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Tetranuclear N-Heterocyclic Carbene Mercury(II) Complexes Containing Triply Deprotonated Acetonitrile: Synthesis and Structural Studies

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In the presence of KO*t*Bu, bis[*N*-(*n*Pr)benzimidazoliumylmethyl]durene bromide (**1a**) and bis[*N*-(*n*Bu)benzimidazoliumylmethyl]durene bromide (**1b**) were treated with $HgBr_2$ in CH_3CN, respectively, to afford two novel tetranuclear NHC–mercury(II) complexes, [durene(CH_2bimy*n*Pr)$_2$Hg$_2$(CCN)Hg$_2$Br$_5$] (**2a**) and [durene(CH_2bimy*n*Bu)$_2$Hg$_2$(CCN)Hg$_2$Br$_5$] (**2b**; durene = 1,2,4,5-tetramethylbenzene, bimy = benzimidazol-2-ylidene, CCN = triply deprotonated acetonitrile). In **2a** or **2b**, a funnel-like molecular structure is formed by a triply deprotonated acetonitrile, a bidentate biscarbene ligand, the Hg^{II} ions, and the bromide ions. Additionally, analysis of the crystal packings of **2a** or **2b** reveals that the double-stranded 1D supramolecular chains are formed through intermolecular weak interactions, including π–π stacking interactions, C–H···Br hydrogen bonds, and weak O···Hg bonds.

Introduction

N-Heterocyclic carbenes (NHCs), such as imidazol-2-ylidenes or benzimidazol-2-ylidenes, have been widely used as ligands in organometallic chemistry since Arduengo and co-workers isolated the first stable N-heterocyclic carbene in 1991.[1] The strong electron-donating ability of NHC ligands leads to metal complexes with high stability against heat, moisture, and air. In addition, NHC ligands can be easily modified by changing the substituents on the nitrogen atoms or the backbone of the carbenes, which provides various ligands for organometallic materials.[2–5] In the family of NHCs, the coordination chemistry of benzimidazol-2-ylidenes has been studied.[6–13] Furthermore, some benzimidazol-2-ylidene metal complexes exhibit superior catalytic performance in C–C coupling reactions[14–16] and transfer hydrogenation.[17]

The first known NHC complex was a mercury(II) compound,[18] and NHC mercury(II) complexes have played an important role in the development of N-heterocyclic carbene chemistry.[19–24] Some compounds containing deprotonated acetonitrile are known, such as, $(Me_3Ge)_2$-CHCN,[25] [Pt(CH_2CN)(PMe$_2$Ph)$_3$]PF$_6$,[26] Pt(CH_2CN)$_2$-(PPh$_3$)$_2$,[27] *trans*-PtCl(CH_2CN)(PPh$_3$)$_2$,[28] and PdCl-(CH_2CN)(PPh$_3$)$_2$;[29] however, to the best of our knowledge, an NHC–mercury(II) complex containing triply deprotonated acetonitrile (CCN) has never been reported. During the course of searching for potential applications of NHC metal complexes, we became interested in developing bidentate bis-NHC ligands based on durene-bridged benzimidazolium salts and their metal complexes. As a continuation of our research on the mercury chemistry of NHCs,[30–32] we herein report the synthesis, structures, and fluorescent emission spectra of two novel tetranuclear NHC–mercury(II) complexes with triply deprotonated acetonitrile, [durene(CH_2bimy*n*Pr)$_2$Hg$_2$(CCN)Hg$_2$Br$_5$] (**2a**) and [durene(CH_2bimy*n*Bu)$_2$Hg$_2$(CCN)Hg$_2$Br$_5$] (**2b**; durene = 1,2,4,5-tetramethylbenzene, bimy = benzimidazol-2-ylidene, CCN = triply deprotonated acetonitrile).

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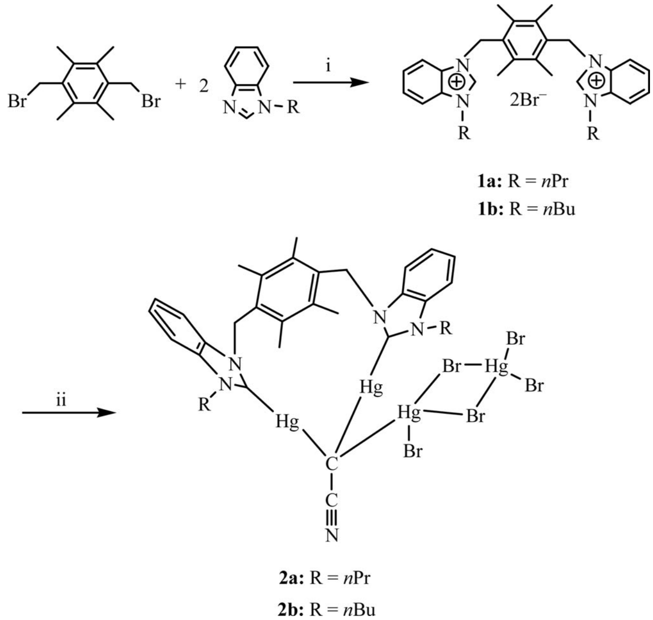
Results and Discussions

