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RESEARCH ARTICLE

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Synthesis and characterization of $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2Hg$, $[4\text{-}(O{=}CH)C_6H_4]_2Hg$ and $[(E)\text{-}4\text{-}(RN{=}CH)C_6H_4]_2Hg$ ($R = 2'\text{-py}, 4'\text{-py}, 2'\text{-pyCH}_2, 4'\text{-pyCH}_2$)

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Abstract

The reaction of $4\text{-}[(CH_2O)_2CH]C_6H_4Br$ (**1**) with *n*-BuLi, followed by addition of $HgCl_2$ to the in situ formed organolithium derivative, affords $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2Hg$ (**2**). Deprotection of the formyl groups of **2** in presence of *p*-TsOH (*p*-Ts = $4\text{-}MeC_6H_4SO_3$) leads to $[4\text{-}(O{=}CH)C_6H_4]_2Hg$ (**3**). Condensation reactions of **3** with 2-aminopyridine (2-pyNH_2), 4-aminopyridine (4-pyNH_2), 2-aminomethylpyridine (2-pyCH_2NH_2), and 4-aminomethylpyridine (4-pyCH_2NH_2), in CH_2Cl_2, affords the novel diorganomercury(II) compounds of type $[(E)\text{-}4\text{-}(RN{=}C)C_6H_4]_2Hg$ [$R = 2'$-py (**4**), $4'$-py (**5**), 2'-pyCH2- (**6**), $4'\text{-pyCH}_2$ (**7**)]. Compounds **2** and **3** were useful precursors for the preparation of the corresponding homocoupling products $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2$ (**8**) and $[4\text{-}(O{=}CH)C_6H_4]_2$ (**9**) in presence of catalytic amounts of palladium(II) acetate. Compounds **2–9** were characterized by multinuclear magnetic resonance (NMR) (^1H, $^{13}C\{^1H\}$, and $^{199}Hg\{^1H\}$, when appropriate) and infrared (IR) spectroscopy and by mass spectrometry. The molecular structures of **3**, **5**, **6**, **8**, and **9** were determined by single-crystal X-ray diffraction.

Highlights

- A quick, easy, and economic synthesis was optimized for bis(4-formylphenyl)mercury(II).
- Syntheses of novel homoleptic diorganomercury(II) compounds with imine functional groups were optimized to give good to excellent yields in mild conditions with easy workup.
- All diorganomercury(II) compounds were characterized by multinuclear (^1H, $^{13}C\{^1H\}$, and $^{199}Hg\{^1H\}$ NMR) and IR spectroscopy as well as mass spectrometry and, for three compounds with imine functional groups, the molecular structure was determined by single-crystal X-ray diffraction.
- The use of diorganomercury(II) compounds as starting materials for homocoupling reactions, in presence of catalytic amounts of palladium(II) acetate, was investigated.

KEYWORDS

^{199}Hg NMR spectroscopy, catalysis, homocoupling, organomercury(II), structural investigation

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1 | INTRODUCTION

Despite the very well-known toxicity of mercury compounds the organomercury chemistry continues to receive notable interest regarding both fundamental and applied topics. Thus, for example, a field of particular development was that related to mercuramacrocycles,[1] that is, (i) studies on supramolecular aspects based on interactions between Lewis acidic mercuramacrocycles and neutral electron-rich substrates as solvents,[2] oxygeneous Lewis bases, for example, carbonylic derivatives, esters, amides, phosphoramides, sulfoxides, nitroxide and nitronyl-nitroxide organic radicals, and crown-ethers,[2e,3] sulfur-containing compounds,[4] azacrowns,[5] or aromatic hydrocarbons, alkynes, and related species,[2c,f,g,6] neutral inorganic metal complexes and organometallics,[7] and anions[2g,8]; (ii) investigation of metallophilic Hg(II) ···M [M = Hg(II), Cu(I), Ag(I), Au(I), Pd(II), Pt(II), and Sb(III)] interactions[1e,f,2d,7a,9]; (iii) potential applications as sensors,[8b,10] anion receptors,[8] molecular recognition,[11] catalysts,[4a,12] and new luminescent materials.[1d,6a–d]

The use of organomercury compounds as precursors in organic and organometallic synthesis also raised considerable interest,[13] mainly due to (i) easy mercuration of functionalized arenes and arene-transition metal complexes using common inorganic mercury(II) salts as $Hg(OAc)_2$, $Hg(TFA)_2$, or $HgCl_2$,[14] and (ii) high selectivity of the transmetallation reaction to either main group or transition metals thus providing organometallic species, which are often inaccessible by classical Grignard and/or lithiation reactions.[14a,15–17] Related to the topic of the present research, organomercury compounds containing aryl groups with at least one substituent with a potential donor nitrogen available for an intramolecular N→M interaction are of interest to be mentioned here. Thus, both homoleptic, Ar_2Hg[14b,c,16] or ArHgX,[1e,9b,c,14c–h,l,16b,d,17] with *ortho*-substituted aromatic groups containing either sp^3 nitrogen[14b,g,16a,b,17a,d–f] or sp^2 nitrogen[1e,9b,c,14c–f,h,16b–d,17a–c,f] as donor atom were used as transmetallating agents to obtain organometallic compounds of other metals, for example, Sn,[17c,18] Te,[14g] Ru,[14e,16a,d,17d–f] Pd,[9b,c,14b–d,f,h,l,16c] Pt,[1e,17b] or Au.[16b,17a] It should also be noted that the unusual reverse transmetallation process, that is, the transfer of an *ortho*-substituted (imino)aryl group from a transition metal to mercury, was reported when a reaction was carried out between an organopalladium(II) chloride and elemental mercury, resulting in the isolation of the organomercury(II) chloride.[18]

Organomercury(II) compounds containing *ortho*-substituted (imino)aryl groups attached to the metal were generally prepared by Schiff base condensation reactions between $[2\text{-}(O{=}CH)C_6H_4]_2Hg$ or $[2\text{-}(O{=}CH)C_6H_4]HgX$ (X = halogen) and primary amines. This includes mercuramacrocycles with at least two metal atoms per heterocycle and their metal complexes,[1e,f,9a–c] as well as monometallic molecular species as $[2\text{-(imino)aryl}]_2Hg$,[1e,16b,19] and [2-(imino)aryl]HgX (X = Cl, Br).[20] In addition, some [2-(imino)aryl]mercury(II) chlorides were isolated as side products during transmetallation reactions, often through splitting of a macrocycle during complexation of transition metal ions.[1e,9b,c,16b,18,21] A few other related organomercury(II) compounds containing (oxazolynyl)aryl[14h,17a] or (imino)ferocenyl[17c,22] substituents were also reported. By contrast, organomercury(II) compounds containing the $[4\text{-}(RN{=}C)C_6H_4]Hg$ fragment have not been described so far, while only a few reports on related compounds containing the $[4\text{-}(RCH{=}N)C_6H_4]Hg$ fragment, prepared either by direct mercuration of Schiff bases[23] or by condensation of $[4\text{-}(H_2N)C_6H_4]HgX$ (X = OAc, Cl) with aromatic aldehydes, are available.[24] Very recently, an article on the synthesis of $4\text{-}(4'\text{-}HO\text{-}C_6H_4CH{=}N)\text{-}5\text{-}F\text{-}2\text{-}NO_2\text{-}C_6H_4]HgCl$ and its use as transmetallating agent in a reaction with $TeBr_4$, to afford a $RTeBr_3$ derivative, was published.[14m]

Within our interest for organometallic supramolecular architectures, we have designed several new organotin(IV),[25] organophosphorus(V),[26] and organobismuth(V)[27] compounds, which might be used as tectons of different geometry for construction of molecular heterometallic species or coordination polymers with different dimensionality. In addition, we have improved the preparation of di(4-pyridyl)mercury(II), which was used as a new organometallic linear tecton in crystal engineering of coordination polymer supramolecular solid-state architectures.[28]

As an extension of this work, we have decided to investigate new related organomercury(II)-based tectons useful as spacers of different dimension and directionality. Herein, we report the synthesis and the spectroscopic characterization of $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2Hg$ (**2**), $[4\text{-}(O{=}CH)C_6H_4]_2Hg$ (**3**) and conversion of the later into various imine derivatives $[(E)\text{-}4\text{-}(RN{=}CH)C_6H_4]_2Hg$ [R = 2′-py (**4**), 4′-py (**5**), 2′-pyCH$_2$ (**6**), 4′-pyCH$_2$ (**7**)], as well as on the use of compounds **2** and **3** as precursors for conversion into the homocoupling products $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2$ (**8**) and $[4\text{-}(O{=}CH)C_6H_4]_2$ (**9**), in presence of catalytic amounts of palladium(II) acetate.

