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Formation of anionic NHC complexes through the reaction of benzimidazoles with mercury chloride. Subsequent protonation and transmetallation reactions

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ABSTRACT

Anionic nitrogen heterocyclic carbene complexes of *C,N*-bound mercuramacrocycles $\{Hg_4Cl_4(R\text{-}Bim)_4\}$ (BimH = benzimidazole; R = Ph, Py) were prepared either from the simple reaction of *N*-substituted benzimidazoles with $HgCl_2$ or from the reaction of *N*-substituted benzimidazoles with $Hg(OAc)_2$ and NaCl. The former reaction is unique as no additional base is required, although in low reaction yield. Under similar reaction conditions, only *N*-bound benzimidazole complexes were obtained when $HgBr_2$ or HgI_2 instead of $HgCl_2$ was employed. The different reactivity could be due to the hard-soft acid-base property of mercury(II) and halides, that facilitates the cleavage of Hg-Cl bond and promotes the *C*-metallation of $HgCl_2$ and benzimidazole. Upon protonation of $\{Hg_4Cl_4(R\text{-}Bim)_4\}$ with $HBF_4{\cdot}OEt_2$, *NH,NR*-NHC complexes of $[HgCl(R\text{-}Bim\text{-}H)][BF_4]$ (R = Ph, Py) were obtained. Preliminary study on the transmetallation reaction of $\{Hg_4Cl_4(Ph\text{-}Bim)_4\}$ with $PdCl_2(CH_3CN)_2$ and LiCl did provide a *C,N*-bound NHC palladium complex.

1. Introduction

Imidazoles interact with metal ions usually through *N*-coordination [1] but to a less extent than via *C*-coordination [2]. *C*-bound imidazoles are a type of *N*-heterocyclic carbenes (NHCs), which have drawn great attention in the chemistry community due to their strong σ-donor ability to metal and their various potential catalytic applications [3]. Several strategies have been developed to promote the production of *C*-bound imidazoles. Oxidative addition of the C2-H bond of azoles by metal ions has been reported [4,5]; incorporating a donor substituent at an imidazole N atom could enhance this reaction [4]. Alternatively, oxidative addition of 2-halogenoazoles to M(0) or M(I) transition metal complexes produces *C,N*-bound azolyl complexes [6]; subsequent *N*-protonation or alkylation could generate NHC complexes. Base induced tautomerization of *N*-coordinated azoles [7] and reactions of base-deprotonated azoles with suitable metal complexes [8] are also known for the synthesis of *C*-bound imidazole-2-yl complexes. In both cases, strong bases are generally required. Interestingly, acid could also promote the tautomerization of *N*-bound azoles [9] to provide *C*-bound azolyl complexes. Recently we reported the preparation of *C,N*-metallated 12-membered mercuramacrocycles $\{Hg_4Br_4(R\text{-}Bim)_4\}$ (R = Me, Py, Bz) from the reaction of *N*-substituted benzimidazoles with $Hg(OAc)_2$ and NaBr, or with $HgBr_2$ and NaOAc [10]. Our result suggests that the reaction is initiated from deprotonation of the C2-H proton of the *N*-bound Hg-benzimidazole complexes by acetate, followed by coordination of the resulting carbenionic C2 atom to second mercury(II) ion to produce the mercuramacrocycles. We demonstrated that the C2-H proton in neutral benzimidazole could be deprotonated by a weak base, acetate, with the assistance of Hg^{2+}. In a continuum to explore the validity of this methodology, we extend our study to the reaction of *N*-substituted benzimidazoles with $Hg(OAc)_2$ and NaCl. Indeed, the *C,N*-metallated 12-membered mercuramacrocycles $\{Hg_4Cl_4(R\text{-}Bim)_4\}$ (R = Ph (**3**), Py (**4**)) were prepared. To our amazement, these compounds could also be obtained via a simple reaction of *N*-substituted benzimidazoles with $HgCl_2$ without the

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presence of NaOAc. Preliminary study on their subsequent protonation to give protic NHC complexes [HgCl(R-Bim-H)][BF_4] (*R* = Ph (**5**), Py (**6**)) and the transmetallation ability of **3** was also reported.

2. Results and discussion

2.1. Formation of {Hg_4Cl_4(R-Bim)$_4$} (R = Ph (**3**), Py (**4**)), and [HgCl(R-Bim-H)][BF_4] (R = Ph (**5**), Py (**6**))