The bidentate ligands bis[*N*-(*n*Pr)benzimidazoliumylmethyl]durene bromide (**1a**) and bis[*N*-(*n*Bu)benzimidazoliumylmethyl]durene bromide (**1b**) were prepared from benzimidazole by alkylation with 1-bromopropane or 1-bromobutane in the presence of NaH in THF at 60 °C for 48 h, followed by quaternization with bis(bromomethyl)durene in sequence in THF under reflux for 48 h (yields: 84% for **1a** and 73% for **1b**; Scheme 1). In the ^1H NMR spectra of **1a** and **1b**, the benzimidazolium proton signals (NCHN) appear at δ = 10.41 ppm for **1a** and at δ = 10.47 ppm for **1b**, which are consistent with the chemical shifts of known benzimidazolium salts.[6–13] Precursors **1a** and **1b** are stable to air and moisture, soluble in polar organic solvents such as dichloromethane, acetonitrile, and methanol, and scarcely soluble in benzene, diethyl ether, and petroleum ether.



Scheme 1. Preparation of compounds **1a**, **1b**, **2a**, and **2b**. Reagents and conditions: (i) THF, reflux, 3 d (84% for **1a**, 73% for **1b**); (ii) $HgBr_2$, KO*t*Bu, CH_3CN, reflux, 24 h (53% for **2a**, 58% for **2b**).

Complexes [durene(CH_2bimy*n*Pr)$_2$Hg$_2$(CCN)Hg$_2$Br$_5$] (**2a**) and [durene(CH_2bimy*n*Bu)$_2$Hg$_2$(CCN)Hg$_2$Br$_5$] (**2b**) were synthesized by the reaction of bis[*N*-(*n*Pr)benzimidazoliumylmethyl]durene bromide (**1a**) and bis[*N*-(*n*Bu)benzimidazoliumylmethyl]durene bromide (**1b**) with $HgBr_2$ in the presence of KO*t*Bu in refluxing CH_3CN for 24 h (yields: 53% for **2a** and 58% for **2b**; Scheme 1). Complexes **2a** and **2b** are stable to air and moisture, soluble in DMSO, and almost insoluble in diethyl ether and hydrocarbon solvents. In the ^{1}H NMR spectra of **2a** and **2b**, the disappearance of the resonances for the benzimidazolium protons (NCHN) shows the formation of the expected metal carbene complexes, and the chemical shifts of other hydrogen atoms are similar to those of the corresponding precursors. In the ^{13}C NMR spectra of **2a** and **2b**, the signals for the carbene carbon appear at δ = 187.8 ppm for **2a** and at δ = 187.6 ppm for **2b**, which are characteristic for metal carbene complexes;[6–13] the signals of the cyano carbon occur at δ = 113.0 ppm for **2a** and at δ = 113.2 ppm for **2b**, which are similar to those of cyano groups in known metal complexes;[33] the signals of the α-carbon atom of acetonitrile appear at δ = 23.2 ppm for **2a** and at δ = 30.6 ppm for **2b**. The IR spectra contain the characteristic bands of the cyano groups at 2140 cm^{-1} for **2a** and at 2136 cm^{-1} for **2b**, and these values are comparable to those of reported complexes containing cyano groups.[25,33–35]

The crystal structures of complexes **2a** and **2b** were demonstrated by X-ray analysis. Pale-yellow crystals of **2a**·DMSO or **2b**·DMSO suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into their DMSO solutions at room temperature. The molecular structure of **2a** is shown in Figure 1a, and the analogous structure of complex **2b** is given as Figure S1a (Supporting Information). An interesting phenomenon during the course of the preparation of **2a** and **2b** is that three α-hydrogen atoms of acetonitrile are completely deprotonated due to the presence of the strong base KO*t*Bu, and then the α-carbon atom of acetonitrile is bonded to three mercury(II) ions to generate a distorted tetrahedron centered at the α-carbon atom [C(35)] of acetonitrile [the bond angles of Hg–C(35)–Hg around the α-carbon atom are in the range of 103.3–117.6°]. As a result, funnel-like tetranuclear complex **2a** or complex **2b** is formed by a triply deprotonated acetonitrile, a bidentate biscarbene ligand, the Hg^{II} ions, and bromide ions. Another notable feature is that five C–Hg bonds [three C(α)–Hg bonds and two C(carbene)–Hg bonds] are formed in a single reaction, which is also interesting in organometallic reactions. In the funnel-like structure of **2a** or **2b**, the α-carbon of acetonitrile lies in the bottom of the funnel, and the side of the funnel is constituted by two benzimidazole rings, one tetramethylbenzene, and one [Hg_2Br_5] unit. The two benzimidazole rings within each molecule form dihedral angles of 116.8° for **2a** and 117.7° for **2b**, and they form dihedral angles of 92.5 and 73.5° for **2a** and 99.3 and 73.5° for **2b** with the durene plane, respectively.