2 | EXPERIMENTAL

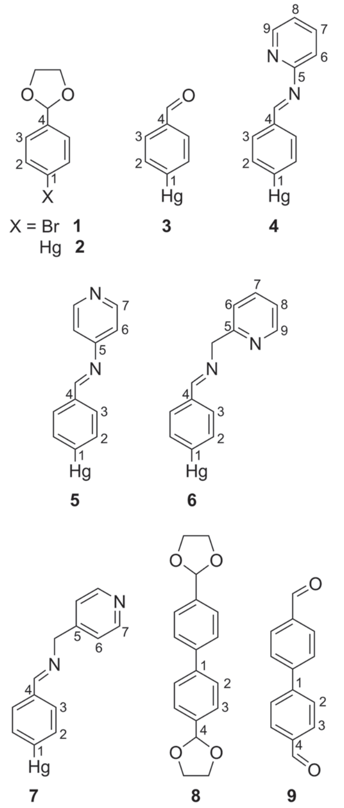
2.1 | Materials and procedures

All reactions were carried out using standard Schlenk techniques under argon atmosphere. Work-ups were done in air using freshly distilled solvents. All chemicals were purchased from commercial sources and used as supplied. THF was pre-dried on KOH pellets, distilled, and refluxed with metallic potassium for 24 h prior to use. Dichloromethane was pre-dried and neutralized by stirring over anhydrous sodium carbonate for 2 days followed by distillation and drying for 24 h over 10% (m/v) 4-Å molecular sieves.[29] Multinuclear magnetic resonance (NMR) (^{1}H, ^{13}C, ^{199}Hg) spectra were recorded in solution at room temperature (r.t.) on Bruker Avance III 400- or 600-MHz instruments. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent ($CDCl_3$, 7.26 and DMSO-d_6 2.50 ppm), while the ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent ($CDCl_3$, 77.16 ppm and DMSO-d_6 39.52 ppm).[30] ^{1}H and ^{13}C resonances were assigned using 2-D NMR experiments (COSY, HSQC, and HMBC) according to the numbering scheme displayed in Scheme 1. The ^{199}Hg chemical shifts are reported in δ units (ppm) relative to Me_2Hg using the chemical shift of the lock solvent as a reference. The NMR spectra were processed using the *MestReNova* software package.[31] The MS APCI+ and ESI+ spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer. Data analysis and calculations of the theoretical isotopic patterns were carried out with the *Xcalibur* software package.[32] Infrared spectra were recorded in the 4000- to 500-cm^{-1} range as KBr pellets on a Bruker FT IR Vector 22 spectrometer or on an FT-IR Bruker Alpha II spectrometer with ATR module. Melting points were recorded in capillary tubes on a Gallenkamp Melting Point Apparatus (MFB 595 030 G).

2.2 | Syntheses

2.2.1 | Synthesis of 4-[$(CH_2O)_2CH$]C_6H_4Br (1)

The protected aryl bromide **1** was prepared using a slightly modified literature method.[33] A reaction mixture of 4-($O{=}CH$)C_6H_4Br (18.520 g, 100 mmol), ethylene glycol (9.311 g, 150 mmol) and *p*-toluenesulfonic acid (0.344 g, 2 mmol) in toluene (100 ml) was refluxed with a Dean-Stark apparatus until the expected amount of water (~1.8 ml) was separated. The remained solution was cooled to r.t., Na_2CO_3 was added, and the mixture was stirred for 30 min. After filtration, the solvent was evaporated to leave colorless oil. Distillation of the crude product at reduced pressure (1×10^{-3} mbar), at 140°C, afforded the title compound **1** as colorless oil, which solidified on standing. Yield 20.25 g (89%; cf. 69% in Mei et al.[33]), m.p. 36–37°C (cf. 37–38°C in Wu et al.[34]; 34–35°C in Dhayalan et al.[35]). **^{1}H NMR** ($CDCl_3$, 400.13 MHz): δ 3.80–4.15 [*m*, 4H, ($CH_2O)_2CH$], 5.77 [*s*, 1H, $(CH_2O)_2CH$], 7.33–7.37 (*m*, 2H, H-3, C_6H_4), 7.49–7.53 (*m*, 2H, H-2, C_6H_4). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.62 MHz): δ 65.42 [*s*, $(CH_2O)_2CH$], 103.12 [*s*, $(CH_2O)_2CH$], 123.34 (*s*, C-1), 128.30 (*s*, C-3), 131.60 (*s*, C-2), 137.08 (*s*, C-4).



SCHEME 1 Numbering scheme for ^{1}H and ^{13}C NMR assignments. In compounds **8** and **9** only non-equivalent positions were labeled

2.2.2 | Synthesis of [4-{$(CH_2O)_2CH$}$C_6H_4]_2Hg$ (2)

A solution of *n*-BuLi (14.5 ml, 1.5 M) in hexane was added under argon to anhydrous THF (40 ml) cooled to −78°C. Then, under stirring, a solution of 4-[$(CH_2O)_2CH$]C_6H_4Br (**1**) (5 g, 21.83 mmol) in THF (40 ml) was added dropwise during about 15 min, and the stirring was continued for 1 h, maintaining the temperature at −78°C. Solid $HgCl_2$ (2.370 g, 8.73 mmol) was added at once, and the reaction mixture was stirred for 1 h at low temperature and then left to reach r.t. overnight. The obtained THF solution was filtered through celite, and the solvent was removed under vacuum. The remaining slightly yellow solid was extracted with $CHCl_3$ (3 × 50 ml), and the organic phase was washed with H_2O (2 × 50 ml) and then dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under vacuum and the obtained yellowish solid was suspended in ethanol (50 ml), sonicated for 15 min, filtered, washed with ethanol (2 × 25 ml), and dried at reduced pressure to give the title compound as a colorless solid. Yield 3.97 g (91%; cf. 50% in Drefahl and Lorenz[36]), m.p. 185–188°C (cf. 184–186°C in ref. Drefahl and Lorenz[36]). **^{1}H NMR** ($CDCl_3$, 400.13 MHz): δ 4.01–4.19 [*m*, 4H, $(CH_2O)_2CH$], 5.82 [*s*, 1H, $(CH_2O)_2CH$], 7.45 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 8.0 Hz), 7.57 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 8.0 Hz). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.62 MHz): δ 65.43 [*s*, $(CH_2O)_2CH$], 103.80 [*s*, $(CH_2O)_2CH$], 126.62 (*s*, C-3, $^3J_{HgC}$ 99.6 Hz), 137.57 (*s*, C-2, $^2J_{HgC}$ 86.9 Hz), 137.73 (*s*, C-4), 171.43 (*s*, C-1, $^1J_{HgC}$ 1187 Hz). **^{199}Hg{^{1}H} NMR** ($CDCl_3$, 71.61 MHz): δ −751.9 (s). **IR** (KBr pellet, *υ*, cm^{-1}): 3302(w), 2953(w), 2883(w), 2853(w), 2752(w), 1595(w), 1477(w), 1414(s), 1375(w), 1310(w), 1219(m), 1103(w), 1082(s), 1061(vs), 1020(m), 959(m), 939(s), 806 (vs), and 677(w). **MS** (APCI+, MeCN), *m/z* (relative intensity, %): 211.07 (4) $[M–Hg–C_4H_7O_2]^+$, 255.10 (24) $[M–Hg–C_2H_3O]^+$, 299.13 (100) $[M–Hg + H]^+$, 457.07 (2) $[M–C_2H_3O]^+$, 501.10 (27) $[M]^+$. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{18}H_{19}HgO_4$ 501.09848. Found: 501.09841.

