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New mercury(II) and silver(I) complexes containing NHC metallacrown ethers with the π–π stacking interactions

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Abstract

The oligoether-linked bis-benzimidazolium salt 1,1′-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[(3-^{sec}butyl)benzimidazolium-1-yl]iodide ($H_2L^1 \cdot I_2$), 1,1′-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[(3-ethyl)benzimidazolium-1-yl]iodide ($H_2L^2 \cdot I_2$) and 1,1′-[1,2-ethanediylbis-(oxy-1,2-ethanediyl)]bis[(3-^{sec}butyl)benzimidazolium-1-yl]hexafluorophosphate ($H_2L^1 \cdot (PF_6)_2$) and their three new mercury(II) and silver(I) complexes containing NHC metallacrown ethers, $HgL^1 \cdot (Hg_2 \cdot I_6)$ (**1**), $HgL^2 \cdot I_2$ (**2**) and $AgL^1 \cdot PF_6$ (**3**) were prepared and characterized. In the packing diagrams of $H_2L^2 \cdot I_2$, **1**, **2** and **3** benzimidazole ring head-to-tail π–π stacking interactions are observed.
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Keywords: Carbene complex; Mercury; Silver; π–π stacking interactions

1. Introduction

Since the discovery of free *N*-heterocyclic carbene (NHC) [1], organometallic chemistry based on imidazol-2-ylidene (imy) or benzimidazol-2-ylidene (bimy) have been receiving considerable attention. The primary characteristic of NHCs is that they are strong σ-donor ligands, which can bind firmly to different metal ions with various oxidation states [2], and a variety of related transition-metal complexes have been synthesized through deprotonation of *N*,*N*′-disubstituted imidazolium (or benzimidazolium) salts [3]. Among these metal–NHC complexes, some reports on the imidazol-2-ylidene (or benzimidazol-2-ylidene) complexes of Hg(II) and Ag(I) have appeared [4]. A new discovery shows that Ag(I)–carbene complexes can be used as effective antimicrobial agents [5], and they are also good carbene transfer agents for synthesis of Ni, Pd, Pt, Cu, Au, Rh, Ir and Ru carbene complexes, such a route affords a convenient method for the preparation of these metal carbene complexes [6]. Also metal–NHC complexes have been demonstrated to be efficient catalysts for some organic reactions, such as Heck, Suzuki, Kumada couplings, and olefin metathesis [7]. *N*-heterocyclic carbene complexes have shown to be remarkably stable toward heat, air, and moisture [8].

Polyether chain phosphine containing metallacrown ethers have been widely studied, because in the complexes the presence of weakly binding oxygen-donor groups can significantly increase the catalytic performance of these systems [9]. The NHC complexes containing metallacrown ethers have structural similarity with related phosphate complexes, and they have potential application as a catalyst and a phase-transfer reagent, therefore, we are interested in the compounds. In the paper, we report the synthesis, structural characterization of new mercury(II) and silver(I) complexes containing NHC metallacrown ethers with a flexible bridging chain, $HgL^1 \cdot (Hg_2 \cdot I_6)$ (**1**), $HgL^2 \cdot I_2$ (**2**) and $AgL^1 \cdot PF_6$ (**3**).

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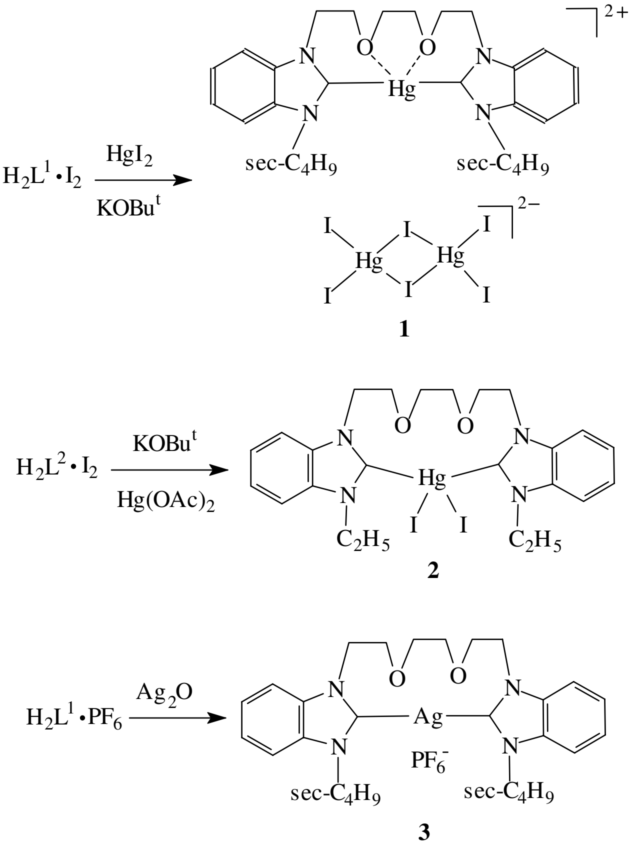
2. Results and discussion