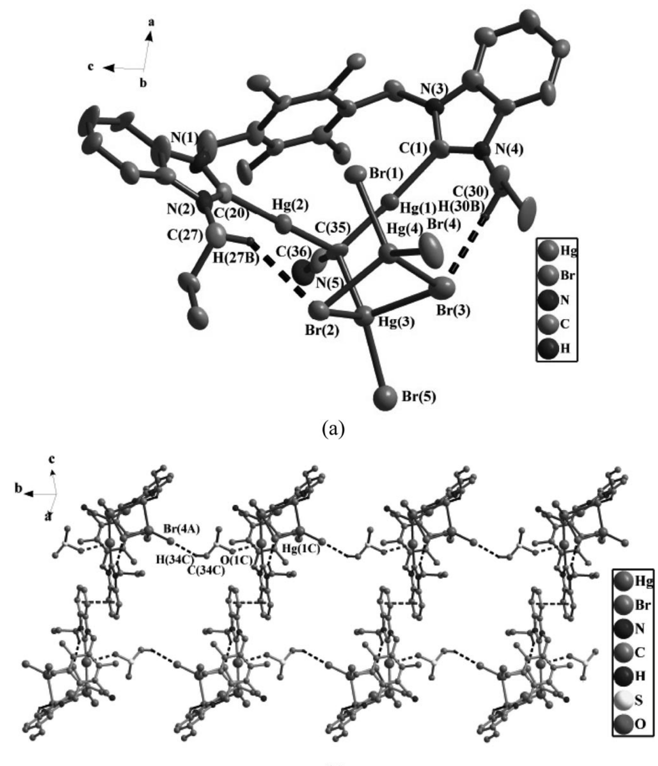


Figure 1. (a) Perspective view of **2a** with anisotropic displacement parameters depicted at 30% probability. Hydrogen atoms are omitted for clarity; (b) double-stranded 1D polymeric chain of **2a**.

In complex **2a** or **2b**, Hg(1) and Hg(2) are bicoordinated with one carbene carbon atom and one α-carbon atom of acetonitrile. The C(1)–Hg(1)–C(35) and C(20)–Hg(2)–C(35) arrays are nearly linear with bond angles of 176.8(6) and 171.2(5)° for **2a** and 176.1(1) and 168.7(1)° for **2b**. The bond

Table 1. Hydrogen bond lengths (Å) and bond angles (°) for **2a** and **2b**.[a]

	D–H···A	D–H	H···A	D···A	D–H···A
2a	C(27)–H(27B)···Br(2)	0.990(1)	2.859(5)	3.714(6)	144.9(7)
	C(30)–H(30B)···Br(3)	0.990(1)	2.579(2)	3.459(3)	148.1(1)
	C(34C)–H(34C)···Br(4A)^{i}	0.980(1)	2.968(2)	3.843(2)	149.2(1)
2b	C(27)–H(27B)···Br(3)	0.990(2)	2.615(5)	3.558(6)	159.2(1)
	C(31)–H(31B)···Br(2)	0.990(2)	2.853(6)	3.709(8)	145.0(1)
	C(37C)–H(37C)···Br(4A)^{i}	1.017(1)	2.829(4)	3.705(5)	145.2(2)

[a] Symmetry code i: $-1 + x$, $-1 - y$, $1 + z$.

lengths of Hg–C(carbene) are 2.095(2) and 2.123(3) Å for **2a** and 2.094(3) and 2.112(4) Å for **2b**, which are similar to those of known NHC mercury(II) complexes.[19–24] The internal ring angles (N–C–N) at the carbene centers vary from 108 to 112° for **2a** and **2b**, which is somewhat larger than those of known NHC mercury(II) complexes.[19–24]