2.2.3 | Synthesis of $[4\text{-}(O{=}CH)C_6H_4]_2Hg$ (3)

p-Toluenesulfonic acid (0.200 g, 1.16 mmol) was added to a solution of **2** (2.000 g, 4 mmol) in THF (35 ml)/H_2O (15 ml) mixture. The reaction mixture was stirred overnight resulting in a colorless precipitate. The precipitate was filtered off and washed with small amounts of cold THF and ethanol and then dried to get **3** as a colorless solid. Yield 1.35 g (82%; cf. 90% in Drefahl and Lorenz[36]), m.p. 260–270°C (decomp.) (cf. 262–264°C in Drefahl and Lorenz[36]). **Elemental analysis** calcd. For $C_{14}H_{10}HgO_2$ (MW 410.82): C, 40.93; H, 2.45%. Found: C, 41.29; H, 2.44%. **^{1}H NMR** ($CDCl_3$, 400.13 MHz): δ 7.64 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 8.0 Hz), 7.96 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 8.0 Hz), 10.02 (*s*, 1H, C*H*=O). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.62 MHz): δ 129.45 (*s*, C-3), 136.21 (*s*, C-4), 138.15 (*s*, C-2), 177.61 (*s*, C-1), 192.72 (*s*, *C*H=O). **^{199}Hg{^{1}H} NMR** ($CDCl_3$, 71.61 MHz): δ −813.7 (s). **^{1}H NMR** (DMSO-*d*$_6$, 400.13 MHz): δ 7.82 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 7.9 Hz), 7.87 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 8.0 Hz), 9.96 (*s*, 1H, C*H*=O). **^{13}C{^{1}H} NMR** (DMSO-*d*$_6$, 100.62 MHz): δ 128.22 (*s*, C-3, $^3J_{HgC}$ 102 Hz), 134.95 (*s*, C-4), 138.80 (*s*, C-2, $^2J_{HgC}$ 80 Hz), 179.10 (*s*, C-1), 193.54 (*s*, *C*H=O). **^{199}Hg{^{1}H} NMR** (DMSO-*d*$_6$, 71.61 MHz): δ −908.8. **IR** (KBr pellet, *υ*, cm^{-1}): 3802(w), 3745(w), 3613(w), 3501(w), 1715(s), 1686(vs), 1583(w), 1555(w), 1516(w), 1493(w), 1423(m), 1394(w), 1300(s), 1182(w), 1128 (w), 1067(w), 999(w), 984(w), 935(w), 814(w), 812(w), 754 (m), 687(m), and 565(w). **MS** (ESI+, MeCN), *m/z* (relative intensity, %): 413.04 (100) $[M + H]^+$. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{14}H_{11}HgO_2$ 413.04598. Found: 413.04241.

2.2.4 | General synthesis of $[4\text{-}(RN{=}CH)C_6H_4]_2Hg$

A Schlenk tube of 50 ml was charged with 1 g of 4-Å molecular sieves, which were then activated for 2 h at 250°C and 1 × 10^{-3} mbar. Compound **3** was then introduced under argon atmosphere in the flask and anhydrous CH_2Cl_2 (10 ml) was added. The obtained suspension was stirred for 15 min, and then the corresponding amine (50% excess) was added. The working up of the reaction mixture is described below:

[(*E*)-4-(2′-pyN=CH)C$_6$H$_4$]$_2$Hg (4): from **3** (0.1 g, 0.243 mmol) and 2-pyNH$_2$ (0.069 g, 0.733 mmol). After stirring overnight, a colorless precipitate was obtained and was filtered off, then washed with acetonitrile (3 × 10 ml) and dried in vacuum to obtain the title compound as a colorless solid. Yield 0.113 g (83%), m.p. 190–200°C (decomp.). **Elemental analysis** calcd. For $C_{24}H_{18}HgN_4$ (MW 563.03): C, 51.20; H, 3.22; N, 9.95%. Found: C, 49.09; H, 3.09; N, 8.80%. **^{1}H NMR** ($CDCl_3$, 400.13 MHz): δ 7.19 (*t*, 1H, H-8, NC_5H_4, $^3J_{HH}$ 6.4 Hz), 7.35 (*d*, 1H, H-6, NC_5H_4, $^3J_{HH}$ 7.9 Hz), 7.59 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 7.6 Hz), 7.77 (*t*, 1H, H-7, NC_5H_4, $^3J_{HH}$ 7.7 Hz), 8.08 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 7.6 Hz), 8.51 (*d*, 1H, H-9, NC_5H_4, $^3J_{HH}$ 5.5 Hz), 9.16 (*s*, 1H, C*H*=N). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.62 MHz): δ 120.01 (*s*, C-6), 122.01 (*s*, C-8), 129.39 (*s*, C-3), 135.81 (*s*, C-4), 137.97 (*s*, C-2), 138.28 (*s*, C-7), 149.04 (*s*, C-9), 161.32 (*s*, C-5), 163.18 (*s*, *C*H=N), and 175.11 (*s*, C-1). **^{199}Hg{^{1}H} NMR** ($CDCl_3$, 71.61 MHz): δ −777.9 (s). **IR** (KBr pellet, *υ*, cm^{-1}): 3298(w), 3044(w), 2988(w), 1620(vs), 1582(vs), 1562(vs), 1547(vs), 1391(w), 1360(w), 1310(w), 1258(m), 1198(m), 1175(m), 1140(w), 1092(w), 1015(w), 989(w), 887(m), 816(s), 787(m), 739(m), and 579(m). **MS** (APCI+, MeCN), *m/z* (relative intensity, %): 181.08 (100) $[R]^+$, 565.13 (50) $[M + H]^+$, $[R = 4\text{-}(2'\text{-}pyN{=}CH)C_6H_4]$. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{24}H_{19}HgN_4$ 565.13105. Found: 565.13019.

[(*E*)-4-(4′-pyN=CH)C_6H_4]$_2$Hg (5): from **3** (0.1 g, 0.243 mmol) and 4-pyNH$_2$ (0.069 g, 0.733 mmol). The reaction mixture was stirred for 5 days when a precipitate is formed. Then the solid was filtered off, washed with acetonitrile (2 × 5 ml) and dried in vacuum to obtain **5** as a colorless solid. Yield 0.081 g (59%), m.p. 200–205°C (decomp.). **Elemental analysis** calcd. For $C_{24}H_{18}HgN_4$ (MW 563.03): C, 51.20; H, 3.22; N, 9.95%. Found: C, 49.88; H, 3.23; N, 8.89%. **^{1}H NMR** ($CDCl_3$, 400.13 MHz): δ 7.04 (*d*, 2H, H-6, NC_5H_4, $^3J_{HH}$ 6.1 Hz), 7.60 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 7.9 Hz), 7.99 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 7.9 Hz), 8.39 (*s*, 1H, C*H*=N), 8.59 (*d*, 2H, H-7, NC_5H_4, $^3J_{HH}$ 6.1 Hz). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.62 MHz): δ 115.86 (*s*, C-6), 129.06 (*s*, C-3), 135.27 (*s*, C-4), 138.10 (*s*, C-2), 150.93 (*s*, C-7), 159.17 (*s*, C-5), 163.09 (*s*, *C*H=N), 175.33 (*s*, C-1). **^{199}Hg{^{1}H} NMR** ($CDCl_3$, 71.61 MHz): δ −786.6 (s). **IR** (KBr pellet, *υ*, cm^{-1}): 3749(w), 3674(w), 3613(w), 3587(w), 1690(w), 1626(m), 1580(s), 1543(s), 1522(m), 1491(w), 1420(w), 1394(w), 1198(w), 1175(w), 1082(m), 1001(vs), 885(w), 831(w), 687(w), and 590(w). **MS** (APCI+, MeCN), *m/z* (relative intensity, %): 182.08 (100) $[R + H]^+$, 363.16 (14) $[M{-}Hg + H]^+$, 565.13 (70) $[M + H]^+$, [R = 4-(4′-pyN=CH)C_6H_4]. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{24}H_{19}HgN_4$ 565.13105. Found: 565.12988.