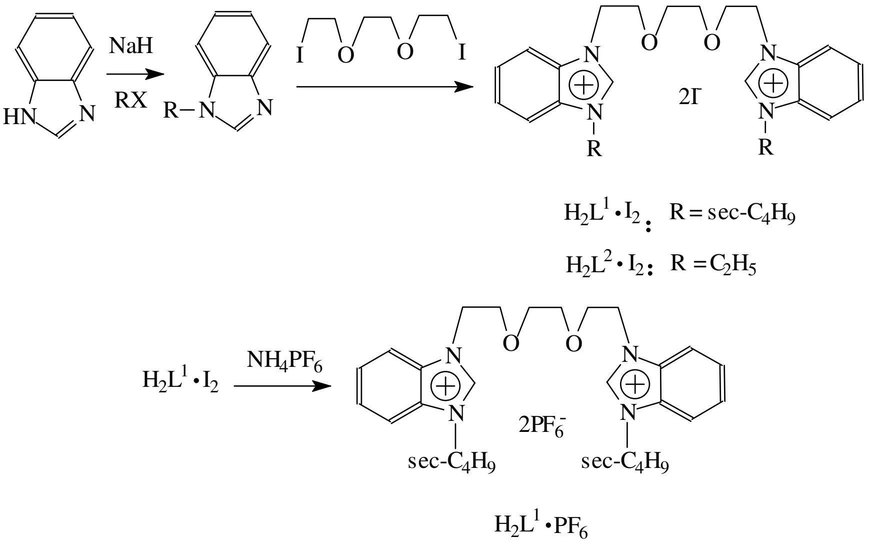
2.1. Synthetic strategy

The bis-benzimidazolium salts, 1,1′-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[(3-^{sec}butyl)benzimidazolium-1-yl] iodide ($H_2L^1 \cdot I_2$) and 1,1′-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[(3-ethyl)benzimidazolium-1-yl]iodide ($H_2L^2 \cdot I_2$) were prepared from benzimidazole by stepwise alkylation with 1-haloalkane followed by 1,2-bis(2-iodoethoxy)ethane in sequence, and 1,1′-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[(3-^{sec}butyl)benzimidazolium-1-yl]hexafluorophosphate ($H_2L^1 \cdot (PF_6)_2$) was obtained by treatment of $H_2L^1 \cdot I_2$ with ammonium hexafluorophosphate in methanol (Scheme 1). Precursors $H_2L^1 \cdot I_2$, $H_2L^2 \cdot I_2$ and $H_2L^1 \cdot (PF_6)_2$ are stable to air and moisture, and soluble in polar organic solvents such as dichloromethane, acetonitrile, methanol, scarcely soluble in benzene, and insoluble in diethyl ether, petroleum ether and water. In the ^{1}H NMR spectra of $H_2L^1 \cdot I_2$, $H_2L^2 \cdot I_2$ and $H_2L^1 \cdot (PF_6)_2$ the benzimidazolium proton signals (NCHN) appear at $\delta = 11.43$ ppm for $H_2L^1 \cdot I_2$, 11.50 ppm for $H_2L^2 \cdot I_2$ and 11.40 ppm for $H_2L^1 \cdot (PF_6)_2$, which are consistent with the chemical shifts of known imidazolium salts or benzimidazolium salts [3].

The $H_2L^1 \cdot I_2$ or $H_2L^2 \cdot I_2$ was treated with HgI_2 or $Hg(OAc)_2$ in the presence of $KOBu^t$ in the solution of CH_3CN and THF to afford macrocycle discarbene complexes $HgL^1 \cdot (Hg_2 \cdot I_6)$ (**1**) and $HgL^2 \cdot I_2$ (**2**). The $AgL^1 \cdot PF_6$ (**3**) was prepared by the reaction of $H_2L^1 \cdot (PF_6)_2$ with Ag_2O in CH_2Cl_2 solution (Scheme 2). The complexes **1**, **2** and **3** are stable in air and moisture, and soluble in DMSO and CH_2Cl_2, and insoluble in diethyl ether, hydrocarbon solvents and water. Complex **3** is light-sensitive in solution, but light-stable as solid. The formation of the metal carbene complexes was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra of **1**, **2** and **3**, 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 hydrogens are similar to those of corresponding precursors. In ^{13}C NMR spectra the signals for the carbene carbon appears at 175 ppm for **1**, 173 ppm



Scheme 2. Preparation of complexes **1**, **2** and **3**.



Scheme 1. Preparation of precursors $H_2L^1 \cdot I_2$, $H_2L^2 \cdot I_2$ and $H_2L^1 \cdot (PF_6)_2$.

for **2**, which are characteristic for carbene metal complexes [4a,4b,4c,4d,4e], but in complex **3**, the resonances for the carbene carbon were not observed. The absence of the carbene carbon resonance is not unusual, and this phenomenon has been reported for some silver–carbene complexes, and given a reason of the fluxional behavior of the NHCs complexes [10].

*2.2. Structure of precursor $H_2L^2 \cdot I_2$, complexes **1**, **2** and **3***

The pale yellow crystals of $H_2L^2 \cdot I_2$ suitable for X-ray diffraction were obtained by evaporating slowly its CH_2Cl_2/CH_3CN solution at room temperature. In molecular structure of $H_2L^2 \cdot I_2$ both benzimidazoles are parallel, and two ethyl chains point to contrary directions (Fig. 1). The internal ring angle (N–C–N) at the carbene center is 110.8(4)°. Analysis of the crystal packing of $H_2L^2 \cdot I_2$ revealed that the 2D supramolecular layers are formed by head-to-tail π–π interactions from intermolecular benzimidazole rings with the inter-planar separation of 3.392 Å (center-to-center separation: 3.535 Å) [11]. In addition, each anionic iodine as a bridge joins two cationic units via I···H–C hydrogen bonds (C(1B)–H(1B)···I(1A)···H(12B)–C(12B), I···H separations being 3.019 and 3.155 Å, and I···H–C angles being 132.3 and 163.4°, and H···I···H angles being 123.6°, respectively) (Fig. 1). The each cationic unit is connected with four anionic iodines via four I···H–C hydrogen bonds (I(1A)···H(1B)–C(1B), I(1C)···H(12C)–C(12C), I(1B)···H(12D)–C(12D) and I(1D)···H(1AB)–C(1AB)), respectively. The adjacent two cationic units are held together by two bridging iodines via I···H–C hydrogen bonds. These hydrogen bonds expand above mentioned 2D supramolecular layers into 3D supramolecular architecture.