In **2a** or **2b**, the four atoms Hg(3), Br(2), Hg(4), and Br(3) form a distorted rhombus, in which the bond angles are in the range 81.1–96.5°. The plane formed by the Hg(3), Br(2), and Hg(4) atoms and the plane formed by the Hg(3), Br(3), and Hg(4) atoms give the same dihedral angle of 34.5° for **2a** and **2b**. The distance of Hg(3)–Br(2) [3.194(2) Å for **2a** and 3.131(4) Å for **2b**] is longer than those of other Hg–Br bonds (the distances of other Hg–Br bonds being in the range of 2.46–2.84 Å). The Hg(3) atom is coordinated by one α-carbon atom of acetonitrile and three bromide ions to form a distorted tetrahedron. The C(35)–Hg(3)–Br(5) is approximately linear with the bond angles of 159.6(5)° for **2a** and 154.3(3)° for **2b**, and the other bond angles around Hg(3) range from 81.7(1) to 159.6(1)° for **2a** and **2b**. In contrast, Hg(4) is coordinated by four bromide atoms to form a distorted tetrahedron. The bond angles of Br–Hg–Br around Hg(4) are in the range 96.5(1)–121.2(2)°, and the bond lengths of Hg–Br vary from 2.501(1) to 2.620(3) Å for **2a** and **2b**.

Notably, the cyanomethyl moiety [C(35)–C(36)–N(5)] is nearly linear with bond angles of 172.0(2)° for **2a** and 171.5(1)° for **2b**. The C(35)–C(36) bond length [1.470(2) Å for **2a** and 1.379(1) Å for **2b**] is shorter than that of the regular C–C single bond (1.54–1.59 Å), and it has partial double-bond character. The C(36)–N(5) bond length [1.120(3) Å for **2a** and 1.151(1) Å for **2b**] is similar to that of other complexes containing cyano groups, and this value is expected for a triple bond with a small amount of double-bond character.[27–29,36,37] Interestingly, two C–H···Br hydrogen bonds in the molecular structure of **2a** or **2b** [C(27)–H(27B)···Br(2) and C(30)–H(30B)···Br(3) for **2a** and C(27)–H(27B)···Br(3) and C(31)–H(31B)···Br(2) for **2b**] are observed (the data for the hydrogen bonds are given in Table 1),[38] which close the side of the funnel and further stabilize the complex.

The crystal packing of **2a** is depicted in Figure 1b, and the analogous structure of complex **2b** is given as Figure S1b (Supporting Information). Two adjacent molecules in **2a** or **2b** are linked by a bridging DMSO molecule through two types of noncovalent bonds, including weak O···Hg bonds[30] [O···Hg separations: 2.777(3) Å for **2a** and 2.914(4) Å for **2b**] and C–H···Br hydrogen bonds (the data for the hydrogen bonds is given in Table 1), to form 1D infinite chains. Additionally, two neighboring 1D chains are further connected together through π–π stacking interactions of the benzimidazole rings, with interplanar separations of 3.380(1) Å for **2a** and 3.377(2) Å for **2b** [center-to-center separations: 3.654(1) Å for **2a** and 3.526(1) Å for **2b**],[39] to generate double-stranded 1D supramolecular chains.

As shown in Figure 2, the fluorescent emission spectra of **1a** and **2a** are obtained upon excitation at 230 nm in dichloromethane at room temperature (the fluorescent emission spectra of **1b** and **2b** are similar to those of **1a** and **2a**). Precursor **1a** exhibits a double emission band centered at 330 and 345 nm, which corresponds to intraligand transitions. Analogously, complex **2a** also shows a double emission band centered at 335 and 348 nm. However, the fluorescent emission of **2a** is stronger than that of precursor **1a**, which probably results from the incorporation of metal–ligand coordination interactions.[40,41] These results show that these metal complexes could be good candidates for potential photoactive materials.

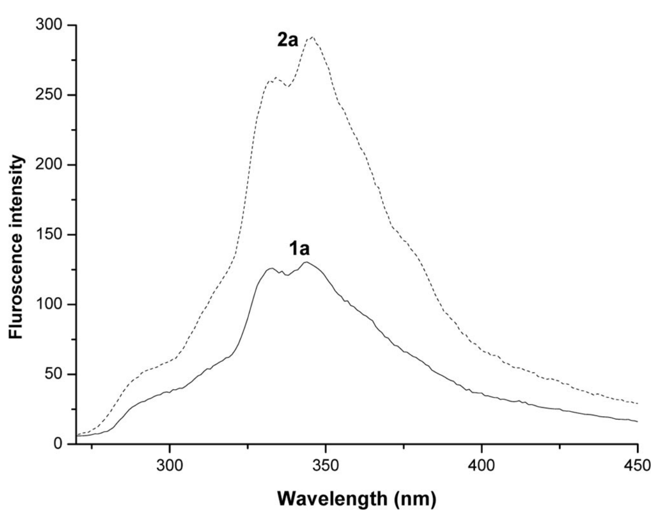


Figure 2. Emission spectra of **1a** (—) and **2a** (---) at 298 K in CH_2Cl_2 (5.0×10^{-6} M) solution.