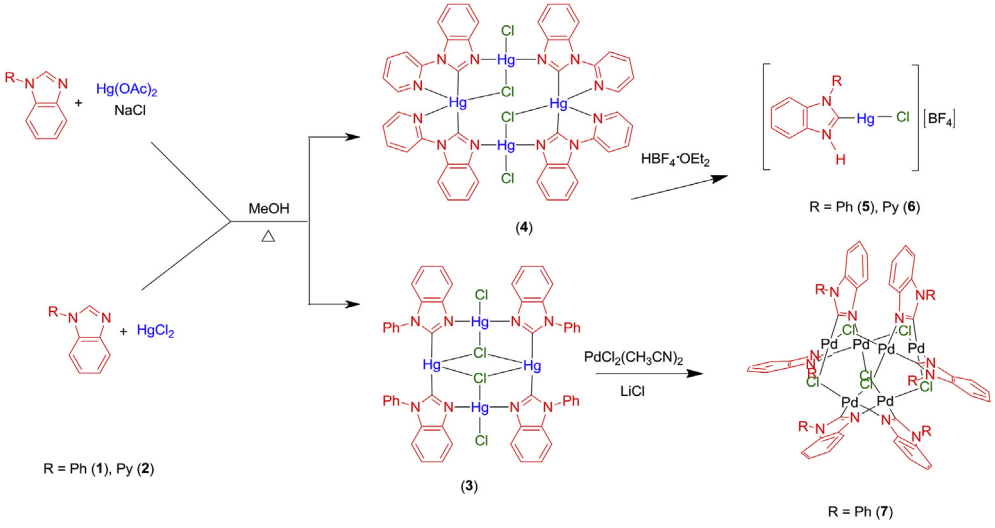
C,N-bound 12-membered mercuramacrocycles of {Hg_4Cl_4(R-Bim)$_4$} (BimH = benzimidazole; R = Ph (**3**), Py (**4**)) were prepared either from the reaction of mono-*N*-substituted benzimidazoles (R-BimH) (R = Ph (**1**), Py (**2**)) [11] with $Hg(OAc)_2$ and NaCl under refluxing methanol solution, or simply from the reaction of mono-*N*-substituted benzimidazoles (R-BimH) with $HgCl_2$ under similar reaction conditions (Scheme 1). The first method has been reported for the preparation of {Hg_4Br_4(R-Bim)$_4$} (R = Me, Py, Bz) [10]. Thus, this methodology can be extended to mercury chloride to prepare the chloro-analogues. The second method produces a lower yield of *C,N*-bound mercuramacrocycle together with *N*-bound benzimidazole complexes of {(Ph-BimH)$_2$$HgCl_2$} and {(Py-Bim-H)$HgCl_2$}$_x$ [12]. We intended to improve the reaction yield of the *C,N*-bound mercuramacrocycle by extending the reaction time, changing the ratio of the reactants or the solvent system. However, the reaction yield of the *C,N*-bound mercuramacrocycle was not improved significantly.

Similar to that observed for the analogous bromo-compounds [10], both complexes **3** and **4** displayed broad proton NMR signals even at high temperature. However, the formation of these *C,N*-bound complexes is corroborated by the absence of the 2H-benzimidazole proton signals at 8.12 ppm in **1** and 8.56 ppm in **2** in the proton NMR spectra, and further supported by the appearance of the carbenic C2 carbon signals in the range of 173.28−185.84 ppm in the ^{13}C NMR spectra. Subsequent protonation of these mercuramacrocycles with HBF_4•OEt_2 produced mononuclear *NH,NR*-NHC complexes [HgCl(R-Bim-H)][BF_4] (R = Ph (**5**), Py (**6**)) (Scheme 1). The acidic N-H proton appeared as broad signals at 12.17 ppm in **5** and 12.38 ppm in **6**. These protons are sensitive for the H/D exchange; their signals disappeared upon addition of D_2O. The carbenic C2 carbon signals appeared at 177.97 ppm in **5** and 178.30 ppm in **6** in the ^{13}C NMR spectra. The N-H IR stretching frequencies of **5** and **6** appeared at 3362 and 3327 cm^{-1}, respectively.

Although in low reaction yield, the formation of **3** and **4** from a simple reaction of **1** and **2** with $HgCl_2$ is unusual, since no additional base is required. Note that reaction of **1** or **2** with either $HgBr_2$ or HgI_2 only produced *N*-metallated complexes (the preparations and characterizations of these *N*-metallated complexes are included in the supporting information). Currently, the mechanism is undetermined. However, a possible explanation to account for this different reactivity could be due to the hard-soft acid-base property of the complexes. As a soft acid, Hg(II) ion displays a strong interaction with both Br^- and I^- ligands, which prevents the breakage of the mercury-halogen bond for further reactions. In contrast, the Cl^- ligand is a hard base, the discordance of the hard-soft interaction could facilitate the cleavage of the Hg-Cl bond. Although the detailed mechanism is still unknown, the acidic nature of the reaction solution of **1** and **2** with $HgCl_2$ measured by the pH test paper may suggest the resulting Cl^- ligand or free anion attacks the C2-H proton of the *N*-metallated azole to form HCl and the coordination of the resulting carbenic C2 atom to second mercury(II) ion produces the mercuramacrocycles.

2.2. Molecular structures of **3**, **5** and **6**

Crystals of **3**·acetone suitable for the X-ray diffraction analysis were isolated from a DMSO/ether/acetone mixed solvent system. Its ORTEP diagram is depicted in Fig. 1, and selected parameters are given in the caption. Complex **3** exists as a 12-membered tetranuclear macrocycle similar to those of the bromo-compound analogues [10], composed of four benzimidazolyl anions bridged by two $HgCl_2$ units and two Hg units through *C,N*-coordination. The macrocycle is puckered in a chair like conformation and contains a crystallographic inversion centre at the midpoint. The mercury ions which coordinate to two nitrogen atoms form a distorted tetrahedral environment. The bond angles around these mercury ions are in the range of 99.28(13)−119.29(13)°, and the Hg-Cl bond distances are 2.3741(16) and 2.5706(14) Å, respectively. The Hg-Cl bond distance of 2.5706(14) Å is slightly longer than generally observed terminal Hg-Cl bond distances found in other *C*-metallated complexes [13], due to the partial bonding interaction of the Cl^- ligands with other two Hg atoms. The Hg-N bond distances are 2.222(5) and 2.243(5) Å, respectively, comparable to those of the



Scheme 1. Synthetic route to prepare mercuramacrocycles and their derivatives from mono-substituted benzimidazoles.