The pale yellow crystals of **1** and **2** · CH_2Cl_2 suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into their CH_2Cl_2/DMSO solution. The white crystals of **3** were obtained by evaporating slowly its CH_2Cl_2 solution at room temperature.

In each cation of **1** a 13-membered NHC metallacrown ether is formed by a didentate chelate bis(carbene) ligand with a long flexible linkage and a mercury(II) as shown in Fig. 2. The both benzimidazole rings form a dihedral angle of 39°. Two *sec*-butyl chains point to contrary directions, and the cationic unit possesses a *trans*-configuration. Each mercury atom is coordinated by two carbene-carbons, two oxygen atoms from flexible linkage and two iodine atoms from two anionic units to form a distorted octahedron arrangement. The C(11A)–Hg(1A)–C(28A) is approximately linear, with the Hg–C(carbene) bond distances of 2.072(11) and 2.078(12) Å, and the bond angel of 175.9(4)°, respectively. These values are comparable to the corresponding values reported for other mercury(II) carbene complexes [4a,4b,4c,4d,4e]. The Hg···O separations are 2.827(10) and 2.799(10) Å, respectively, which are within the range of distances observed in HgX_2 crown ether and polyethylene glycol complexes [12]. The Hg···I distance of ca. 3.4 Å are longer than normal values (regular Hg–I bond length being 2.7–2.9 Å) [4e] but shorter than the sum of the van der Waals radii (3.7 Å), showing a weak interaction between cationic units and anionic units. The

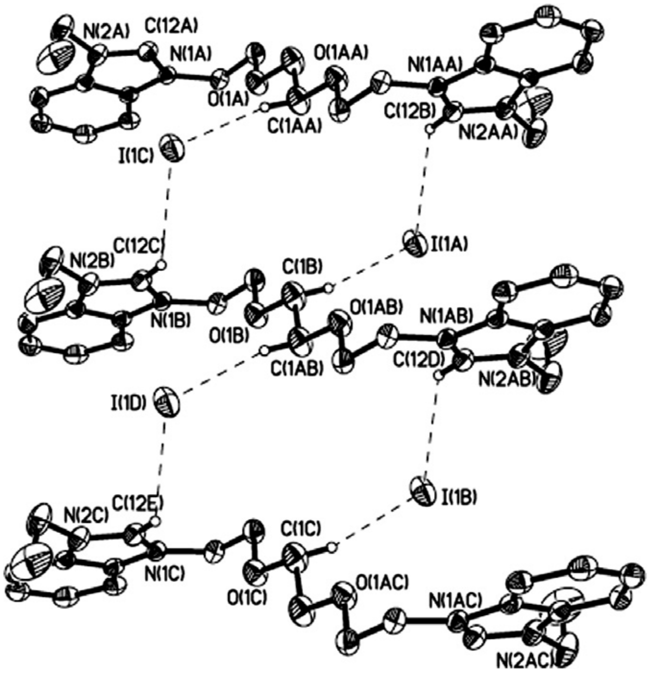


Fig. 1. Intermolecular I···H–C interactions in $H_2L^2 \cdot I_2$. The unrelated hydrogen atoms have been omitted for clarity.

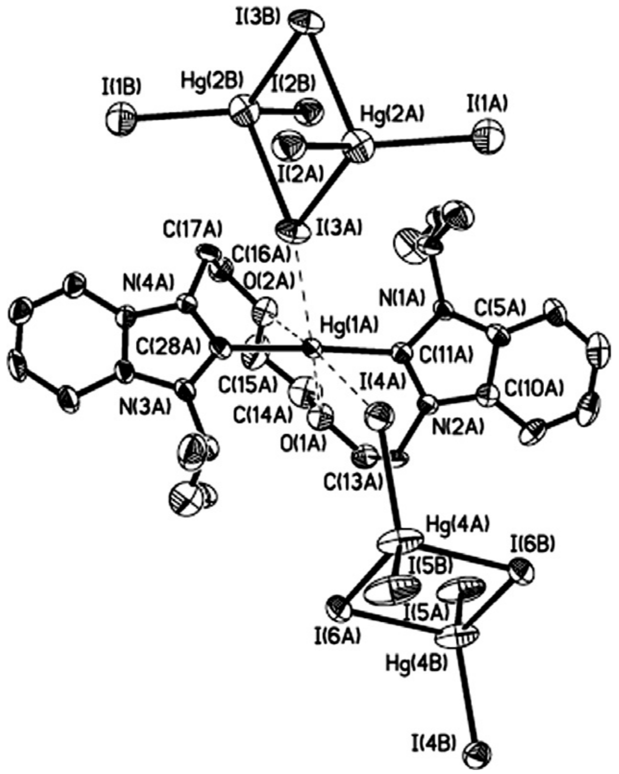


Fig. 2. Perspective view of **1** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

internal ring angle (N(1)–C(11)–N(2)) at the carbene center is 108.7°.

In the anionic unit of **1** two mercury atoms and six iodine atoms (two bridging iodines I(3A) and I(3B), and four terminal iodines I(1A), I(2A), I(1B), I(2B)) form the building unit $[Hg_2I_6]^{2-}$ (Fig. 2). The coplanar four atoms Hg(2A), I(3A), Hg(2B) and I(3B) form a quadrangle Hg_2I_2 arrangement (I(3A)–Hg(2A)–I(3B) = 95.3° and Hg(2A)–I(3A)–Hg(2B) = 84.6°). The four terminal iodine atoms (1A), I(1B), I(2A) and I(2B) lie in both flanks of the quadrangle plane (I(1A)–Hg(2A)–I(2A) = 122.9°), respectively. The distances of terminal iodine and mercury (Hg(2A)–I(1A) = 2.674(1) Å and Hg(2A)–I(2A) = 2.694(1) Å) are relatively shorter than those of bridging iodine and mercury (Hg(2A)–I(3A) = 2.8652(12) and Hg(2A)–I(3B) = 3.092(4) Å). The Hg···Hg separation of 4.016 Å shows no metal–metal interactions. The both quadrangle Hg_2I_2 planes from both different anionic units lying in both flanks of cationic unit form a dihedral angle of 67.8°. It was known that mercury(II) ions have a strong tendency to form complexes, principally linear two-coordinate $[HgX_2]$, or tetrahedral four-coordinate $[HgX_4]^{2-}$ systems [4a,4b,4c,4d,4e], but $[Hg_2I_6]^{2-}$ is a rare anionic complex.