[(*E*)-4-(2′-pyCH$_2$N=CH)C_6H_4]$_2$Hg (6): from **3** (0.100 g, 0.243 mmol) and 2-pyCH$_2$NH$_2$ (0.079 g, 0.731 mmol). The reaction mixture was stirred over night, when a colorless precipitate was obtained. It was filtered off, then washed with acetonitrile (3 × 5 ml) and dried in vacuum to obtain **6** as a colorless solid. Yield 0.126 g (88%), m.p. 205–210°C (decomp.). **Elemental analysis** calcd. For $C_{26}H_{22}HgN_4$ (MW 591.08): C, 52.83; H, 3.75; N, 9.48%. Found: C, 50.75; H, 3.80; N, 8.07%. **^{1}H NMR** ($CDCl_3$, 600.13 MHz): δ 4.98 (*s*, 2H, C*H*$_2$), 7.19 (dd, 1H, H-8, NC_5H_4, $^3J_{HH}$ 7.7, $^3J_{HH}$ 4.7 Hz), 7.45 (*d*, 1H, H-6, NC_5H_4, $^3J_{HH}$ 7.9 Hz), 7.51 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 7.7 Hz), 7.69 (*t*, 1H, H-7, NC_5H_4, $^3J_{HH}$ 7.7 Hz), 7.89 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 7.8 Hz), 8.48 (*s*, 1H, C*H*=N), 8.58 (*d*, 1H, H-9, NC_5H_4, $^3J_{HH}$ 5.2 Hz). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz): δ 67.03 (*s*, *C*H$_2$), 122.17 (*s*, C-8), 122.45 (*s*, C-6), 128.34 (*s*, C-3), 136.00 (*s*, C-4), 136.81 (*s*, C-7), 137.83 (*s*, C-2), 149.45 (*s*, C-9), 159.51 (*s*, C-5), 163.36 (*s*, *C*H=N), 173.76 (*s*, C-1). **^{199}Hg{^{1}H} NMR** ($CDCl_3$, 71.61 MHz): δ −765.3 (s). **IR** (KBr pellet, *υ*, cm^{-1}): 3045 (w), 2889(w), 2895(w), 2870(w), 2839(w), 1691(w), 1634 (vs), 1587(s), 1570(m), 1549(w), 1475(w), 1433(m), 1335 (w), 1302(w), 1263(w), 1215(w), 1096(w), 1051(w), 1045 (w), 1018(m), 995(m), 872(w), 833(m), 818(m), 775(s), 752(w), and 615(w). **MS** (ESI+, MeCN), *m/z* (relative intensity, %): 198.10 (58) $[C_{14}H_{14}O]^+$, 503.10 (100) $[M{-}C_6H_6N + OH]^+$, 593.16 (40) $[M + H]^+$, [R = 4-(2′-pyCH$_2$N=CH)C_6H_4]. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{26}H_{13}HgN_4$ 593.16235. Found: 593.16311.

[(*E*)-4-(4′-pyCH$_2$N=CH)C_6H_4]$_2$Hg (7): from **3** (0.100 g, 0.243 mmol) and 4-pyCH$_2$NH$_2$ (0.079, 0.731 mmol). The reaction mixture was stirred overnight, and then the obtained colorless solution was concentrated to ~5 ml and acetonitrile (20 ml) was added. The resulted solid was filtered off and washed with acetonitrile (2 × 5 ml) and diethyl ether (2 × 5 ml), then dried in vacuum to obtain **7** as a colorless solid. Yield 0.10 g (70%), m.p. 190–200°C (decomp.). **Elemental analysis** calcd. For $C_{26}H_{22}HgN_4$ (MW 591.08): C, 52.83; H, 3.75; N, 9.48%. Found: C, 49.94; H, 3.91; N, 7.15%. **^{1}H NMR** ($CDCl_3$, 600.13 MHz): δ 4.83 (*s*, 2H, C*H*$_2$), 7.30 (*d*, 2H, H-6, NC_5H_4, $^3J_{HH}$ 5.4 Hz), 7.53 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 7.9 Hz), 7.88 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 8.0 Hz), 8.41 (*s*, 1H, C*H*=N), 8.58 (*d*, 2H, H-7, NC_5H_4, $^3J_{HH}$ 5.9 Hz). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz): δ 63.69 (*s*, *C*H$_2$), 122.90 (*s*, C-6), 128.29 (*s*, C-3), 135.65 (*s*, C-4), 137.91 (*s*, C-2), 148.62 (*s*, C-5), 150.03 (*s*, C-7), 163.46 (*s*, *C*H=N), 173.98 (*s*, C-1). **^{199}Hg{^{1}H} NMR** ($CDCl_3$, 71.61 MHz): δ −770.8 (s). **IR** (KBr pellet, *υ*, cm^{-1}): 3022(w), 2874(w), 2839(w), 1641(s), 1599(vs), 1587(s), 1551(m), 1481(w), 1420(m), 1414(s), 1379(w), 1348(w), 1302(w), 1217(w), 1065(w), 1016(w), 993(w), 837(w), 808 (vs), 795(s), 727(w), and 609(w). **MS** (APCI+, MeCN), *m/z* (relative intensity, %): 197.11 (90) $[R + H]^+$, 389.18 (30) $[M{-}Hg{-}H]^+$, 593.16 (76) $[M + H]^+$, [R = 4-(4′-pyCH$_2$N=CH)C_6H_4]. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{26}H_{23}HgN_4$ 593.16235. Found: 593.16322.

2.2.5 | Synthesis of [4-{$(CH_2O)_2CH$}C_6H_4]$_2$ (8)

A mixture of **2** (0.234 g, 0.5 mmol) and a catalytic amount of Pd(OAc)$_2$ (0.010 g, 0.0445 mmol) in 10 ml CH_2Cl_2 was stirred overnight, under protection against light. The obtained dark suspension was mixed with anhydrous $MgSO_4$ and then filtered. The solvent was evaporated from the clear solution providing a colorless solid, which was washed with 3 × 5 ml EtOH, followed by extraction with 2 × 10 ml Et_2O. The solvent was removed in vacuum from the resulting clear solution to provide 0.105 g of **8** as a colorless crystalline product (yield 70% of isolated pure product), m.p. 281–283°C. **^{1}H NMR** ($CDCl_3$, 600.13 MHz): δ 4.01–4.20 [*m*, 4H, (C*H*$_2$O)$_2$CH], 5.87 [*s*, 1H, (CH$_2$O)$_2$C*H*], 7.55 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 8.3 Hz), 7.61 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 8.3 Hz). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz): δ 65.50 [*s*, (*C*H$_2$O)$_2$CH], 103.70 [*s*, (CH$_2$O)$_2$*C*H], 127.03 (*s*, C-3), 127.38 (*s*, C-2), 137.25 (*s*, C-4), 141.86 (*s*, C-1). **IR** (ATR, *υ*, cm^{-1}): 2941 (w), 2871(m), 2351(vs), 2332(vs), 1607(m), 1499(w), 1406(m), 1310(m), 1216(m), 1065(s), 1016(m), 961(m), 930(m), 879(w), 812(vs), 718(w), and 526(w). **MS** (APCI+, MeCN), *m/z* (relative intensity, %): 255.10 (10) $[M{-}C_2H_4O]^+$, 299.13 (100) $[M + H]^+$. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{18}H_{19}O_4$ 299.12779. Found: 299.12722.

2.2.6 | Synthesis of $[4\text{-}(O{=}CH)C_6H_4]_2$ (9)

A mixture of **3** (0.205 g, 0.5 mmol) and a catalytic amount of $Pd(OAc)_2$ (0.010 g, 0.0445 mmol) in 10 ml CH_2Cl_2 was stirred overnight, under protection against light. The resulted dark suspension was mixed with anhydrous $MgSO_4$ and then filtered. The solvent was evaporated from the clear solution providing a colorless solid, which was extracted with 4 × 5 ml EtOH. Then the solvent was removed and the solid was dried in vacuum for 3 h to give 0.062 g of **9** as a colorless microcrystalline product (yield 59% of isolated pure product), m.p. 146–147°C (cf. 146–148°C in Dwivedi et al.[37a], 150–151°C in Kaboudin et al.[37b]). **^{1}H NMR** ($CDCl_3$, 400.13 MHz): δ 7.81 (*d*, 2H, H-2, C_6H_4, $^3J_{HH}$ 8.3 Hz), 8.00 (*d*, 2H, H-3, C_6H_4, $^3J_{HH}$ 8.3 Hz), 10.09 (*s*, 1H, C*H*=O). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.62 MHz): δ 128.19 (*s*, C-2), 130.53 (*s*, C-3), 136.13 (*s*, C-4), 145.72 (*s*, C-1), 191.88 (*s*, *C*H=O). **IR** (ATR, υ, cm^{-1}): 3337(w), 2826(w), 2733(w), 1683(vs), 1596(s), 1556(m), 1384(w), 1308(w), 1207(m), 1165(w), 1003(w), 857(w), 829(w), 809(m), 656(w), 548(w), and 498(w). **MS** (APCI+, MeCN), *m/z* (relative intensity, %): 155.09 (95) $[C_{12}H_{11}]^+$, 211.07 (100) $[M + H]^+$. **HRMS** (APCI+, MeCN): $[M + H]^+$ calcd. For $C_{14}H_{11}O_2$ 211.07536. Found: 211.07495.

