N, 10.59.

Synthesis of  $[Pd(L^3)](PF_6)_2(9)$ 

(H4L<sup>3</sup>)(PF<sub>6</sub>)4 (318 mg, 0.25 mmol), Pd(OAc)<sub>2</sub> (56 mg, 0.25 mmol) and sodium acetate (82 mg, 1.0 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 1 h. Then, 5 mL of DMSO was added into the mixture and stirred for one day at 50 °C. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL of water and a dark brown solid precipitated which was collected by filtration and dry under vacuum to give **9** as a brown solid (203 mg, yield 75.2%). Slow evaporation of the solvent from an acetonitrile solution of the compound gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C): δ 7.76-7.80 (m, 8H, Ph-*H*), 7.31-7.35 (m, 8H, Ph-*H*), 5.31-5.38 (m, 8H, N-C*H*<sub>2</sub>), 4.78-4.84 (m, 8H, N-C*H*<sub>2</sub>), 2.33-2.35 (m, 8H, C*H*<sub>2</sub>), 1.91-2.03 (m, 8H, C*H*<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN, 25 °C): δ 176.95 (carbene-*C*), 134.64 (imidazole-ring-*C*), 124.40 (PhC), 112.04 (Ph*C*),

45.04 (N-*C*H<sub>2</sub>), 24.05 (*C*H<sub>2</sub>), MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 939.35. Anal. Calcd for C<sub>44</sub>H<sub>48</sub>N<sub>8</sub>F<sub>12</sub>PdP<sub>2</sub> (1085.24 g mol<sup>-1</sup>): C, 48.70; H, 4.46; N, 10.33. Found: C, 48.70; H, 4.44; N, 10.31.

Synthesis of  $[Pt(L^1)](PF_6)_2$  (10)

 $(H_4L^1)(PF_6)_4$  (304 mg, 0.25 mmol), Pt(acac)<sub>2</sub> (98 mg, 0.25 mmol) and sodium acetate (82 mg, 1.0 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 2 h,. Then 5 mL of DMSO was added into the mixture and stirred for 2 days. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL of water and a yellow-green solid precipitated which was collected by filtration and dried under vacuum to give 10 as a light yellow solid (252 mg, yield 90.2%). Slow evaporation of the solvent from an acetonitrile solution of the compound gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C): δ 7.51-7.56 (m, 8H, Ph-*H*), 7.30-7.35 (m, 8H, Ph-*H*), 5.07-5.13 (m, 8H, N-C $H_2$ ), 4.83-4.88 (dt,  ${}^{2}J_{H,H} = 8$  Hz, 16 Hz, 4 Hz, 8H, N-CH<sub>2</sub>), 2.78-2.86 (m, 4H, CH<sub>2</sub>), 2.06-2.11 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 173.33 (carbene-C), 132.47 (imidazole -ring -C), 121.78 (PhC), 109.47 (PhC), 48.08 (N-CH<sub>2</sub>), 28.73 (CH<sub>2</sub>), MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 972.35. Anal. Calcd for C<sub>40</sub>H<sub>40</sub>N<sub>8</sub>F<sub>12</sub>PtP<sub>2</sub> (1117.83 g mol<sup>-1</sup>): C, 42.98; H, 3.61; N, 10.02. Found: C, 42.97; H, 3.58; N, 10.03.

Synthesis of  $[Pt(L^2)](PF_6)_2$  (11)

(H<sub>4</sub>L<sup>2</sup>)(PF<sub>6</sub>)<sub>4</sub> (311 mg, 0.25 mmol), Pt(acac)<sub>2</sub> (98 mg, 0.25 mmol) and sodium acetate (82 mg, 1.0 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 2 h. Then 5 mL of DMSO was added into the mixture and stirred for 2 days. The solution was cooled to room temperature and filtered through Celite. The filtrate was poured into 300 mL of water and a yellow-green solid precipitated which was collected by filtration and dried under vacuum to give 11 as a light yellow solid (267 mg, yield 93.3%). Slow evaporation of the solvent from an acetonitrile solution of the compound gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C): δ 7.52-7.59 (m, 8H, Ph-*H*), 7.30-7.35 (m, 8H, Ph-*H*), 5.25-5.36 (m, 8H, N-CH<sub>2</sub>), 4.84-4.89 (dt,  ${}^{2}J_{H,H} = 8$  Hz, 16 Hz, 4 Hz, 4H, N-CH<sub>2</sub>), 4.62-4.69 (m, 4H, N-CH<sub>2</sub>), 2.75-2.82 (m, 2H, CH<sub>2</sub>), 2.17-2.27 (m, 4H, CH<sub>2</sub>), 2.17-2.27 (m, 4H, CH<sub>2</sub>), 1.45-1.54 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 172.83 (carbene-C), 134.62, 133.74 (imidazole-ring-C), 124.18, 124.08 (PhC), 112.19, 111.60 (PhC), 50.24 (N-CH<sub>2</sub>), 44.11 (CH<sub>2</sub>), 29.91 (CH<sub>2</sub>), 24.39 (CH<sub>2</sub>). MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 1000.35. Anal. Calcd for C<sub>42</sub>H<sub>44</sub>N<sub>8</sub>F<sub>12</sub>PtP<sub>2</sub> (1145.88 g mol<sup>-1</sup>): C, 44.02; H, 3.87; N, 9.78. Found: C, 44.05; H, 3.90; N, 9.79.

### Synthesis of $[Pt(L^3)](PF_6)_2$ (12)

(H4L<sup>3</sup>)(PF<sub>6</sub>)4 (318 mg, 0.25 mmol), Pd(acac)<sub>2</sub> (98 mg, 0.25 mmol) and sodium acetate (82 mg, 1.0 mmol) were added to a 100 mL Schlenk flask. The mixture was dried under vacuum at 90 °C for 2 h. Then 5 mL of DMSO was added into the mixture and stirred for 2 days. The solution was cooled to room temperature and filtered through

Celite. The filtrate was poured into 300 mL of water and a yellow-green solid precipitated which was collected by filtration and dried under vacuum to give **12** as a light yellow solid (262 mg, yield 89.5%). Slow diffusion of diethyl ether into a solution of dimethyl formamide gave colorless prism crystals suitable for X-ray diffraction study. <sup>1</sup>H NMR(400 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  7.59-7.71 (m, 8H, Ph-*H*), 7.21-7.24 (m, 8H, Ph-*H*), 5.68-5.76 (m, 8H, N-C*H*<sub>2</sub>), 4.75-4.82 (dt, <sup>2</sup>*J*<sub>H,H</sub> = 8 Hz, 16 Hz, 4 Hz, 8H, N-C*H*<sub>2</sub>), 2.19-2.39 (m, 8H, C*H*<sub>2</sub>), 1.34-1.41 (m, 8H, C*H*<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C):  $\delta$  169.38 (carbene-*C*), 133.90 (imidazole-ring-*C*), 127.19 (Ph*C*), 114.15 (Ph*C*), 46.31 (N-CH<sub>2</sub>), 25.65 (*C*H<sub>2</sub>), MS (ESI): m/z [M-PF<sub>6</sub>]<sup>+</sup>: 1029.10. Anal. Calcd for C<sub>44</sub>H<sub>48</sub>N<sub>8</sub>F<sub>12</sub>PtP<sub>2</sub> (1173.93 g mol<sup>-1</sup>): C, 45.02; H, 4.12; N, 9.55. Found: C, 45.02; H, 4.10; N, 9.54.

#### Supplementary materials are available

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