An interesting feature in the packing diagrams of **1** is that 1D chains are formed by the head-to-tail π–π stacking interactions from inter-molecular benzimidazole rings, with the inter-planar separation of 3.711 Å (center-to-center separation: 4.090 Å). In addition, anionic building unit $[Hg_2I_6]^{2-}$ are packed between successive the cationic NHC metallacrown ethers, and held together the cations via weak Hg···I interactions, which extends the above 1D chains into 2D supramolecular layers. Thus aromatic π–π stacking interactions from benzimidazole rings, and Hg···I interactions from cationic mercurys and anionic iodides are mainly responsible for forming 2D supramolecular layers in **1**.

Compared with **1**, complex **2** contains also a macrocycle NHC metallacrown ether formed by a didentate chelate bis(carbene) ligand with a long flexible linkage and a mercury(II) (Fig. 3). The both benzimidazole rings within each molecule form a dihedral angle of 70.8°. Two ethyl chains point to same direction, and the molecule possesses a *cis*-configuration. The coordinated environment of mercury atom has some different from the one in **1**. In **2** each mercury atom is coordinated by two carbene–carbons and two iodine atoms to form a distorted tetrahedron arrangement. The C(9B)–Hg(1B)–C(22B) is approximately linear with bond angle of 147.3(3)°, and this value is obviously smaller than 175.9(4)° in **1**. The average Hg–C bond distances of 2.137 Å are slightly longer than those of 2.075 Å in **1** due to the variation of coordination environment. The I(1B)–Hg(1B)–I(2B) bond angle is 97.9(1)°, and the Hg(1B)–I(1B) and Hg(1B)–I(2B) bond distances are 2.939(6) Å and 3.141(6) Å, respectively, comparable to the values of $[Hg_2I_6]^{2-}$ in **1**. The internal ring angle (N(1B)–C(9B)–N(2B)) at the carbene center is 107.3(6)°, which is somewhat smaller than that of corresponding precursor $H_2L^2 \cdot I_2$ (110.8(4)°) and similar to those of some known mercury complexes. The relative long Hg···O separations of 3.195(5) Å and 4.134(6) Å show no Hg···O interactions.

In the crystal packing of complex **2** like the cation of **1**, 1D infinite chains are also formed through the head-to-tail π–π stacking interactions from inter-molecular benzimidazole rings, with the inter-planar separation of 3.442 Å (center-to-center separation: 4.295 Å). In addition, the intermolecular I···H–C hydrogen bonds (I···H separation = 3.213 Å, I···H–C angle = 168.6°) between 1D infinite chains are observed (Fig. 3), which expand the above 1D infinite chains into 2D supramolecular layers. Thus, 2D supramolecular layers are stabilized by aromatic π–π stacking interactions from benzimidazole rings and I···H–C hydrogen bonds from inter-molecules in **2**.

Similar to **1** and **2**, complex **3** contains also a macrocycle NHC metallacrown ether formed by a didentate chelate bis(carbene) ligand with a long flexible linkage and a silver(I) as shown in Fig. 4. The both benzimidazole rings within each molecule form a dihedral angle of 69.2°. Two *sec*-butyl chains point to contrary directions, and the cationic unit possesses a *trans*-configuration, comparable to the cationic configuration of **1**. The coordination geometry on the silver atom is nearly linear with the Ag–carbene bond distances of 2.088(6) Å and 2.090(6) Å, and with the bond angle C(11)–Ag(1)–C(18) of 174.0(2)°. The internal ring angle (N(1)–C(7)–N(2)) at the carbene center is 105.8(5)°. These values are quite normal when compared to the corresponding values reported for other NHC silver complexes [4f,4g,4h,4i,4j,4k,4l,4m,4n,4o,4p,4q,4r]. The Ag···O contacts are 2.885(4) and 3.678(5) Å, showing that Ag···O interactions can be neglected. In the crystal packing of complex **3**, the 1D infinite chains are also formed by the head-to-tail π–π stacking interactions from intermolecular benzimidazole rings, with the inter-planar separation of 3.302 Å (center-to-center separation: 4.705 Å).

*2.3. Thermogravimetric analysis of complexes **1**, **2** and **3***

Complexes **1**, **2** and **3** are air stable at ambient conditions and the thermogravimetric experiments were performed to explore their thermal stabilities. The TGA curve of **1** reveals that the complex starts to decompose beyond 175 °C with two steps of weight losses (peaks at 251.4 °C and 366.8 °C) and does not stop until heating ends at 700 °C. The TGA curve of **2** suggests that the first weight loss of 8.90% in the region of 185–232 °C (peaking at 225 °C) corresponds to the expulsion of the lattice dichloromethane molecules (calculated: 8.98%). The starting decomposition of the residuary section occurs at 240 °C with two steps of weight losses (peaks at 259.1 °C and 366.2 °C) and does not stop until heating ends at 700 °C. The TGA curve of **3** reveals that the complex starts to decompose beyond 240 °C with two steps of weight losses (peaks at 256.4 °C and 333.9 °C) and does not stop until heating ends at 700 °C.