Conclusions

In summary, a couple of funnel-like tetranuclear NHC–mercury(II) complexes with triply deprotonated acetonitrile, [durene(CH_2bimy*n*Pr)$_2$$Hg_2(CCN)Hg_2Br_5$] (**2a**) and [durene($CH_2$bimy*n*Bu)$_2$$Hg_2(CCN)Hg_2Br_5$] (**2b**), have been synthesized and characterized. The results show that three α-hydrogen atoms of acetonitrile can be completely substituted by three mercury(II) ions in the presence of KO*t*Bu. In the crystal packing of **2a** or **2b**, the double-stranded 1D supramolecular chains are formed by intermolecular weak interactions, including π–π stacking interactions, C–H···Br hydrogen bonds, and weak O···Hg bonds. Analysis of the fluorescent emission spectra of **1a** and **2a** reveals that the fluorescent emission of **2a** is stronger than that of precursor **1a**. The resultant structures of the complexes will provide valuable experimental data for crystal engineering and supramolecular chemistry. Further studies on new organometallic compounds from precursors **1a**, **1b**, and analogous ligands are underway.

Experimental Section

General Procedures: Bis(bromomethyl)durene was prepared according to the literature.[42] All manipulations were performed by using Schlenk techniques, and solvents were purified by standard procedures. All the reagents for syntheses and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. IR spectra were measured with a Bruker IR Equinox-55 infrared spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Varian Mercury Vx 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported relative to the internal standard TMS for both ^1H and ^{13}C NMR. Elemental analyses were measured by using a Perkin–Elmer 2400C Elemental Analyzer. The luminescent spectra were conducted with a Cary Eclipse fluorescence spectrophotometer.

Bis[*N*-(*n*Pr)benzimidazoliumylmethyl]durene Bromide (1a): A THF solution (20 mL) of benzimidazole (2.000 g, 16.9 mmol) was added to a suspension of oil-free sodium hydride (0.480 g, 20.3 mmol) in THF (50 mL), and the mixture was stirred for 1 h at 60 °C. Then, a THF (40 mL) solution of *n*-propyl bromide (2.288 g, 18.6 mmol) was added dropwise to the above solution. The mixture was stirred for 48 h at 60 °C and a yellow solution was obtained. The solvent was removed under reduced pressure and H_2O (100 mL) was added to the residue. Then, the solution was extracted with CH_2Cl_2 (3 × 30 mL), and the extracting solution was dried with anhydrous $MgSO_4$. After removing CH_2Cl_2, a pale-yellow liquid of *N*-(*n*Pr)-benzimidazole was obtained. Yield: 2.530 g (89%). A solution of *N*-(*n*Pr)benzimidazole (2.203 g, 14.0 mmol) and bis(bromomethyl) durene (2.000 g, 6.3 mmol) in THF (150 mL) was stirred for 3 d at reflux, and a precipitate was formed. The product was filtered and washed with THF. Product **1a** was obtained as a white powder after recrystallization (methanol/diethyl ether). Yield: 3.342 g (84%). M.p. 300–302 °C. $C_{32}H_{40}Br_2N_4$ (640.50): calcd. C 60.00, H 6.29, N 8.75; found C 60.14, H 6.33, N 8.64. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.63 (t, J = 7.2 Hz, 6 H, CH_3), 1.53 (m, 4 H, CH_2), 2.36 (s, 12 H, CH_3), 4.82 (t, J = 7.2 Hz, 4 H, CH_2), 5.94 (s, 4 H, CH_2), 7.72 (m, 6 H, PhH), 8.55 (d, J = 8.1 Hz, 2 H, PhH), 10.41 (s, 2 H, 2-bimiH) ppm (bimi: benzimidazole).