2.3 | Crystal structure determination

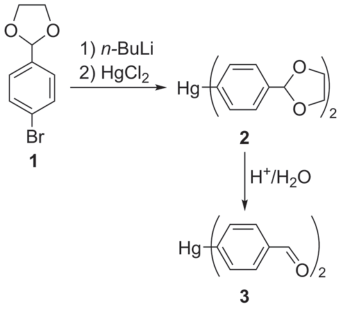
Single crystals of **3**, **5**·$3H_2O$, **6**, **8**, and **9** were obtained by slow evaporation of the solvent from solutions of **3** in acetone, **5** in CH_2Cl_2, **6** in $CHCl_3$, and **8** and **9** in CH_2Cl_2/EtOH (1:1) mixture, in open atmosphere. Table S1 (see Supporting Information) provides a summary of the crystallographic data together with refinement details for compounds. Crystallographic measurements were carried out with Rigaku Oxford-Diffraction XCALIBUR E CCD (**3**, **5**·$3H_2O$, and **6**) or Bruker D8 VENTURE (**8** and **9**) diffractometers equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The unit cell determination and data integration for **3**, **5**·$3H_2O$, and **6** were carried out using the CrysAlis package of Oxford Diffraction,[38] and the structures were solved by direct methods using Olex2 software[39] with the SHELXT structure solution program and refined by full-matrix least squares on F^2 with SHELXL-2015.[40] For structure solving and refinement of **8** and **9**, the Bruker APEX3 Software Package was used.[40] Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms have been placed in fixed, idealized positions accounting for the hybridation of the supporting atoms. The crystal structure of **5**·$3H_2O$ contains large channels hosting severely disordered water molecules. Nevertheless, their positional parameters were successfully determined from difference Fourier maps and refined isotropically with fractional s.o.f. In the structures of **5** and **6**, the molecules lie on a center of inversion. The asymmetric unit of **8** contains two complete molecules and two molecules located on inversion centers, thus the overall value of *Z* is 12. The drawings were created with the Diamond program.[41]

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

Compounds **1–3** were prepared according to Scheme 2. The aryl bromide $4\text{-}[(CH_2O)_2CH]C_6H_4Br$ (**1**) was obtained from 4-bromobenzaldehyde and ethylene glycol using a slightly modified literature method[33]: to avoid the contact with water (i.e., extraction with cold water/ethyl acetate mixture and treatment with brine) and acidic media (i.e., separation by silica gel column chromatography), which might decompose the desired product, the crude material was distilled at reduced pressure. This resulted in considerable (~20%) increased yield in pure **1**, isolated as a viscous colorless oil which solidified on standing; the solid was kept under argon atmosphere at −24°C, to reduce its decomposition. Alternative methods for the preparation and working-up of **1** were also reported.[34,35]

In an earlier work, compound $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2Hg$ (**2**) was obtained in 50% yield through a



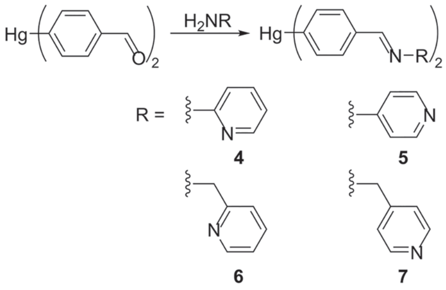
SCHEME 2 Synthesis of compounds **2** and **3**

reaction between the Grignard reagent 4-[$(CH_2O)_2CH$]C_6H_4MgBr and $HgBr_2$, in THF, at r.t., but no spectroscopic characterization was reported.[36] We have carried out the preparation of the same compound **2** using the organolithium reagent 4-[$(CH_2O)_2CH$]C_6H_4Li and $HgCl_2$, in anhydrous THF, at −78°C. After working up the crude reaction mixture, **2** was isolated in excellent yield (90%). The deprotection of **2** was achieved using a standard procedure (i.e., hydrolysis with THF/H_2O mixture, in presence of p-toluenesulfonic acid, at r.t.) resulting in a high yield of pure [4-(O=CH)C_6H_4]$_2$Hg (**3**), a useful intermediate in the synthesis of the target [4-(RN=CH)C_6H_4]$_2$Hg compounds.

Imines of type [(*E*)-4-(RN=C)C_6H_4]$_2$Hg [R = 2′-py (**4**), 4′-py (**5**), 2′-pyCH_2 (**6**), 4′-pyCH_2 (**7**)] were obtained in good to excellent yield (60%–90%) by reacting **3** with an excess of the corresponding amine, in dry and acid free CH_2Cl_2, at r.t. (Scheme 3). All four compounds **4–7** were isolated as colorless solids. Satisfactory analytical results and HRMS data were obtained for all these organomercury(II) compounds. Compounds **4–6** exhibit good stability in the solid state, but slowly decompose in solution, in non-anhydrous solvents, to starting material **3** and the corresponding amine, as was easily observed by NMR studies. Compound **7** was found to decompose after few days even in solid state, when unidentified yellow oily products were formed.

3.2 | Spectroscopic characterization

Compounds **2–7** were investigated by mass spectrometry, IR, and NMR spectroscopy. In the APCI+ or ESI+ mass spectra (see Supporting Information) the protonated molecular ions $[M + H]^+$ was observed for all the compounds. In the IR spectra of **2** and **3**, typical medium to very strong bands were assigned to the acetal moiety (959, 939 cm^{-1}) and C=O stretching vibration (1686 cm^{-1}).[42] For compounds **4–7**, a strong band in the region 1620–1641 cm^{-1} was assigned to the stretching vibration of the C=N double bond as typical for compounds containing Schiff-base ligands.[42]



SCHEME 3 Synthesis of compounds **4–7**

The solution characterization of compounds **2–7** was achieved by multinuclear (^1H, $^{13}C\{^1H\}$ and $^{199}Hg\{^1H\}$) NMR spectroscopy, the spectra being recorded in $CDCl_3$ at r.t.. Owing to the low solubility in $CDCl_3$, the spectra for compound **3** were also recorded in DMSO-d_6, without significant changes in terms of chemical shifts of the observed resonance signals. The $^{199}Hg\{^1H\}$ NMR spectra for compounds **2–7** exhibit one singlet resonance, thus indicating the presence of only one organomercury(II) species in $CDCl_3$ solution. The δ_{Hg} chemical shifts range from −751.9 ppm for **2** to −813.7 ppm for **3**, with intermediate values for the imines **4–7**. The ^1H and $^{13}C\{^1H\}$ NMR spectra show in all cases only one set of expected resonances both in the aliphatic and the aromatic regions, thus being consistent with the equivalence of the organic groups attached to the same mercury atom. An indicative ^1H chemical shift for compounds **2–7** is that of the resonance signal assigned to the hydrogen of the C*H* group placed in position 4 of the aromatic substituent. Thus, the change in this chemical shift from δ 5.82 ppm for **2** [$(CH_2O)_2CH$] to δ 10.02 ppm for **3** (C*H*=O) is useful to follow the deprotection of the carbonyl function in **2**, while the shift of the corresponding resonance to δ 9.16 ppm for **4**, δ 8.39 ppm for **5**, δ 8.48 ppm for **6**, and δ 8.41 ppm for **7** (C*H*=N) can be used for easy monitorization by ^1H NMR spectroscopy of the conversion of the aldehyde function to the imine one. A similar significant shift of the singlet resonance for the carbon of the same *C*H group was observed in the ^{13}C NMR spectra of compounds **2–7**, that is, δ 103.80 ppm for **2** [$(CH_2O)_2CH$], 192.72 ppm for **3** (*C*H=O), and 163.18 ppm for **4**, 163.09 ppm for **5**, 163.36 ppm for **6**, or 163.46 ppm for **7** (*C*H=N), respectively.

3.3 | Solid-state structures

The molecular structures of the diorganomercury(II) compounds **3**, **5**, and **6** were established by single-crystal X-ray diffraction. The ORTEP-like representations of the molecular structure of these compounds, with the atom numbering scheme, are depicted in Figures 1–3. Selected interatomic distances and bond angles, as well as dihedral angles, are listed in Tables 1 and 2.