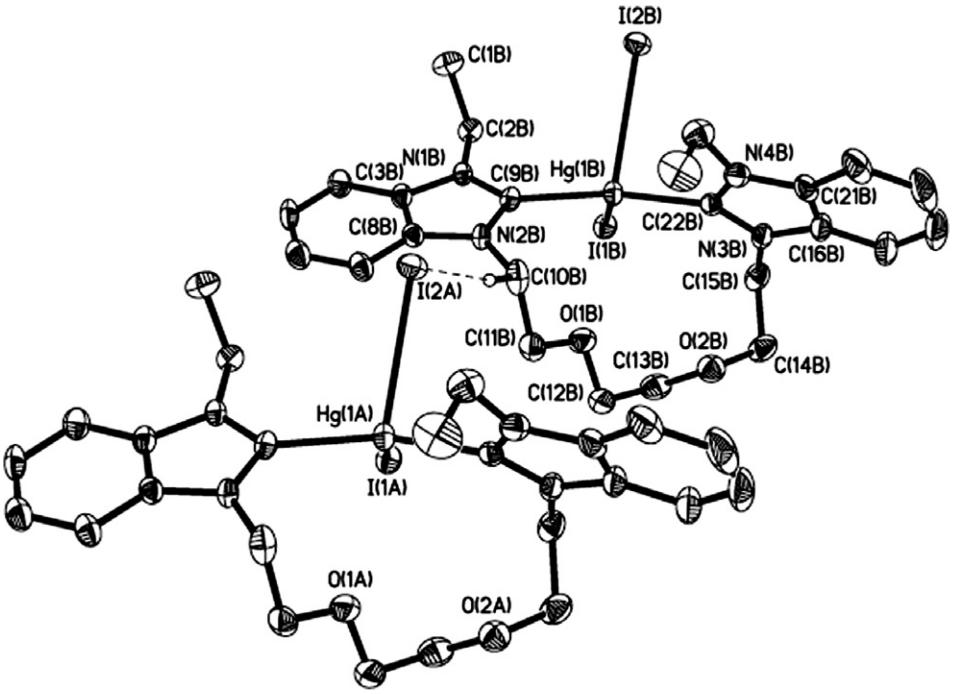


Fig. 3. Intermolecular I···H–C hydrogen bonds in **2**. The unrelated hydrogen atoms have been omitted for clarity.

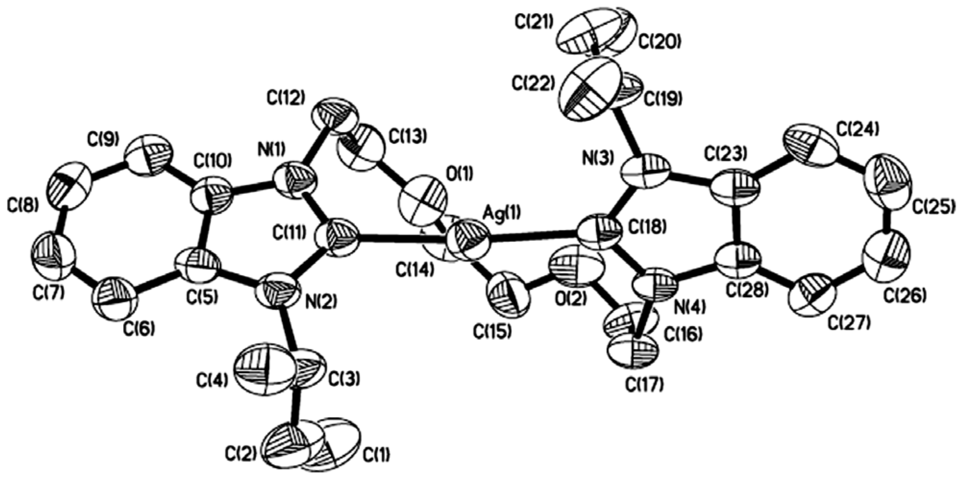


Fig. 4. Perspective view of **3** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

3. Conclusion

In summary, carbene precursors and their three new flexible bidentate NHCs bridged mercury(II) and silver(I) macrocyclic complexes have been synthesized and characterized. In packing diagrams of $H_2L^2 \cdot I_2$, **1**, **2** and **3** benzimidazole ring head-to-tail π–π stacking interactions are observed. In packing diagrams of $H_2L^2 \cdot I_2$ and **1** there exist intermolecular I···H–C hydrogen bonds. These weak interactions are helpful to forming 2D supramolecular layers or 3D supramolecular architecture. Complex **3** is stable toward light and air in the solid state at room temperature, which may offer convenient carbene precursor for the preparation of other transition metal complexes. Further studies on new organometallic compounds from precursors and analogous ligands are underway.

4. Experimental

4.1. General procedures

1,2-Bis(2-iodoethoxy)ethane was prepared according to the literature methods [13]. All manipulations were performed 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. ^1H and $^{13}C\{^1H\}$

NMR spectra were recorded on a Varian Mercury Vx 300 spectrometer at 300 MHz and 75 MHz, respectively. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. J values are given in Hz. Elemental analyses were measured using a Perkin–Elmer 2400C Elemental Analyzer.

4.2. Preparation of $H_2L^1 \cdot I_2$

A THF solution of benzimidazole (1.000 g, 8.5 mmol) was added to a suspension of oil-free sodium hydride (0.244 g, 10.2 mmol) in THF (25 mL) and stirred for 1 h at 60 °C. Then THF (20 mL) solution of *sec*-butyl bromide (1.276 g, 9.3 mmol) was dropwise added to above solution. The mixture was continued to stir for 48 h at 60 °C and a yellow solution was obtained. The solvent was removed with a rotary evaporator and H_2O (30 mL) was added to the residue. Then the solution was extracted with CH_2Cl_2 (3×20 mL), and the extracting solution was dried with anhydrous $MgSO_4$. After removing CH_2Cl_2, a pale yellow liquid 1-^{sec}butylbenzimidazole was obtained. Yield: 1.360 g (92%).