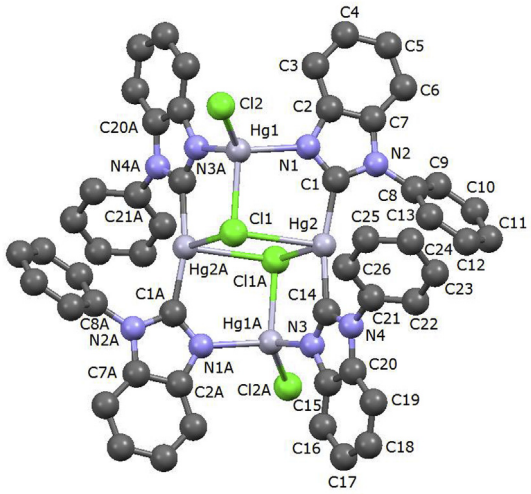


Fig. 1. Molecular structure of **3**·acetone. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)-N(3)#1, 2.222(5); Hg(1)-N(1), 2.243(5); Hg(1)-Cl(2), 2.3741(16); Hg(1)-Cl(1), 2.5706(14); Hg(2)-C(1), 2.072(6); Hg(2)-C(14), 2.086(5); Hg(2)-Cl(1), 2.9556(15); Cl(1)-Hg(2)#1, 2.9946(15); N(3)#1-Hg(1)-N(1), 106.72(18); N(3)#1-Hg(1)-Cl(2), 119.29(13); N(1)-Hg(1)-Cl(2), 115.59(14); N(3)#1-Hg(1)-Cl(1), 99.28(13); N(1)-Hg(1)-Cl(1), 99.39(14); Cl(2)-Hg(1)-Cl(1), 113.65(5); C(1)-Hg(2)-C(14), 166.7(2); C(1)-Hg(2)-Cl(1), 95.07(17); C(14)-Hg(2)-Cl(1), 95.66(16); Hg(1)-Cl(1)-Hg(2), 90.63(4); Hg(1)-Cl(1)-Hg(2)#1, 90.86(4); Hg(2)-Cl(1)-Hg(2)#1, 99.02(4); N(1)-C(1)-N(2), 109.9(5); N(3)-C(14)-N(4), 110.6(5).

related mercury complexes [1e,14]. The other two mercury ions which coordinate to two carbanions are in an almost linear arrangement. The C-Hg-C angle is 166.7(2)° and the Hg-C distances are 2.072(6) and 2.086(5) Å, respectively, consistent with those reported in the literature [13,15]. These two mercury ions also exhibit partial interaction with chloride ions bound to the other two mercury atoms and the Hg···Cl distances are 2.9946(15) and 2.9556(15) Å.

Crystals of **4**·OEt_2 were also isolated from a DMSO/ether/acetone mixed solvent system, but with poor crystal quality, its ORTEP diagram and bond parameters are included in the supporting information (Fig. S1). The molecular structure of **4** is similar to that of **3**, except that the nitrogen atoms of substituted pyridine units also interact with the mercury atoms coordinated to two carbanions.

Crystals of **5**·1/4(Hg_2Cl_4) were isolated from dichloromethane solution, and two molecules of **5** and a half molecule of Hg_2Cl_4 were found in the unit cell. The ORTEP diagram is depicted in Fig. 2, and the selected parameters are listed in the caption. The molecular structures of the two cations are similar, except for the second cation also interacts with the Hg_2Cl_4 molecule and the BF_4^- anion (supporting information, Fig. S2). The cations adopt a two-coordinated linear geometry at Hg atom. Their C-Hg-Cl angles are 174.2(2) and 176.9(2)°, respectively. The Hg-C and Hg-Cl bond distances are 2.041(7) and 2.264(2) Å, respectively, in one cation (Fig. 2a), and 2.055(8) and 2.262(3) Å, respectively, in the second cation (Fig. 2b). The Hg-C bond distances are slightly shorter than those found in **3** but are comparable to those of reported mercury NHC complexes [10,13b,d,e]. The Hg-Cl bond distances are slightly shorter than those reported in the literature which falls in the range of 2.301(6)–2.324(1) Å [13b,d,e]. The Cl^- ligand in the second cation also coordinates to a mercury atom in Hg_2Cl_4. The bridging Hg(3) ··· Cl(1) distance is 2.924(4) Å.

Crystals of **6** were isolated from liquid diffusion of dichloromethane into an acetonitrile solution. ORTEP diagrams of the cationic NHC complex is depicted in Fig. 3, and the selected parameters are listed in the caption. The cationic structure of **6** is similar to that of **5**, which also adopts a two-coordinated linear geometry at the Hg atom. The C-Hg-Cl angle is linear (177.98(15)°) and the Hg-C and Hg-Cl bond distances are 2.052(5) and 2.2728(14) Å, respectively. The N-H distance is 0.875(10) Å. Hydrogen bonding interactions are also found, in which the NH···F(BF_3) distances are in the range of 2.052–2.611 Å.

2.3. Transmetallation reaction

Transmetallation is an alternative way to prepare the metal carbene complexes [16]. Recently, Baker et al. reported the reaction of mercury carbene complex with $Pd(PPh_3)_4$ to produce palladium carbene complexes [17]. To test the possible metal translation of our *C,N*-metallated mercuramacrocycles, we performed the reaction of **3** with $PdCl_2(CH_3CN)_2$ and lithium chloride (Scheme 1). The crude product could not be purified completely. However, after repeating extraction with dichloromethane, an NMR pure compound could be obtained, and a crystal with the composition $\{PdCl(Ph\text{-}Bim)\}_6\cdot CH_3CN$ (**7**·CH_3CN) was isolated from acetonitrile solution.

Proton NMR spectrum of **7** is complicated in which most of the signals are overlapped together, however, the existence of three isomers in a ratio of 5:4:1 at 7.87, 8.06, and 8.12 ppm as doublets could be found. The carbon signals of the two major species were listed in the experimental section, in which only one C2 carbon signal at 161.29 ppm was observed. This chemical shift is comparable to those of $\{PdBr_2(NHC)(Py)\}$ (Py = pyridine) complexes of benzimidazole-based *N*-heterocyclic carbenes which appeared in the range of 163.1–163.9 ppm [18]. Although the isolated crystal of **7**·CH_3CN possesses poor quality and precise cell parameters are not available, the structure is clearly constituted by six (Ph-Bim)PdCl units. As shown in Fig. S3, in addition to the Cl^- ligand and the C2 atom of the Ph-Bim ligand in the (Ph-Bim)PdCl unit, each Pd atom also coordinates to the adjacent Cl^- ligand and the N atom of the Ph-Bim ligand to form a trigonal prismatic structure.