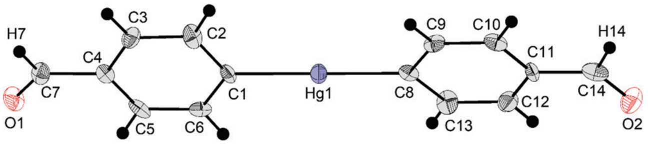


FIGURE 1 Molecular structure of [4-(O=CH)C_6H_4]$_2$Hg (**3**). Thermal ellipsoids are drawn at 40% probability

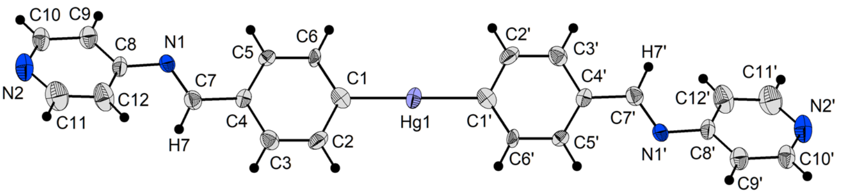


FIGURE 2 Molecular structure of [(*E*)-4-(4′-pyN=CH)C_6H_4]$_2$Hg·3H_2O (**5**·3H_2O). Thermal ellipsoids are drawn at 40% probability (water molecules are not shown)

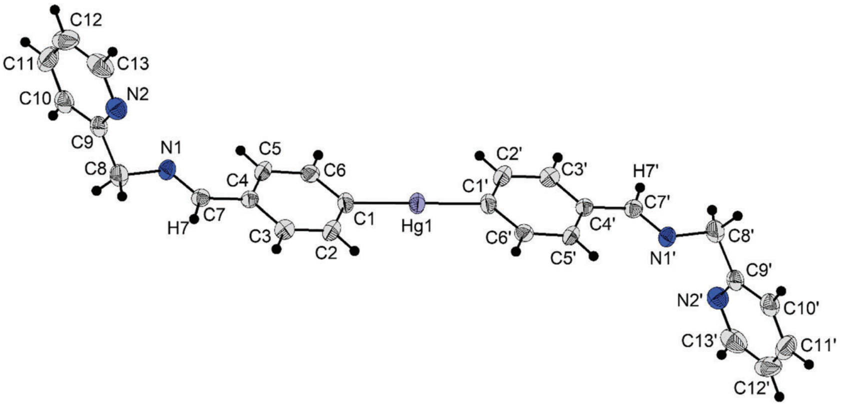


FIGURE 3 Molecular structure of [(E)-4-(2′-pyCH2N=CH)C6H4]2Hg] (**6**). Thermal ellipsoids are drawn at 40% probability

TABLE 1 Selected interatomic distances (Å) and angles (°) in compound **3**

Hg1–C1	2.073(8)	C1–Hg1–C8	178.3(3)
Hg1–C8	2.066(8)		
		C4–C7–O1	124.9(9)
C7–O1	1.187(11)	C4–C7–H7	118
C14–O2	1.217(12)	O1–C7–H7	118
		C11–C14–O2	126.3(9)
		C11–C14–H14	117
		O2–C14–H14	117
Dihedral angles			
{C1–C6}/{C8–C13}	9.4	{C1–C6}/{C7,H7,O1}	7.1
{C4,C7,H7,O1}/{C11,C14,H14,O2}	5.0	{C8–C13}/{C14,H14,O2}	7.2

Common structural features for these organomercury compounds are (i) the lengths of the covalent Hg–C bonds, which fit in the reported range (2.06–2.15 Å) for diarylmercury compound[43]; (ii) the expected linear arrangement of the Hg–C bonds within a molecule, that is, C–Hg–C 178.3(3)° for **3**, and 180° for **5** and **6**, respectively; and (iii) the isolation as *E*-imino isomers of compounds **5** and **6**, as consequence of the existence of the inversion centers. In the molecule of **3**, the two aromatic rings attached to a mercury atom are slightly twisted to each other (dihedral angle {C1–C6}/{C8–C13} of 9.4°), as are the carbonyl (O=CH–C) groups (dihedral angle {C4,C7, H7,O1}/{C11,C14,H14,O2} of 5.0°). By contrast, both corresponding systems, that is, aromatic rings attached to mercury atom and the imino (C–N=CH–C) groups, are co-planar within a molecular unit of **5** and **6** (see Tables 1 and 2 for the corresponding dihedral angles). The pyridyl rings are twisted (33.0° and 77.5° for **5** and **6**, respectively) with respect to the planar Ar_2Hg skeleton.

A major structural difference that should be noted is the relative orientation of the C=E (E = O, N) double bonds with respect to the *quasi* planar arrangement of the aromatic rings attached to mercury: they are *trans* in the molecule of **3**, but *cis* in those of the di(imino) arilmercury compounds **5** and **6**.

A closer check of the crystal structures of these diorganomercury(II) compounds revealed different supramolecular architectures. For both compounds **3** and **5**, the planar (or almost planar) molecules are stacked to allow the formation of chain polymers through two Hg⋯π interactions per metal atom (with almost orthogonal Hg⋯$Ar_{centroid}$ vectors as evaluated through the γ angle between the normal to the aromatic ring and the line defined by the metal atom and $Ar_{centroid}$): Hg(1)⋯

TABLE 2 Selected interatomic distances (Å) and angles (°) in compounds **5**·$3H_2O$ and **6**

5·$3H_2O$[a]		**6**[b]	
Hg1–C1	2.100(11)	Hg1–C1	2.090(5)
N1–C7	1.27(2)	N1–C7	1.262(6)
N1–C8	1.403(17)	N1–C8	1.475(7)
N2–C10	1.34(2)	N2–C9	1.338(7)
N2–C11	1.36(2)	N2–C13	1.302(9)
C1–Hg1–C1′	180	C1–Hg1–C1′	180
C4–C7–N1	122.9(13)	C4–C7–N1	124.3(5)
C4–C7–H7	119	C4–C7–H7	118
N1–C7–H7	118	N1–C7–H7	118
C7–N1–C8	120.3(12)	C7–N1–C8	117.0(5)
C10–N2–C11	114.8(14)	C9–N2–C13	116.1(5)
Dihedral angles			
{C1-C6}/{C1′–C6′}	0.0	{C1–C6}/{C1′–C6′}	0.0
{C1–C6}/{C7,H7,N1,C8}	6.8	{C1–C6}/{C7,H7,N1,C8}	4.7
{C1–C6}/{C8-C12,N2}	33.0	{C1–C6}/{C9–C13,N2}	77.5
{C7,H7,N1,C8}/{C8–C12,N2}	36.6	{C7,H7,N1,C8}/{C9–C13,N2}	80.8
{C4,C7,H7,N1,C8}/{C4′,C7′,H7′,N1′,C8′}	0.0	{C4,C7,H7,N1,C8}/{C4′,C7′,H7′,N1′,C8′}	0.0
{C8–C12,N2}/{C8′–C12′,N2′}	0.0	{C9–C13,N2}/{C9′–C13′,N2′}	0.0

[a] Symmetry equivalent atoms (*1–x, –3–y, 3–z*) are given by "prime."
[b] Symmetry equivalent atoms (*–x, –y, –z*) are given by "prime."

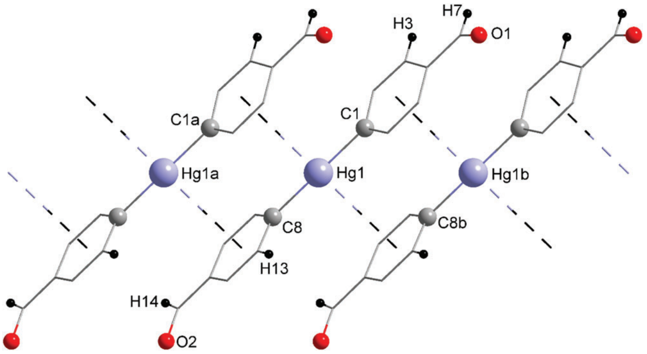


FIGURE 4 View along *c* axis of the supramolecular chain polymer association build through Hg···π interactions in the crystal of $[4\text{-}(O{=}CH)C_6H_4]_2Hg$ (**3**) (only hydrogen atoms of the carbonyl groups and those involved in intermolecular interactions are shown) [symmetry equivalent atoms (*–1+x, y, z*) and (*1+x, y, z*) are given by "a" and "b"]

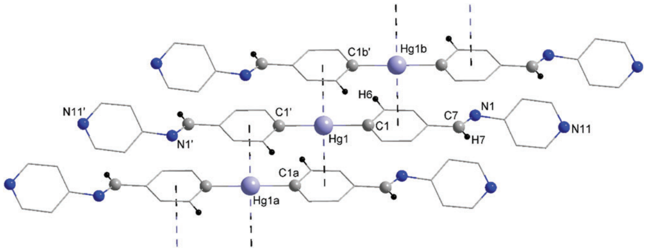


FIGURE 5 View of the supramolecular chain polymer association build through Hg···π interactions in the crystal of $[(E)\text{-}4\text{-}(4'\text{-}pyN{=}CH)C_6H_4]_2Hg{\cdot}3H_2O$ (**5**·$3H_2O$) (only hydrogen atoms of the imino groups and those involved in intermolecular interactions are shown; due to disorder, water molecules are not shown) [symmetry equivalent atoms (*1–x, –3–y, 3–z*), (*x,–1+y, z*), (*x, 1+y, z*) and (*1–x, –2–y, 3–z*) are given by "prime," "a," "b," and "b prime"]