Bis[*N*-(*n*Bu)benzimidazoliumylmethyl]durene Bromide (1b): Precursor **1b** was prepared in a manner analogous to that for **1a**, only with *n*-butyl bromide instead of *n*-propyl bromide. Compound **1b** was obtained as a white powder. Yield: 3.060 g (73%). M.p. 266–268 °C. $C_{34}H_{44}Br_2N_4$ (668.55): calcd. C 61.08, H 6.63, N 8.38; found C 61.15, H 6.68, N 8.41. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.3 Hz, 6 H, CH_3), 1.41 (m, 4 H, CH_2), 1.96 (m, 4 H, CH_2), 2.30 (s, 12 H, CH_3), 4.79 (t, J = 7.3 Hz, 4 H, CH_2), 5.93 (s, 4 H, CH_2), 7.81 (m, 6 H, PhH), 8.60 (d, J = 8.3 Hz, 2 H, PhH), 10.47 (s, 2 H, 2-bimiH) ppm (bimi: benzimidazole).

[Durene(CH_2bimy*n*Pr)$_2$$Hg_2(CCN)Hg_2Br_5$] (2a): A suspension of KO*t*Bu (0.226 g, 2.0 mmol), **1a** (0.200 g, 0.3 mmol), and anhydrous mercury(II) bromide (0.457 g, 1.3 mmol) in acetonitrile (30 mL) was heated at reflux for 24 h. A brown solution was formed, and the solvent was removed under reduced pressure. Water (30 mL) was added to the residue, and the solution was extracted with CH_2Cl_2 (3 × 20 mL). The extracting solution was dried with anhydrous $MgSO_4$ and concentrated to 10 mL, and hexane (2 mL) was added to precipitate a pale-yellow powder. Isolation by filtration yielded complex **2a**. Yield: 0.298 g (53%). M.p. 292–294 °C. $C_{34}H_{38}Br_5Hg_4N_5$ (1718.58): calcd. C 23.76, H 2.23, N 4.08; found C 23.80, H 2.44, N 4.16. IR (KBr): $\tilde{\nu}$ = 2140 ν(CN) cm^{-1}. ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 0.94 (t, J = 7.1 Hz, 6 H, CH_3), 1.98 (m, 4 H, CH_2), 2.09 (s, 12 H, CH_3), 4.61 (m, 2 H, CH_2), 4.71 (m, 2 H, CH_2), 5.78 (d, J = 7.5 Hz, 2 H, CH_2), 5.95 (d, J = 7.5 Hz, 2 H, CH_2), 7.74 (m, 4 H, PhH), 8.08 (d, J = 7.2 Hz, 2 H, PhH), 8.28 (d, J = 7.2 Hz, 2 H, PhH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$] DMSO): δ = 187.8 ($C_{carbene}$), 137.5, 136.6, 133.4, 132.7, 132.2, 126.1, 126.0 and 125.8 (PhC), 113.0 (CN), 46.4 (NCH_2Ph), 30.6 (NCH_2CH_2), 23.2 (HgCCN), 17.6 (CCH_2C), 16.1 ($PhCH_3$), 11.0 (CH_2CH_3) ppm.

[Durene(CH_2bimy*n*Bu)$_2$$Hg_2(CCN)Hg_2Br_5$] (2b): Complex **2b** was prepared in a manner analogous to that for **2a**, only with **1b** instead of **1a**. Complex **2b** was obtained as a pale-yellow powder. Yield: 0.315 g (58%). M.p. 266–268 °C. $C_{36}H_{42}Br_5Hg_4N_5$ (1746.63): calcd. C 24.76, H 2.42, N 4.01; found C 24.83, H 2.54, N 4.16. IR (KBr): $\tilde{\nu}$ = 2136 ν(CN) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.4 Hz, 6 H, CH_3), 1.38 (m, 4 H, CH_2), 1.92 (m, 4 H, CH_2), 2.48 (s, 12 H, CH_3), 4.57 (m, 2 H, CH_2), 4.73 (m, 2 H, CH_2), 5.74 (d, 2 H, CH_2), 5.94 (d, 2 H, CH_2), 7.70 (m, 4 H, PhH), 8.05 (d, J = 7.2 Hz, 2 H, PhH), 8.27 (d, J = 7.6 Hz, 2 H, PhH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO): δ = 187.6 ($C_{carbene}$), 137.4, 136.6, 133.4, 132.6, 132.2, 126.1, 125.9 (PhC), 113.2 (CN), 48.0 (NCH_2Ph), 31.7 (NCH_2CH_2), 30.6 (HgCCN), 19.5 (CCH_2C), 17.5 (CCH_2C), 16.0 ($PhCH_3$), 13.7 (CH_2CH_3) ppm.