3. Conclusions

While the reaction of *N*-substituted benzimidazoles R-BimH (R = Ph, Py) with $HgBr_2$ or HgI_2 only produced *N*-metallated complexes, the *C,N*-metallated mercuramacrocycles can be isolated from the reaction of *N*-substituted benzimidazoles with $HgCl_2$. The difference between these two reactions could be due to the hard-soft acid-base property of the mercury halides. These *C,N*-metallated complexes are precursors of NHC carbene complexes; protonation of these mercuramacrocycles with $HBF_4\cdot OEt_2$ affords the NH,NR-NHC complexes. These *C,N*-metallated complexes are also candidates for transmetallation reaction; preliminary study indicates that the mercuramacrocycle $\{Hg_4Cl_4(Ph\text{-}Bim)_4\}$ is able to transfer the benzimidazolyl anion to palladium(II) metal ion.

4. Experimental

4.1. General procedures

Dichloromethane and acetonitrile were distilled and purified prior to use according to standard methods. Methanol and other chemicals were analytic reagent grade and were used as obtained from the commercial suppliers. The compounds 1-phenylbenzimidazole (**1**) and 1-pyridylbenzimidazole (**2**) were synthesized according to literature procedures [11]. Elemental analyses were carried out on a Hitachi 270-30 spectrometer. ^1H NMR spectra (δ (TMS) = 0.00 ppm) were recorded on either a Bruker Avance DPX300 or a Bruker Avance II 400 spectrometer operating at 300.13 and 400.13 MHz, respectively. ^{13}C NMR spectra were recorded on either a Bruker Avance DPX300 or a Bruker Avance II

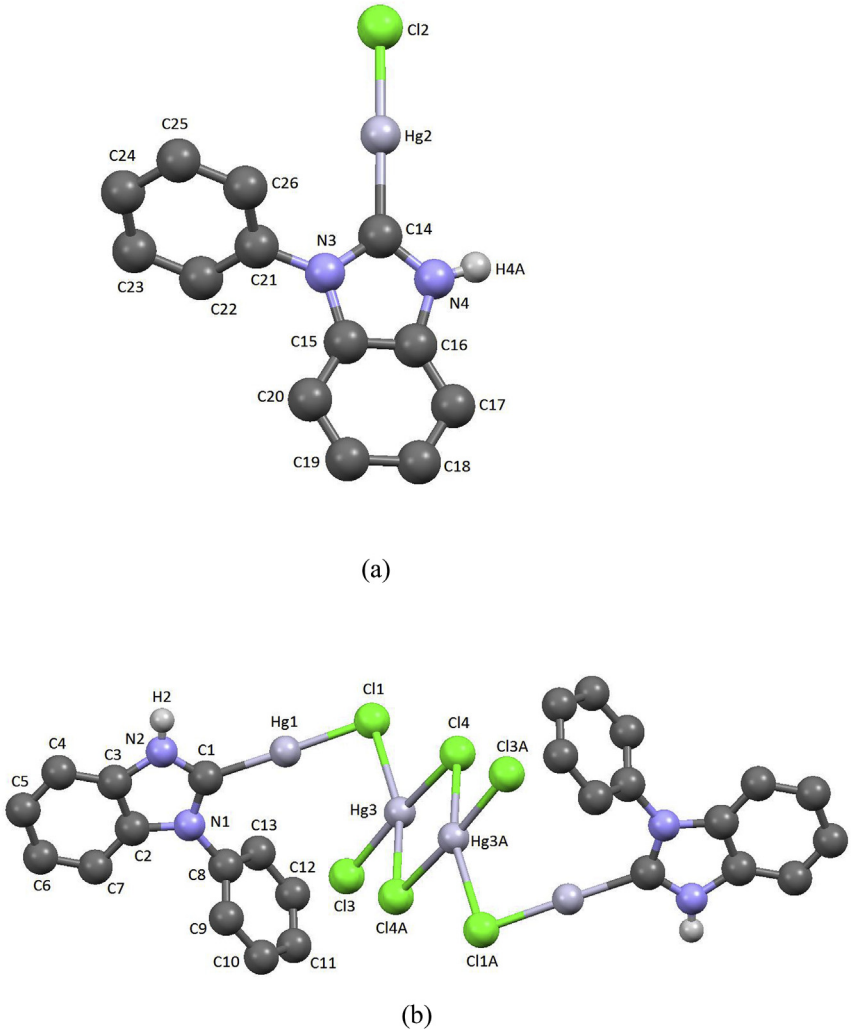


Fig. 2. Molecular structure of **5**. Except for NH hydrogen, hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)-C(1), 2.055(8); Hg(2)-C(14), 2.041(7); Hg(1)-Cl(1), 2.262(3); Hg(2)-Cl(2), 2.264(2); Hg(3)-Cl(1), 2.924(4); Hg(3)-Cl(3), 2.324(4); Hg(3)-Cl(4), 2.654(9); Hg(3)-Cl(4)#1, 2.794(8); C(1)-Hg(1)-Cl(1), 176.9(2); C(14)-Hg(2)-Cl(2), 174.2(2); N(2)-C(1)-N(1), 108.4(7); N(4)-C(14)-N(3), 107.5(6); Hg(1)-Cl(1)-Hg(3), 93.87(11); Hg(3)-Cl(4)-Hg(3)#1, 92.20(18); Cl-Hg(3)-Cl: 80.5(2)~168.1(2).