$Ar_{centroid}$\{C(1a)–C(6a)\} 3.48 Å ($\gamma = 5.0°$) and Hg(1)···$Ar_{centroid}$\{C(8b)-C(13b)\} 3.50 Å ($\gamma = 14.1°$) for **3** (Figure 4), and Hg(1)···$Ar_{centroid}$\{C(1a)-C(6a)\} 3.43 Å ($\gamma = 2.7°$) for **5** (Figure 5). Although somewhat longer than other reported intra- or intermolecular Hg···π interactions in organomercury(II) compounds,[43–45] these Hg···$Ar_{centroid}$ distances in the crystals of **3** and **5** are shorter than the sum of the van der Waals radii of mercury (recently reported as 2.45 Å)[46] and that estimated for an arene ring, that is, 1.9 Å.[47]

The resulting chains of molecules of **3** are connected through Hg···O interactions [Hg(1)···O(1b") 3.01 Å, *c.f.* Σr_{vdW} (Hg,O) 3.95 Å[46]] into a 3-D network supported by further C–H_{aryl}···O contacts [range 2.57–2.61 Å, cf. Σr_{vdW}(O,H) 2.70 Å[46]; see Figures S44 and S45]. The C_2HgO core has a slightly distorted T-shape [C(1)-Hg

(1)···O(1b″) 92.8°; C(8)-Hg(1)···O(1b″) 88.9°], while the overall $C_2HgO(Ar_{centroid})_2$ core is distorted square pyramidal.

By contrast, in the crystal of **5** there are no further interactions between heavy atoms, but the chain polymers based on Hg···π interactions are connected into a layer through $C–H_{aryl}···N$ contacts [$C(6)–H(6)_{aryl}···N$ (1A) 2.78 Å, cf. $\Sigma r_{vdW}(N,H)$ 2.86 Å[46]; see Figures S46 and S47].

No Hg···π interactions or other interactions between heavy atoms are present in the crystal of **6**, but a network of $C–H_{imino}···\pi$ interactions [$C(7)–H(7)_{imino}···Ar_{centroid}$ {C(9a)–C(13a), N(2a)} 2.90 Å, $\gamma = 3.9°$; cf. $H···Ar_{centroid}$ contacts shorter than 3.1 Å and an angle γ between the normal to the aromatic ring and the line defined by the H atom and $Ar_{centroid}$ smaller than 30°][48] connects the molecules into a layer (Figure 6). Further, $C–H_{aryl}···\pi$ and $C–H_{Py}···\pi$ interactions between layers result in a 3-D supramolecular architecture (see Figures S48–S50).

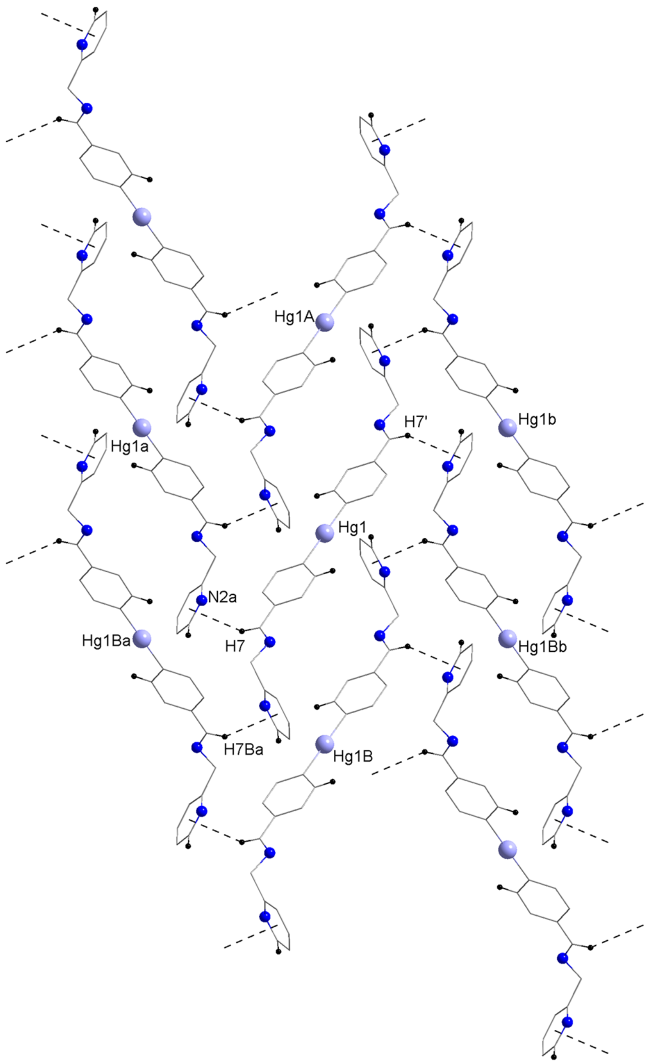
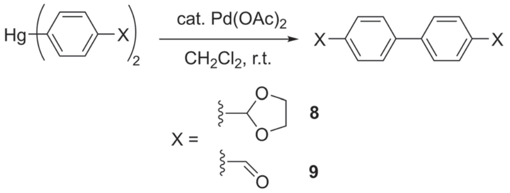


FIGURE 6 View along *c* axis of the supramolecular layer build through $C–H_{imino}···\pi$ interactions in the crystal of $[(E)\text{-}4\text{-}(2'\text{-}pyCH_2N{=}CH)C_6H_4]_2Hg$ (**6**) (only hydrogen atoms of the imino groups and those involved in intermolecular interactions are shown) [symmetry equivalent atoms (*−x, −y, −z*), (*x, 1+y, z*), (*x, −1+y, z*), (*−1−x, 0.5+y, 0.5−z*), (*1−x, 0.5 y, −0.5−z*), (*−1−x, −0.5+y, 0.5−z*) and (*1−x, −0.5+y, −0.5−z*) are given by "prime," "A," "B," "a," "b," "Ba," and "Bb")

3.4 | Investigation of transmetallation versus homocoupling

As pointed out in Section 1, the imine derivatives **4–7** might be useful as divergent, linear organometallic tectons in crystal engineering of coordination polymers, as was already proved for di(4-pyridyl)mercury(II).[28] On the other hand, the use of organomercury(II) is well known as transmetallating agents of organic substituents to either main group or transition metals,[14–18] for example, several homoleptic Ar_2Hg,[49] including compounds with *ortho*-substituted aromatic groups,[14b,c,16c] were reported as source for aryl substituents in the synthesis of organopalladium(II) compounds. This potential reactivity should be also taken into account when synthesis of coordination polymers is designed.

Therefore, we have performed reactions between $Pd(OAc)_2$ and several diarylmercury(II) compounds reported in this work, in 1:1 molar ratio, in order to check the potential use of the title diorganomercury compounds as linkers between Pd-containing nodes or as transmetallating agents. The reaction carried out with the imino derivative **6** produced a complex reaction mixture, including some black material suggesting decomposition to naked metal, and its work-up did not resulted in pure compounds. When the reaction was carried using the compounds **2** or **3**, the NMR data recorded on the crude reaction mixture suggested that instead of a coordination polymer or a transmetallation of the aryl substituent from mercury to palladium, a C–C coupling reaction occurred to produce the homocoupling products $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2$ (**8**) and $[4\text{-}(O{=}CH)C_6H_4]_2$ (**9**) (Scheme 4). In fact, such a reaction pathway should have been also anticipated taking into account previous reports regarding the use of some arylmercury compounds as starting materials for synthesis of pure organic



SCHEME 4 Synthesis of compounds **8** and **9** via homocoupling reactions

compounds, in the presence of catalytic amounts of palladium salts.[50] Indeed, treatment of compounds **2** and **3** with a catalytic amount of $Pd(OAc)_2$ allowed isolation in good yields of compounds **8** and **9**.