A solution of 1-^{sec}butylbenzimidazole (1.550 g, 8.9 mmol) and 1,2-dis(2-iodoethoxy)ethane (1.500 g, 4.1 mmol) in THF (50 mL) was stirred for three days under reflux, and a pale yellow precipitate was formed. The product was filtred and washed with THF. The pale yellow powder of bis-benzimidazolium iodide ($H_2L^1 \cdot I_2$) are obtained by recrystallization from methanol/diethyl ether. Yield: 2.290 g (78.6%). M.p.: 156–158 °C. Anal. Calc. for $C_{28}H_{40}I_2N_4O_2$: C, 46.81; H, 5.61; N, 7.80. Found: C, 46.76; H, 5.48; N, 7.66%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, $J = 5.4$, 6H, CH_3), 1.79 (d, $J = 5.1$, 6H, CH_3), 2.14 (m, 4H, CH_2), 4.15 (m, 2H, CH), 4.53 (t, $J = 4.0$, 4H, CH_2), 4.72 (t, $J = 4.0$, 4H, CH_2), 5.20 (t, $J = 4.0$, 4H, CH_2), 7.71 (m, 6H, PhH), 7.94 (t, $J = 6.4$, 2H, PhH), 11.43 (s, 2H, 2-benzimiH) (benzimi = benzimidazole). ^{13}C NMR (75 MHz, DMSO-d_6): δ 138.2 (NCHN), 136.4, 121.3 and 116.2 (PhC), 70.1 and 68.8 (OCH_2), 54.7 and 53.5 (NCH_2), 29.6 (CCH_2), 17.9 (CCH_3), 10.3 (CCH_3).

4.3. Preparation of $H_2L^2 \cdot I_2$

The $H_2L^2 \cdot I_2$ was prepared in a manner analogous to that for $H_2L^1 \cdot I_2$, only with ethyl bromide instead of *sec*-butyl bromide. Compound $H_2L^2 \cdot I_2$ was obtained as a pale yellow powder. Yield: 2.060 g (76.6%). M.p.: 192–194 °C. Anal. Calc. for $C_{24}H_{32}I_2N_4O_2$: C, 43.52; H, 4.87; N, 8.46. Found: C, 43.34; H, 4.56; N, 8.72%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.62 (t, $J = 5.5$, 6H, CH_3), 3.36 (t, $J = 4.2$, 4H, CH_2), 3.78 (t, $J = 4.2$, 4H, CH_2), 4.72 (t, $J = 4.2$, 4H, CH_2), 4.86 (q, $J = 5.5$, 4H, CH_2), 7.68 (m, 4H, PhH), 7.90 (d, $J = 6.3$, 2H, PhH), 7.97 (d, $J = 6.3$, 2H, PhH), 11.50 (s, 2H, 2-benzimiH) (benzimi = benzimidazole). ^{13}C NMR (75 MHz, DMSO-d_6): δ 139.8 (NCHN), 136.2, 123.3 and 114.8 (PhC), 69.1 and 68.4 (OCH_2), 52.8 and 46.2 (NCH_2), 12.8 (CCH_3).

4.4. Preparation of $H_2L^1 \cdot (PF_6)_2$

NH_4PF_6 (2.720 g, 16.8 mmol) was added to a methanol solution of $H_2L^1 \cdot I_2$ (3.000 g, 4.2 mmol) whilst stirring and a white precipitate formed immediately. The product was collected by filtration, washed with small portions of cold methanol, and dried in vacuum to give 2.820 g of $H_2L^1 \cdot (PF_6)_2$. Yield: 89.5%. M.p.: 140–142 °C. Anal. Calcd for $C_{28}H_{40}F_{12}N_4O_2P_2$: C, 44.57; H, 5.34; N, 7.43. Found: C, 44.64; H, 5.55; N, 7.31%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, $J = 5.4$, 6H, CH_3), 1.78 (d, $J = 5.0$, 6H, CH_3), 2.18 (m, 4H, CH_2), 4.15 (m, 2H, CH), 4.50 (t, $J = 4.0$, 4H, CH_2), 4.77 (t, $J = 4.0$, 4H, CH_2), 5.26 (t, $J = 4.0$, 4H, CH_2), 7.70 (m, 6H, PhH), 7.95 (t, $J = 6.5$, 2H, PhH), 11.40 (s, 2H, 2-benzimiH) (benzimi = benzimidazole). ^{13}C NMR (75 $MH_{Z,}$ DMSO-d_6): δ 138.8 (NCHN), 137.2, 120.8 and 113.9 (PhC), 69.4 and 68.3 (OCH_2), 55.1 and 53.2 (NCH_2), 28.8 (CCH_2), 17.6 (CCH_3), 9.3 (CCH_3).

4.5. Preparation of $HgL^1 \cdot (Hg_2I_6)$ (**1**)

A suspension of $KOBu^t$ (0.090 g, 0.8 mmol), precursor $H_2L^1 \cdot I_2$ (0.200 g, 0.28 mmol) and mercury(II) iodide (0.409 g, 0.90 mmol) in THF (20 mL) and acetonitrile (20 mL) was refluxed for 24 h. A brown solution was formed and the solvent was removed with a rotary evaporator. The water (30 mL) was added to the residue and the solution extracted with CH_2Cl_2 (3×20 mL). The extracting solution was dried with anhydrate $MgSO_4$, then the solution was concentrated to 10 ml and hexane (2 mL) was added, as a result a pale yellow powder was obtained. Yield: 0.180 g (35.4%). M.p.: 220–222 °C. Anal. Calc. for $C_{28}H_{38}Hg_3I_6O_2N_4$: C, 18.42; H, 2.10; N, 3.07. Found: C, 18.65; H, 2.43; N, 3.21%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (t, $J = 5.4$, 6 H, CH_3), 1.71 (d, $J = 5.2$, 6H, CH_3), 2.16 (m, 4H, CH_2), 4.23 (m, 2H, CH), 4.56 (t, $J = 4.0$, 4H, CH_2), 4.75 (t, $J = 4.0$, 4H, CH_2), 5.23 (t, $J = 4.0$, 4H, CH_2), 7.77 (m, 6H, PhH), 7.95 (t, $J = 6.2$, 2H, PhH).