400 spectrometer operating at 75.46 and 100.61 MHz, respectively. Infrared spectra were recorded on a Jasco FT/IR-460 Plus spectrometer with 4 cm^{-1} resolution. As the complexes **5** and **6** contained large amounts of fluoride in the form of BF_4^- counter anion, elemental analysis was not obtained [19]. However, high resolution mass spectra are supplied. Mass spectrometric analyses are performed using an Applied Biosystem QSTAR XL ESI-QTOF mass spectrometer. The transmetallation reaction was carried out under a nitrogen atmosphere.

4.2. X-ray structure determination

Crystallographic data collections were carried out on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150(2) or 296(2) K. Unit cell parameters were retrieved and refined using DENZO-SMN [20] software on all reflections. Data reduction was performed with the DENZO-SMN [20] software. An empirical absorption was based on the symmetry-equivalent reflections and was applied to the data using the SORTAV [21] program. The structure was solved using the SHELXS-97 [22] program and refined using the SHELXL-97 [23] program by full matrix least squares on F^2 values. All non-hydrogen

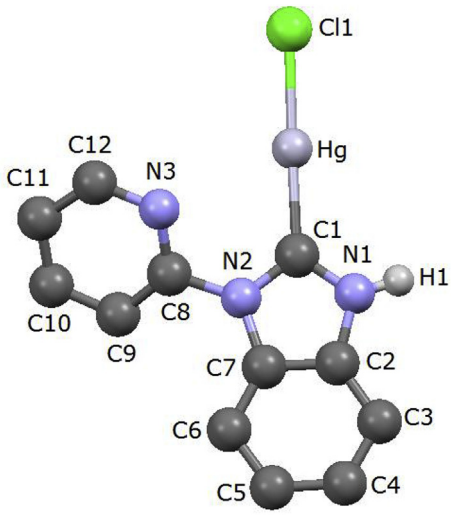


Fig. 3. Molecular structure of **6**. Except for NH hydrogen, hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Hg-C(1), 2.052(5); Hg-Cl(1), 2.2728(14); N(1)-H(1), 0.875(10); C(1)-Hg-Cl(1), 177.98(15); N(1)-C(1)-N(2), 107.8(4).

atoms were refined anisotropically. Except for NH proton in **6**, all of the other hydrogen atoms were fixed at calculated positions and refined using a riding mode. Crystal data and details of data collection and structure refinement for the different compounds are given in supporting information. Crystal data, details of data collection and structure refinement for compounds **3**, **5**, **6** (CCDC 1882659–1882661) can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.3. Preparations of complexes

4.3.1. Preparation of {Hg_4Cl_4(Ph-Bim)$_4$} (**3**)

Method A. A mixture of 1-phenylbenzimidazole (196.9 mg, 1.01 mmol), $Hg(OAc)_2$ (327.6 mg, 1.03 mmol), and NaCl (61.0 mg, 1.04 mmol) in 40 mL MeOH was refluxed for 36 h to afford a white precipitate. The solution was removed by filtration, and the solids were washed four times with methanol (4 × 20 mL) and dried under vacuum to obtain a white crude product. The crude product was dissolved in DMSO and layered with acetone and ether to obtain a 97.2 mg (22% yield) white crystals of {Hg_4Cl_4(Ph-Bim)$_4$}·acetone.

Method B. A mixture of 1-phenylbenzimidazole (268.2 mg, 1.38 mmol) and $HgCl_2$ (367.6 mg, 1.35 mmol) in 20 mL MeOH was refluxed for 48 h to afford a white precipitate. The solution was removed by filtration and the solids were washed four times with methanol (4 × 20 mL) and dried under vacuum to obtain a white crude product. Crystals of {Hg_4Cl_4(Ph-Bim)$_4$}·acetone (28.4 mg, 5% yield) were obtained from DMSO/ether/acetone three-layered solvent mixture. ^{1}H NMR (DMSO–d_6, 100 °C): major, δ 7.73 (m, 1H, Ar), 7.65 (m, 4H, Ar), 7.58 (m, 1H, Ar), 7.36 (m, 1H, Ar), 7.30 (m, 2H, Ar) ppm; minor, δ 7.65 (m, 1H, Ar), 7.50 (m, 1H, Ar), 7.41 (m, 2H, Ar), 7.36 (m, 3H, Ar), 7.30 (m, 2H, Ar) ppm. ^{13}C NMR (DMSO–d_6, 100 °C): major, δ 175.55 (NCN), 143.49 (Ar), 137.88 (Ar), 135.57 (Ar), 130.56 (Ar), 129.36 (Ar), 126.74 (Ar), 124.05 (Ar), 123.06 (Ar), 118.81 (Ar), 111.04 (Ar) ppm; minor, δ 137.16 (Ar), 135.28 (Ar), 130.62 (Ar), 129.60 (Ar), 126.12 (Ar), 124.65 (Ar), 124.27 (Ar), 123.83 (Ar), 122.80(Ar), 120.44 (Ar), 118.00 (Ar), 111.42 (Ar) ppm. Anal. Calc. for $C_{55}H_{42}Cl_8Hg_4N_8O$: C, 37.21; H, 2.38; N, 6.31. Found: C, 36.81; H, 2.52; N, 6.20%.

4.3.2. Preparation of {Hg_4Cl_4(Py-Bim)$_4$} (**4**)

Method A. Complex **4** was prepared in a similar manner as that of complex **3** from 1-pyridylbenzimidazole (207.2 mg, 1.06 mmol), $Hg(OAc)_2$ (330.2 mg, 1.04 mmol), NaCl (61.2 mg, 1.05 mmol), and 40 mL MeOH. Crystals of {Hg_4Cl_4(Py-Bim)$_4$}·ether (121.4 mg, 25% yield) were obtained from DMSO/ether/acetone three-layered solvent mixture.