X-ray Structure Determinations: For complexes **2a** and **2b**, selected single crystals were mounted on a Rigaku Saturn diffractometer at 113(2) K with Mo-K_α radiation (λ = 0.71073 Å) by ω scan mode. Data collection and reduction were performed by using the SMART and SAINT software[43] with frames of 0.6° oscillation in the θ range $1.8 < \theta < 25°$. An empirical absorption correction was applied by using the SADABS program.[44] The structures were solved by direct methods, and all non-hydrogen atoms were subjected to an anisotropic refinement by full-matrix least-squares on F^2 by using the SHELXTL package.[45] All hydrogen atoms were generated geometrically (C–H bond lengths = 0.96 Å), assigned appropriated isotropic thermal parameters, and included in the final calculations. Selected bond lengths and angles are shown in Table 2, and crystallographic data are summarized in Table 3.

CCDC-713154 (for **2a**) and -713155 (for **2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Perspective view and double-stranded 1D polymeric chain of **2b**.

Table 2. Selected bond lengths (Å) angles (°) for **2a** and **2b**.

2a		**2b**	
N(5)–C(36)	1.120(3)	N(5)–C(36)	1.151(1)
C(35)–C(36)	1.470(2)	C(35)–C(36)	1.379(1)
Hg(1)–C(1)	2.096(2)	Hg(1)–C(1)	2.094(1)
Hg(1)–C(35)	2.103(1)	Hg(1)–C(35)	2.108(9)
Hg(2)–C(35)	2.075(2)	Hg(2)–C(35)	2.113(1)
Hg(2)–C(20)	2.123(2)	Hg(2)–C(20)	2.113(1)
Hg(3)–C(35)	2.102(1)	Hg(3)–C(35)	2.142(9)
N(3)–C(1)–N(4)	107.9(1)	N(1)–C(1)–N(2)	108.4(9)
N(1)–C(20)–N(2)	112.0(1)	N(3)–C(20)–N(4)	110.1(1)
Hg(1)–C(35)–Hg(2)	107.5(6)	Hg(1)–C(35)–Hg(2)	104.7(4)
C(36)–C(35)–Hg(3)	103.3(1)	C(36)–C(35)–Hg(3)	106.5(7)
N(5)–C(36)–C(35)	172.0(2)	N(5)–C(36)–C(35)	171.5(1)
C(1)–Hg(1)–C(35)	176.8(6)	C(35)–Hg(1)–C(1)	176.2(4)
C(35)–Hg(2)–C(20)	171.3(6)	C(20)–Hg(2)–C(35)	168.7(4)
C(35)–Hg(3)–Br(5)	159.6(5)	C(35)–Hg(3)–Br(5)	154.3(3)

Table 3. Summary of crystallographic data for **2a** and **2b**.

	2a·DMSO	**2b**·DMSO
Chemical formula	$C_{34}H_{38}Br_5Hg_4N_5$·DMSO	$C_{36}H_{42}Br_5Hg_4N_5$·DMSO
Fw	1796.73	1824.78
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.558(4)	11.775(2)
b (Å)	13.861(1)	14.219(2)
c (Å)	16.247(6)	16.086(3)
α (°)	73.199(1)	72.101(9)
β (°)	89.393(1)	88.242(1)
γ (°)	67.745(7)	66.065(7)
V (Å^3)	2291.9 (1)	2328.7(7)
Z	2	2
D_{calcd} (Mg m^{-3})	2.604	2.602
Abs. coeff. (mm^{-1})	17.793	17.515
F(000)	1628	1660
Cryst size (mm)	0.12 × 0.10 × 0.08	0.22 × 0.20 × 0.08
θ_{min}, θ_{max} (°)	1.92, 27.88	2.16, 29.13
T (K)	113(2)	113(2)
No. of data collected	22749	24897
No. of unique data	10699	12017
No. of refined param.	489	530
Goodness-of-fit on F^2[a]	1.043	1.032
Final R indices[b] [$I > 2\sigma(I)$]		
R_1	0.0737	0.0500
wR_2	0.2273	0.1417
R indices (all data)		
R_1	0.0932	0.0744
wR_2	0.2435	0.1541

[a] GOF = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined. [b] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$, where $P = (F_o^2 + 2F_c^2)/3$.

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[1] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[2] J. C. Garrison, W. J. Youngs, *Chem. Rev.* **2005**, *105*, 3978–4008.

[3] E. Assen, B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813.

[4] D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92.

[5] D. S. McGuinness, K. J. Cavell, B. W. Skekton, A. H. White, *Organometallics* **1999**, *18*, 1596–1605.

[6] H. V. Huynh, C. Holtgrewe, T. Pape, L. L. Koh, *Organometallics* **2006**, *25*, 245–249.

[7] F. E. Hahn, C. Radloff, T. Pape, A. Hepp, *Organometallics* **2008**, *27*, 6408–6410.

[8] F. E. Hahn, C. G. Plumed, M. Münder, T. Lügger, *Chem. Eur. J.* **2004**, *10*, 6285–6293.