Table 1
Selected bond lengths (Å) angles (°) for $H_2L^2 \cdot I_2$ and **1**

$H_2L^2 \cdot I_2$		**1**	
O(1)–C(1)	1.431(6)	Hg(1A)	2.072(11)
O(1)–C(2)	1.413(6)	Hg(1A)	2.078(12)
N(1)–C(3)	1.468(5)	Hg(2A)	2.6744(14)
N(1)–C(4)	1.390(5)	Hg(2A)	2.6948(13)
N(1)–C(12)	1.321(5)	Hg(2A)	2.8652(12)
N(2)–C(9)	1.387(6)	Hg(2A)	3.0922(12)
N(2)–C(10)	1.481(6)	O(1A)	1.391(16)
N(2)–C(12)	1.321(6)	O(1A)	1.390(19)
N(1)–C(12)–N(2)	110.8(4)	N(1A)	1.352(14)
C(1)–O(1)–C(2)	111.8(4)	C(11A)	175.9(4)
C(3)–N(1)–C(4)	123.9(3)	N(1A)	108.7(10)
C(3)–N(1)–C(12)	128.1(4)	I(1A)	122.96(4)
C(4)–N(1)–C(12)	107.9(4)	I(1A)	119.32(4)
C(9)–N(2)–C(12)	108.2(4)	I(2A)	106.87(4)
C(10)–N(2)–C(12)	124.1(4)	C(13A)	116.3(12)
C(9)–N(2)–C(10)	127.6(4)	C(15A)	114.9(12)

^{13}C NMR (75 MH$_Z$, DMSO-d_6): δ 175.0 (C$_{carbene}$), 128.2, 117.4 and 113.8 (PhC), 69.8 (OCH$_2$), 53.2 (NCH$_2$), 47.8 (NCH), 28.2 (CCH$_2$C), 19.1 (CCH$_3$), 9.1 (CCH$_3$).

4.6. Preparation of $HgL^2 \cdot I_2$

A suspension of KOBu^t (0.090 g, 0.8 mmol), precursor $H_2L^2 \cdot I_2$ (0.200 g, 0.3 mmol) and anhydrous mercury(II) acetate (0.106 g, 0.3 mmol) in THF (20 mL) and acetonitrile (20 mL) was refluxed for 24 h. A brown solution was formed and the solvent was removed with a rotary evaporator. The water (30 mL) was added to the residue and the solution extracted with CH_2Cl_2 (3×20 mL). The extracting solution was dried with anhydrate $MgSO_4$, then the solution was concentrated to 10 mL and hexane (5 mL) was added, as a result a pale yellow powder was obtained. Yield: 0.980 g (37.7%). M.p.: 262–264 °C. Anal. Calc. for $C_{24}H_{30}HgI_2N_4O_2$: C, 33.48; H, 3.51; N, 6.51. Found: C, 33.56; H, 3.73; N, 6.33%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.64 (t, $J = 5.6$, 6H, CH$_3$), 3.40 (t, $J = 4.2$, 4H, CH$_2$), 3.79 (t, $J = 4.2$, 4H, CH$_2$), 4,76 (t, $J = 4.2$, 4H, CH$_2$), 4.80 (q, $J = 5.6$, 4H, CH$_2$), 7.68 (m, 4H, PhH), 7.92 (d, $J = 6.3$, 2H, PhH), 7.98 (d, $J = 6.3$, PhH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 173.0 (C$_{carbene}$), 127.9, 116.0 and 113.4 (PhC), 70.1 and 69.3 (OCH$_2$), 53.4 (NCH$_2$), 46.2 (NCH$_2$), 13.4 (CCH$_3$).

4.7. Preparation of $AgL^1 \cdot PF_6$

Silver oxide (0.031 g, 0.14 mmol) was added to a solution of compound $H_2L^1 \cdot (PF_6)_2$ (0.200 g, 0.27 mmol) in dichloromethane (30 mL) and the suspension solution was stirred for 24 h at refluxing. The resulting solution was filtered and concentrated to 10 mL, and Et$_2$O (5 mL) was added to precipitate a white powder. Isolation by filtration yields $AgL^1 \cdot PF_6$. Yield: 0.098 g (43.8%). M.p.: 160–162 °C. Anal. Calc. for $C_{28}H_{38}F_6AgN_4O_2P$: C, 47.01; H, 5.35; N, 7.83. Found: C, 47.23; H, 5.44; N, 7.79%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.91 (t, $J = 5.2$, 6H, CH$_3$), 1.74 (d, $J = 5.0$, 6H, CH$_3$), 2.12 (m, 4H, CH$_2$), 4.20 (m, 2H, CH), 4.55 (t, $J = 3.8$, 4H, CH$_2$), 4.77 (t, $J = 3.8$, 4H, CH$_2$), 5.26 (t, $J = 3.8$, 4H, CH$_2$), 7.73 (m, 6H, PhH), 7.92 (t, $J = 6.4$, 2H, PhH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 127.8, 118.0 and 114.5 (PhC), 69.6 and 69.3 (OCH$_2$), 55.3 (NCH$_2$), 54.8 (NCH), 28.8 (CCH$_2$C), 18.7 (CCH$_3$), 9.0 (CCH$_3$). The carbene carbon was not observed.