Method B. Complex **4** was prepared in a similar manner as that of complex **3** from 1-pyridylbenzimidazole (216.4 mg, 1.11 mmol), $HgCl_2$ (292.4 mg, 1.08 mmol), and 20 mL MeOH. Crystals of {Hg_4Cl_4(Py-Bim)$_4$}·ether (66.0 mg, 13% yield) were obtained from DMSO/ether/acetone three-layered solvent mixture. ^{1}H NMR (DMSO–d_6, 80 °C): major, δ 8.56 (d, J = 4.6 Hz, 1H, Py), 8.13 (t, J = 7.8 Hz, 1H, Py), 7.94 (d, J = 8.1 Hz, 1H, Py), 7.85 (d, J = 7.6 Hz, 1H, Bim), 7.76 (d, J = 7.7 Hz, 1H, Bim), 7.51 (dd, J = 7.1 Hz, J = 5.2 Hz, 1H, Py), 7.32 (m, 2H, Bim) ppm; minor, δ 8.22 (d, J = 4.1 Hz, 1H, Py), 8.06 (d, J = 7.9 Hz, 1H, Py), 7.94 (d, J = 8.1 Hz, 1H, Py), 7.85 (d, J = 7.6 Hz, 1H, Bim), 7.80 (d, J = 8.0 Hz, 1H, Bim), 7.32 (m, 1H, py, 2H, Bim) ppm. ^{13}C NMR (DMSO–d_6, 80 °C): major, δ 173.28 (NCN), 150.24 (Py), 149.14 (Py), 145.54 (C_6H_4), 140.77 (Py), 133.25 (C_6H_4), 124.20 (C_6H_4), 123.45 (Py), 123.33 (C_6H_4), 119.55 (C_6H_4), 116.79 (Py), 111.96 (C_6H_4) ppm; minor, δ 185.84 (NCN), 150.00 (Py), 148.95 (Py), 144.91 (C_6H_4), 140.57 (Py), 133.20 (C_6H_4), 124.48 (C_6H_4), 123.72 (Py), 123.33 (C_6H_4), 118.91 (C_6H_4), 116.68 (Py), 112.18 (C_6H_4) ppm. Anal. Calc. For $C_{48}H_{32}Cl_4Hg_4N_{12}$: C, 33.50; H, 1.87; N, 9.77. Found: C, 33.37; H, 1.91; N, 9.69%.

4.3.3. Preparation of [HgCl(Ph-Bim-H)][BF_4]·1/4(Hg_2Cl_4) (**5**·1/4(Hg_2Cl_4))

In a dry box, 226.4 mg (0.13 mmol) of {Hg_4Cl_4(Ph-Bim)$_4$} and 10 mL of dichloromethane were added into a 50 mL flask, then a 150 μL (0.55 mmol) of HBF_4·OEt_2 was added to the flask at room temperature. The solution was stirred for 1 h and filtered. Crystallization was performed by slow evaporation of a solution of **5**·1/4(Hg_2Cl_4) in dichloromethane at ambient temperature. 98.8 mg (0.15 mmol, 58% yield) of white microcrystalline were obtained. ^{1}H NMR (CD_3CN): δ 12.17 (br s, 1H, NH), 8.04 (d, J = 8.2 Hz, 1H, C_6H_4), 7.74 (m, 2H, C_6H_4), 7.65 (m, 3H, C_6H_4, C_6H_5), 7.55 (m, 3H, C_6H_5). ^{13}C NMR (CD_3CN): δ 177.97 (NCN), 135.42, 131.03, 126.89, 126.15, 112.89 (C_6H_5), 133.68, 132.27, 130.83, 127.08, 114.40 (C_6H_4). HRMS (ESI, positive ions): m/z = 431.0231 (calcd: 431.0239). IR: N-H: 3362 cm^{-1}.

4.3.4. Preparation of [HgCl(Py-Bim-H)][BF_4] (**6**)

Complex **6** was prepared and purified by following a similar procedure as that of **5**, starting from {Hg_4Cl_4(Py-Bim)$_4$} (237.6 mg, 0.14 mmol) and HBF_4·OEt_2 (160 μL, 0.59 mmol). The solution was stirred for 6 h and filtered. The solvent was removed, and the resulting solids were dissolved in acetonitrile and diffused with dichloromethane for crystallization. 114.0 mg (0.22 mmol, 40% yield) of light purple crystals were obtained. ^{1}H NMR (CD_3CN): δ 12.38 (br s, 1H, NH), 8.23 (m, 2H, Py), 8.17 (m, 2H, Py, C_6H_4), 8.07 (m, 1H, C_6H_4), 7.75 (m, 2H, C_6H_4), 7.54 (m, 1H, Py). ^{13}C NMR (CD_3CN): δ 178.30 (NCN), 149.44, 147.81, 141.32 (Py), 133.71, 130.94, 127.26, 127.19 (C_6H_4), 125.66, 117.34 (Py), 114.99, 113.73 (C_6H_4). HRMS (ESI, positive ions): m/z = 432.0195 (calcd: 432.0191). IR: N-H: 3327 cm^{-1}.