[9] F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W. P. Fehlhammer, *Chem. Eur. J.* **2003**, *9*, 704–712.

[10] F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935.

[11] F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. L. Van, *Angew. Chem. Int. Ed.* **2005**, *44*, 3759–3763.

[12] F. E. Hahn, L. Wittenbecher, D. L. Van, R. Fröhlich, *Angew. Chem. Int. Ed.* **2000**, *39*, 541–544.

[13] F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241–245.

[14] F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2007**, *26*, 150–154.

[15] F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2006**, *25*, 5927–5936.

[16] F. E. Hahn, M. C. Jahnke, V. G. Benitez, D. M. Morales, T. Pape, *Organometallics* **2005**, *24*, 6458–6463.

[17] F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, *Organometallics* **2005**, *24*, 2203–2209.

[18] H. W. Wanzlick, H. J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142.

[19] K. M. Lee, J. C. C. Chen, I. J. B. Lin, *J. Organomet. Chem.* **2001**, *364*, 617–618.

[20] X. J. Wan, F. B. Xu, Q. S. Li, H. B. Song, Z. Z. Zhang, *Organometallics* **2005**, *24*, 6066–6068.

[21] U. J. Scheele, S. Dechert, F. Meyer, *Inorg. Chim. Acta* **2006**, *359*, 4891–4900.

[22] T. Weskamp, V. P. W. Böhm, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12–22.

[23] J. C. Garrison, R. S. Simons, J. M. Talley, C. Wesdemiotis, C. A. Tessier, W. J. Youngs, *Organometallics* **2001**, *20*, 1276–1278.

[24] A. Caballero, E. Díez-Barra, F. A. Jalón, S. Merino, J. Tejeda, *J. Organomet. Chem.* **2001**, *395*, 617–618.

[25] S. Inoue, Y. Sato, *Organometallics* **1986**, *5*, 1197–1201.

[26] P. S. Pregosin, *Inorg. Chim. Acta* **1980**, *45*, L7–L9.

[27] H. William, G. O. Allen, *Acta Crystallogr., Sect. C* **1999**, *55*, 1406–1408.

[28] A. D. Pra, G. Zanotti, G. Bombieri, R. Ros, *Inorg. Chim. Acta* **1979**, *36*, 121–125.

[29] M. Robert, F. George, A. J. McAlees, M. Parvez, P. J. Roberts, *J. Chem. Soc., Dalton Trans.* **1982**, 1699–1708.

[30] Q. X. Liu, L. N. Yin, X. M. Wu, J. C. Feng, J. H. Guo, H. B. Song, *Polyhedron* **2008**, *27*, 87–94.

[31] Q. X. Liu, X. J. Zhao, X. M. Wu, J. H. Guo, X. G. Wang, *J. Organomet. Chem.* **2007**, *692*, 5671–5679.

[32] Q. X. Liu, L. N. Yin, J. C. Feng, *J. Organomet. Chem.* **2007**, *692*, 3655–3663.

[33] I. B. Michael, T. W. Hambley, R. S. Michael, A. G. Swincer, *Organometallics* **1985**, *4*, 494–500.

[34] F. J. Lalor, S. A. O'Neill, *J. Organomet. Chem.* **2003**, *684*, 249–253.

[35] F. Weller, *Z. Anorg. Allg. Chem.* **1975**, *415*, 233–240.

[36] L. Pauling, *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, NY, **1960**, p. 269.

[37] G. Read, M. Urgelles, A. M. R. Galas, B. H. Michael, *J. Chem. Soc., Dalton Trans.* **1983**, 911–913.

[38] N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182.

[39] C. K. Lee, J. C. C. Chen, K. M. Lee, C. W. Liu, I. J. B. Lin, *Chem. Mater.* **1999**, *11*, 1237–1242.

[40] J. Tao, M. L. Tong, J. X. Shi, X. M. Chen, S. W. Ng, *Chem. Commun.* **2000**, 2043–2044.
[41] A. P. de Silva, H. Q. N. Lgunaratne, T. L. Gunnlangsson, A. J. M. Unzley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566.
[42] A. W. van der Made, R. H. van der Made, *J. Org. Chem.* **1993**, *58*, 1262–1263.
[43] *SMART 5.0 and SAINT 4.0 for Windows NT, Area Detector Control and Integration Software*, Bruker Analytical X-ray Systems, Inc., Madison, WI, USA, **1998**.
[44] G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.
[45] G. M. Sheldrick, *SHELXTL 5.10 for Windows NT, Structure Determination Software*, Bruker Analytical X-ray Systems, Inc., Madison, WI, USA, **1997**.

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