4.8. X-ray structure determinations

For compounds $H_2L^2 \cdot I_2$, **1**, **2** and **3**, selected single crystals were mounted on a Bruker APEX II CCD diffractometer at 293(2) K with Mo Kα radiation ($\lambda = 0.71073$ Å) by ω scan mode. Data collection and reduction were performed using the SMART and SAINT software [14] with frames of 0.6° oscillation in the θ range $1.8 < \theta < 25°$. An empirical absorption correction was applied using the SADABS program [15]. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package [16]. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters and included in structure factor calculations. Selected bond lengths and angles were showed in

Table 2
Selected bond lengths (Å) angles (°) for **2** and **3**

2		**3**	
Hg(1)–C(9)	2.148(7)	Ag(1)–C(11)	2.088(6)
Hg(1)–C(22)	2.127(7)	Ag(1)–C(18)	2.090(6)
Hg(1)–I(1)	2.9392(6)	N(1)–C(10)	1.368(7)
Hg(1)–I(2)	3.1413(6)	N(1)–C(11)	1.373(7)
N(1)–C(2)	1.473(9)	N(1)–C(12)	1.459(7)
N(1)–C(3)	1.406(9)	N(2)–C(3)	1.482(8)
N(1)–C(9)	1.351(9)	N(2)–C(5)	1.399(8)
N(2)–C(8)	1.390(9)	N(2)–C(11)	1.342(7)
N(2)–C(9)	1.351(9)	C(11)–Ag(1)–C(18)	174.0(2)
N(2)–C(10)	1.483(10)	N(1)–C(11)–N(2)	105.8(5)
N(1)–C(9)–N(2)	107.3(6)	C(10)–N(1)–C(11)	110.7(5)
C(9)–Hg(1)–C(22)	147.3(3)	C(10)–N(1)–C(12)	125.8(5)
C(9)–Hg(1)–I(1)	96.52(17)	C(11)–N(1)–C(12)	123.5(5)
C(9)–Hg(1)–I(2)	103.40(19)	C(3)–N(2)–C(5)	126.9(5)
C(22)–Hg(1)–I(1)	111.3(2)	C(3)–N(2)–C(11)	122.8(6)
C(22)–Hg(1)–I(2)	89.89(19)	C(5)–N(2)–C(11)	110.3(5)
I(1)–Hg(1)–I(2)	97.911(17)		

Table 3
Summary of crystallographic data for $H_2L^2 \cdot I_2$ and **1**

	$H_2L^2 \cdot I_2$	**1**
Chemical formula	$C_{24}H_{32} \cdot I_2N_4O_2$	$C_{28}H_{38}Hg_3I_6N_4O_2$
F$_w$	662.34	1825.79
Crystal system	Monoclinic	Triclinic
Space group	*P2(1)/c*	$P\bar{1}$
a (Å)	6.8232(17)	10.8243(13)
b (Å)	12.545(3)	12.1816(14)
c (Å)	15.976(4)	16.3255(19)
α (°)	90	93.155(2)
β (°)	100.181(4)	96.977(2)
γ (°)	90	97.284(2)
V (Å^3)	1345.9(6)	2114.0(4)
Z	2	2
D_{calc} (Mg/m^3)	1.634	2.868
Absorption coefficient (mm^{-1})	2.363	15.276
F(000)	652	1616
Crystal size (mm)	$0.24 \times 0.20 \times 0.16$	$0.24 \times 0.22 \times 0.20$
θ_{min}, θ_{max}, deg	2.08, 25.03	1.69, 25.03
T (K)	293(2)	293(2)
Number of data collected	6641	10862
Number of unique data	2363	7421
Number of refined parameters	146	387
Goodness-of-fit on F^{2a}	1.071	1.034
Final R indices[b] [$I > 2\sigma(I)$]		
R_1	0.0414	0.0474
wR_2	0.0963	0.1184
R indices (all data)		
R_1	0.0469	0.0713
wR_2	0.0999	0.1335

[a] Goof $= [\sum\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined.

[b] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 4
Summary of crystallographic data for **2** and **3**

	2	**3**
Chemical formula	$C_{24}H_{30}HgI_2N_4O_2 \cdot CH_2Cl_2$	$C_{28}H_{38}AgF_6N_4O_2P$
F_w	945.84	715.46
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*P2(1)/c*
a (Å)	8.8646(5)	10.3238(6)
b (Å)	8.9060(5)	18.9279(10)
c (Å)	20.1169(11)	16.2906(9)
α (°)	88.1020(10)	90
β (°)	81.4130(10)	97.3370(10)
γ (°)	77.8530(10)	90
V (Å^3)	1535.23(15)	3157.2(3)
Z	2	4
D_{calc} (Mg/m^3)	2.046	1.505
Absorption coefficient (mm^{-1})	7.226	0.756
$F(000)$	1690	1464
Crystal size (mm)	0.24 × 0.22 × 0.16	0.24 × 0.22 × 0.18
θ_{min}, θ_{max} (°)	1.02, 25.03	1.66, 25.03
T (K)	293(2)	293(2)
Number of data collected	7979	15971
Number of unique data	5426	5581
Number of refined parameters	327	383
Goodness-of-fit on F^2[a]	1.064	1.078
Final R indices[b] $[I > 2\sigma(I)]$		
R_1	0.0351	0.0530
wR_2	0.0874	0.1381
R indices (all data)		
R_1	0.0443	0.0900
wR_2	0.0990	0.1582

[a] Goof $= [\sum\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined.

[b] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Tables 1 and 2, and crystallographic data were summarised in Tables 3 and 4 for $H_2L^2 \cdot I_2$, **1**, **2** and **3**.

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Appendix A. Supplementary material

CCDC 657127, 657128, 657129 and 657130 contain the supplementary crystallographic data for $H_2L^2 \cdot I_2$, **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.09.027.

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