4.3.5. Reaction of **3** with $PdCl_2(CH_3CN)_2$

A mixture of **3** (471.2 mg, 0.27 mmol), $PdCl_2(CH_3CN)_2$ (284.6 mg, 1.10 mmol), and LiCl (84.8 mg, 2.00 mmol) in 15 mL acetonitrile was stirred overnight. The precipitate was removed by filtration, and an orange solution was obtained. The solution was dried under a dynamic pump, and the resulted solids were extracted with about 2 mL of dichloromethane. Then the solvent was removed under a dynamic pump, and the resulted solids were extracted with dichloromethane (about 2.0 mL) again. The solution was kept at room temperature overnight and a light yellow solid contaminated with black species was obtained. The solution was filtered, and the resulting solid was dissolved in acetonitrile to remove the black species. The acetonitrile was removed from this pale yellow solution, and 203.2 mg of pale yellow solid was obtained. Single crystals of {PdCl(Ph-Bim)}$_6$·CH_3CN were isolated from acetonitrile solution. ^{1}H NMR (CD_3CN): δ 8.12 (d, J = 8.1 Hz, 0.1H, Ar), 8.06 (d, J = 8.1 Hz, 0.4H, Ar), 7.87 (d, J = 8.1 Hz, 0.5H, Ar), 7.68–7.62 (m, 5H, Ar), 7.31–7.07 (m, 3H, Ar) ppm. ^{13}C NMR (CD_3CN): δ 161.29 (NCN), 141.04 (Ar), 141.02 (Ar), 137.42 (Ar), 135.51 (Ar), 135.38 (Ar), 129.80 (Ar), 129.73 (Ar), 127.63 (Ar), 127.50 (Ar), 123.10 (Ar), 123.05 (Ar), 122.21 (Ar), 115.40 (Ar), 110.38 (Ar), 109.93 (Ar) ppm.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.02.015.

References

[1] (a) H. Nozary, C. Piguet, J.-P. Rivera, P. Tissot, G. Bernardinelli, N. Vulliermet, J. Weber, J.-C.G. Bünzli, Inorg. Chem. 39 (2000) 5286–5298;
(b) A. Ikezaki, M. Nakamura, Inorg. Chem. 41 (2002) 6225–6236;
(c) L. Li, T.-L. Hu, J.-R. Li, D.-Z. Wang, Y.-F. Zeng, X.-H. Bu, CrystEngComm 9 (2007) 412–420;
(d) N.H. Tarte, H.Y. Cho, S.I. Woo, Macromolecules 40 (2007) 8162–8167;
(e) C.-Y. Su, A.M. Goforth, M.D. Smith, H.-C. zur Loye, Inorg. Chem. 42 (2003) 5685–5692;
(f) V. Miranda-Soto, D.B. Grotjahn, A.L. Cooksy, J.A. Golen, C.E. Moore, A.L. Rheingold, Angew. Chem. Int. Ed. 50 (2011) 631–635.

[2] (a) G. Sini, O. Eisenstein, R.H. Crabtree, Inorg. Chem. 41 (2002) 602–604;
(b) J. Ruiz, B.F. Perandones, J.F. Van der Maelen, S. García-Granda, Organometallics 29 (2010) 4639–4642.

[3] (a) A.T. Biju, N. Kuhl, F. Glorius, Acc. Chem. Res. 44 (2011) 1182–1195;
(b) S. Würtz, F. Glorius, Acc. Chem. Res. 41 (2008) 1523–1533;
(c) S.P. Nolan, Acc. Chem. Res. 44 (2011) 91–100;
(d) M. Tobisu, N. Chatani, Acc. Chem. Res. 48 (2015) 1717–1726;
(e) C.I. Ezugwu, N.A. Kabir, M. Yusubov, F. Verpoort, Coord. Chem. Rev. 307 (2016) 188–210;
(f) R. Zhong, A.C. Lindhorst, F.J. Groche, F.E. Kühn, Chem. Rev. 117 (2017) 1970–2058;
(g) O. Schuster, L. Yang, H.G. Raubenheimer, M. Albrecht, Chem. Rev. 109 (2009) 3445–3478;
(h) A. Nasr, A. Winkler, M. Tamm, Coord. Chem. Rev. 316 (2016) 68–124.

[4] (a) K. Araki, S. Kuwata, T. Ikariya, Organometallics 27 (2008) 2176–2178;
(b) F.E. Hahn, A.R. Naziruddin, A. Hepp, T. Pape, Organometallics 29 (2010) 5283–5288;
(c) F. He, P. Braunstein, M. Wesolek, A.A. Danopoulos, Chem. Commun. 51 (2015) 2814–2817;
(d) T. Toda, S. Kuwata, T. Ikariya, Chem. Eur J. 20 (2014) 9539–9542;
(e) A.R. Naziruddin, A. Hepp, T. Pape, F.E. Hahn, Organometallics 30 (2011) 5859–5866;
(f) V. Miranda-Soto, D.B. Grotjahn, A.G. DiPasquale, A.L. Rheingold, J. Am. Chem. Soc. 130 (2008) 13200–13201;
(g) S.E. Flowers, B.M. Cossairt, Organometallics 33 (2014) 4341–4344;
(h) S. Kuwata, T. Ikariya, Chem. Commun. 50 (2014) 14290–14300.

[5] (a) J.C. Lewis, S.H. Wiedemann, R.G. Bergman, J.A. Ellman, Org. Lett. 6 (2004) 35–38;
(b) K.L. Tan, R.G. Bergman, J.A. Ellman, J. Am. Chem. Soc. 124 (2002) 3202–3203.

[6] (a) H. Jin, T.T.Y. Tan, F.E. Hahn, Angew. Chem., Int. Ed. 54 (2015) 13811–13815;
(b) H. Jin, T.T.Y. Tan, F.E. Hahn, Angew. Chem. 127 (2015) 14016–14020;
(c) T. Kösterke, T. Pape, Hahn, Chem. Comm. 47 (2011) 10773–10775;
(d) R. Das, C.G. Daniliuc, F.E. Hahn, Angew. Chem. Int. Ed. 53 (2014) 1163–1166;
(e) R. Das, A. Hepp, C.G. Daniliuc, F.E. Hahn, Organometallics 33 (2014) 6975–6987;
(f) T. Kösterke, J. Kösters, E.-U. Würthwein, C. Mück-Lichtenfeld, C. Schulte to Brinke, F. Lahoz, F.E. Hahn, Chem. Eur J. 18 (2012) 14594–14598;
(g) T. Kösterke, T. Pape, F.E. Hahn, J. Am. Chem. Soc. 133 (2011) 2112–2115;
(h) P.J. Fraser, W.R. Roper, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1974) 102–105.