In fact, treatment of compounds **2** and **3** with a catalytic amount of $Pd(OAc)_2$ allowed isolation in good yields of **8** and **9** as colorless, crystalline solids. Their identity was confirmed by multinuclear NMR and MS studies. While our work was under preparation a report was published[51] on unexpected boronic acid homocoupling products, including compounds **8** and **9**, formed during Suzuki–Miyaura cross-coupling reactions of 2-bromo-1,3-$(CF_3)_2C_6H_3Br$ with various arylboronic acids, using Pd complexes. Our spectroscopic data fit very well with those reported in this recent article. It should be noted here that **8** was prepared in good yield (74%) by nickel-catalyzed Ullmann coupling of 4-$[(CH_2O)_2CH]C_6H_4Br$, but no spectroscopic characterization was provided.[52] For compound **9**, there were previously reported different synthetic procedures based on (i) $[4\text{-}(O{=}CH)C_6H_4]B(OH)_2$ via a Suzuki cross-homocoupling reaction mediated by $Pd(OAc)_2$,[37a,53a] or $CuSO_4$[37b]; (ii) 4-$[(CH_2O)_2CH]C_6H_4I$ via an Ullmann cross-homocoupling reaction using palladium on activated charcoal as catalyst,[53b] or Suzuki-coupling reaction between 4-$[(CH_2O)_2CH]C_6H_4Br$ and $[4\text{-}(O{=}CH)C_6H_4]B(OH)_2$ in the presence of $Pd(PPh_3)_4$.[53c]

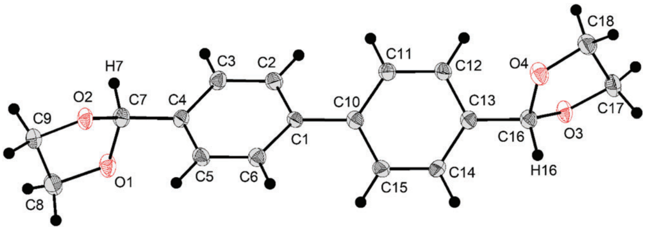


FIGURE 7 Molecular structure of $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2$ (**8a**). Thermal ellipsoids are drawn at 40% probability

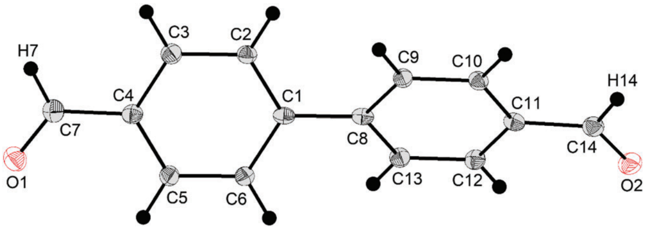


FIGURE 8 Molecular structure of $[4\text{-}(O{=}CH)C_6H_4]_2$ (**9**). Thermal ellipsoids are drawn at 40% probability

The molecular structures of both compounds **8** and **9** were established by single-crystal X-ray diffraction. Their molecular structures as ORTEP-like representations, with the atom numbering scheme, are depicted in Figures 7 and 8. Selected interatomic distances and bond angles are listed in Table 3.

The crystal of **8** contains four independent, very similar, molecules noted as **8a** (Figure 7) to **8d**. The molecules

TABLE 3 Selected interatomic distances (Å) and angles (°) in compounds **8** and **9**

8a[a]		**9**	
C1–C10	1.486(4)	C1–C8	1.463(3)
C7–O1	1.430(3)	C7–O1	1.222(2)
C7–O2	1.416(3)		
C16–O3	1.416(3)	C14–O2	1.223(2)
C16–O4	1.431(3)		
O1–C7–O2	105.5(2)		
C4–C7–O1	111.2(2)	C4–C7–O1	124.48(19)
C4–C7–O2	111.2(2)		
C4–C7–H7	110	C4–C7–H7	118
O3–C16–O4	106.2(2)		
C13–C16–O3	111.1(2)	C11–C14–O2	124.35(19)
C13–C16–O4	111.1(2)		
C13–C16–H16	109	C11–C14–H14	118
Dihedral angles			
{C1–C6}/{C10–C15}	27.1	{C1–C6}/{C8–C13}	32.3
{C1–C6}/{C7,O1,O2}	84.8	{C1–C6}/{C7,H7,O1}	5.0
{C10–C15}/{C16,O3,O4}	82.3	{C8–C13}/{C14,H14,O2}	3.7
{C7,O1,O2}/{C16,O3,O4}	3.5	{C7,H7,O1}/{C14,H14,O2}	26.2

[a] The molecular parameters are given for molecule **8a** of the four independent molecules from the unit cell.

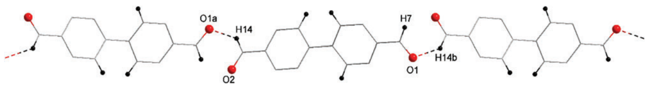


FIGURE 9 View along *a* axis of the supramolecular chain polymer association build through O···$H_{carbonyl}$ interactions in the crystal of $[4\text{-}(O{=}CH)C_6H_4]_2$ (**9**) (only hydrogen atoms involved in intermolecular interactions are shown) [symmetry equivalent atoms (*0.5–x, 1–y, 0.5+z*) and (*0.5–x, 1–y, −0.5+z*) are given by "a" and "b"]

labeling is consistent to the atom labels. Two molecules in the asymmetric unit (**8a** and **8c**) are complete, whereas the other two (**8b** and **8d**) lie on inversion centers. The molecular parameters in Table 3 refer only to molecule **8a**.

In the molecules located on the inversion centers, the torsion angles between the aryl groups are 180°, in contrast to those complete (**8a**: 27.1°, **8c**: 29.4°). The C–C bond lengths between the two aryl groups are slightly longer in the residues with planar diaryl unit (**8b:** 1.496 (3), and **8d**: 1.497(4) Å), than in **8a** or **8d** (1.486(4), and 1.473(4) Å, respectively).

In the crystal of **8**, the four independent molecules are connected through a network of C–H···O (range 2.31–2.51 Å, cf. Σr_{vdW}(O,H) 2.70 Å[46]) and C–H···π (range 2.55–2.93 Å, cf. H···$Ar_{centroid}$ contacts shorter than 3.1 Å[48]) interactions into a complex 3-D supramolecular architecture (for details, see Figure S51).

In the crystal of **9**, the molecules are associated through C–$H_{carbonyl}$···O hydrogen bonds [C(14b)–H $(14b)_{carbonyl}$···O(1) 2.44 Å] into chain polymers (Figure 9), which are connected into a 2-D layer through additional inter-chains C–$H_{carbonyl}$···O interactions [C(7a″)–H $(7a'')_{carbonyl}$···O(2) 2.51 Å] (see Figure S52). Further, weaker inter-layers C–H_{aryl}···O contacts (range 2.55–2.60 Å) resulted in a 3-D supramolecular association (for details, see Figure S53).

It is worth to mention here the recent report of the crystal structure of a supramolecular complex which consists of an octacarbene-based tetranuclear silver(I) metallacage and a molecule of **9** located outside of the cavity and connected to it through multiple C–H···O interactions.[54]

4 | CONCLUSIONS

We report an improved synthetic protocol, with higher yield than previously reported, for $[4\text{-}(O{=}CH)C_6H_4]_2Hg$ (**3**) using $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2Hg$ (**2**) as staring material. Compound **3** was used for the synthesis in good to excellent yields, in mild conditions, for the series of organometallic derivatives with imine functional groups $[(E)\text{-}4\text{-}(RN{=}CH)C_6H_4]_2Hg$ [R = 2′-py (**4**), 4′-py (**5**), 2′-pyCH$_2$ (**6**), 4′-pyCH$_2$ (**7**)]. Compounds **4–7** might be used as divergent organometallic tectons in crystal engineering of coordination polymers as previously shown.

Oxidative demercuration reactions of **2** and **3** in presence of catalytic amounts of palladium(II) acetate affords $[4\text{-}\{(CH_2O)_2CH\}C_6H_4]_2$ (**8**) and $[4\text{-}(O{=}CH)C_6H_4]_2$ (**9**), respectively. This approach represents an alternative synthetic pathway for the two useful organic derivatives.

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AUTHOR CONTRIBUTIONS

Levente Kiss: Investigation; methodology. **Alexandra Pop:** Data curation; formal analysis. **Shova Sergiu:** Data curation; formal analysis. **Ciprian Rat:** Project administration; visualization. **Cristian Silvestru:** Project administration; supervision.

DATA AVAILABILITY STATEMENT

Data are available upon request from the authors. CCDC-2027584 for **3**, 2027585 for **5**·3H_2O, 2027586 for **6**, 2027587 for **8** and 2027588 for **9** contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (via www.ccdc.cam.ac.uk/data_request/cif). Represented in the supporting information are the ^{1}H, $^{13}C\{^{1}H\}$ and $^{199}Hg\{^{1}H\}$ (where applicable) NMR spectra of compounds **1–9** (Figures S1–S27), the high-resolution mass spectra (Figures S28–S35), and the IR spectra (Figures S36–S43) of compounds **2–9**.

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