[7] (a) C.-H. Hsieh, R. Pulukkody, M.Y. Darensbourg, Chem. Commun. 49 (2013) 9326–9328;
(b) M.A. Huertos, J. Pérez, L. Riera, A. Menéndez-Velázquez, J. Am. Chem. Soc. 130 (2008) 13530–13531;
(c) J. Ruiz, B.F. Perandones, J. Am. Chem. Soc. 129 (2007) 9298–9299;
(d) M.A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, Angew. Chem. Int. Ed. 49 (2010) 6409–6412;
(e) M. Brill, J. Díaz, M.A. Huertos, R. López, J. Pérez, L. Riera, Chem. Eur J. 17 (2011) 8584–8595;
(f) J. Ruiz, Á. Berros, B.F. Perandones, M. Vivanco, Dalton Trans. (2009) 6999–7007;
(g) G.E. Dobereiner, C.A. Chamberlin, N.D. Schley, R.H. Crabtree, Organometallics 29 (2010) 5728–5731.

[8] (a) H.G. Raubenheimer, S. Cronje, J. Organomet. Chem. 617–618 (2001) 170–181;
(b) N. Meier, F.E. Hahn, T. Pape, C. Siering, S.R. Waldvogel, Eur. J. Inorg. Chem. (2007) 1210–1214;
(c) P.C. Kunz, C. Wetzel, S. Kögel, M.U. Kassack, B. Spingler, Dalton Trans. 40 (2011) 35–37;
(d) F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 375 (1989) 147–160.

[9] R.J. Sundberg, R.F. Bryan, I.F. Taylor Jr., H. Taube, J. Am. Chem. Soc. 96 (1974) 381–392.

[10] M.-H. Yu, H.-H. Yang, A.R. Naziruddin, S. Kanne, B.-H. Wang, F.-C. Liu, I.J.B. Lin, G.-H. Lee, Eur. J. Inorg. Chem. (2016) 4829–4834.

[11] (a) A.K. Verma, J. Singh, V.K. Sankar, R. Chaudhary, R. Chandra, Tetrahedron Lett. 48 (2007) 4207–4210;
(b) Q. Xia, W. Chen, H. Qiu, J. Org. Chem. 76 (2011) 7577–7582.

[12] The reaction yields of the *N*-bound benzimidazole complexes $\{HgCl_2(Ph\text{-}BimH)_2\}$ and $\{HgCl_2(Py\text{-}Bim\text{-}H)\}_x$ isolated from the high temperature reaction are 46 and 38%, respectively. The *N*-bound products are also isolated from the room temperature reaction, their characterizations are included in the supporting information.

[13] (a) B. Soro, S. Stoccoro, G. Minghetti, A. Zucca, M.A. Cinellu, S. Gladiali, M. Manassero, M. Sansoni, Organometallics 24 (2005) 53–61;
(b) N.-C. Lin, H.J.H. Syu, A.R. Naziruddin, F.-C. Liu, I.J.B. Lin, RSC Adv. 7 (2017) 11652;
(c) E.C. Constable, T.A. Leese, D.A. Tocher, J. Chem. Soc., Chem. Commun. (1989) 570;
(d) S. Pelz, F. Mohr, Organometallics 30 (2011) 383–385;
(e) M.M.D. Roy, M.J. Ferguson, E. Rivard, Anorg. Allg. Chem. 642 (2016) 1232.

[14] C.J. Matthews, W. Clegg, S.L. Heath, N.C. Martin, M.N.S. Hill, J.C. Lockhart, Inorg. Chem. 37 (1998) 199–207.

[15] A.S. Borovik, A.R. Barron, J. Am. Chem. Soc. 124 (2002) 3743–3748.

[16] (a) J.C.Y. Lin, R.T.W. Huang, C.S. Lee, A. Bhattacharyya, W.S. Hwang, I.J.B. Lin, Chem. Rev. 109 (2009) 3561–3598;
(b) J.C. Garrison, W.J. Youngs, Chem. Rev. 105 (2005) 3978–4008;
(c) S.-T. Liu, T.-Y. Hsieh, G.-H. Lee, S.-M. Peng, Organometallics 17 (1998) 993–995;
(d) A.G. Nair, R.T. McBurney, D.B. Walker, M.J. Page, M.R.D. Gatus, M. Bhadbhade, B.A. Messerle, Dalton Trans. 45 (2016) 14335–14342.

[17] M.V. Baker, D.H. Brown, R.A. Haque, P.V. Simpson, B.W. Skelton, A.H. White, C.C. Williams, Organometallics 28 (2009) 3793–3803.

[18] Y.-C. Lin, H.-H. Hsueh, S. Kanne, L.-K. Chang, F.-C. Liu, I.J.B. Lin, G.-H. Lee, S.-M. Peng, Organometallics 32 (2013) 3859–3869.

[19] V.P. Fadeeva, V.D. Tikhova, O.N. Nikulicheva, J. Anal. Chem. 63 (2008) 1094–1106.

[20] Z. Otwinowsky, W. Minor, DENZO-SMN, Methods Enzymol. 276 (1997) 307–326.

[21] (a) R.H. Blessing, Acta Crystallogr. A51 (1995) 33–38;
(b) R.H. Blessing, J. Appl. Crystallogr. 30 (1997) 421–426.

[22] SHELXS-97, G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467–473.

[23] G.M. Sheldrick, SHELXL-97, University of Göttingen: Göttingen, Germany, 1997.