Supporting Information

Pd and Pt Catalyst Poisoning in the Study of Reaction Mechanisms: What Does the Mercury Test Mean for Catalysis?

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S1. General Information

**Caution:** Mercury and its compounds are highly toxic. An efficient hood must be used when handling these compounds. Residues should be utilized according to local regulations for mercury wastes.

1,4-Dioxane and THF were dried over metallic sodium and distilled twice under an argon and stored under 4 Å molecular sieves. Other solvents and all reagents were obtained from commercial sources and used without further purification, unless stated otherwise. Compounds 1a-d, bis(1,3-dimethyl-1,3-dihydro-2H-benzimidazol-2-ylidene)diodopalladium (2a), and (1,3-dimethyl-1,3-dihydro-2H-benzimidazol-2-ylidene)(diiodo)(pyridine) platinum (3) were synthesized as described elsewhere. Unless otherwise noted, all experiments with metallic Hg were conducted under an argon atmosphere via standard Schlenk techniques.

¹H and ¹³C{¹H} NMR spectra were recorded using a Bruker DRX 500 instrument at 500 MHz and 125 MHz, respectively, or a Bruker AVANCE II 600 instrument at 600 MHz and 150 MHz, correspondingly. ¹H NMR chemical shifts (δ) are given in ppm relative to the resonance shifts of solvents (CDCl₃, 7.26 ppm; THF-d₈, 3.58 ppm; DMSO-d₆, 2.50 ppm). Coupling constants (J) are given in Hz. Multiplicities of signals are described as follows: s = singlet, d = doublet, t = triplet, m = multiplet. ¹³C{¹H} chemical shifts (δ) are reported in ppm relative to the resonance shifts of solvents (CDCl₃, 77.16 ppm; DMSO-d₆, 39.52 ppm).

Electrospray ionization mass spectra (ESI-MS) were obtained using a Bruker maXis Q-TOF instrument equipped with an electrospray ionization (ESI) ion source. The measurements were acquired in positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: −500 V) with a scan range of m/z 50 – 1500. External calibration of the mass spectrometer was achieved using a low-concentration tuning mix solution (Agilent Technologies). Direct syringe injection was used for the analyzed solutions at flow rate 3 μL min⁻¹. Nitrogen was applied as the nebulizer gas (0.4 bar) and dry gas (4.0 L min⁻¹).

GC-MS spectra were collected using an Agilent 7890A GC system, equipped with an Agilent 5975C mass-selective detector (electron impact, 70 eV) and a HP-5MS column (30 m × 0.25 mm × 0.25 μm film) using He as carrier gas at a flow rate of 0.6 mL/min for 0.5 min, then 1 mL/min per min to 1.7 mL/min for 0 min. The temperature program for all GC-MS measurements: initial temperature 40 °C for 1 min, then 60 °C/min to 280 °C for 5 min. Obtained GC-MS spectra were compared with authentic samples and spectra in the NIST mass spectral library. Retention times of analyzed compounds were 4.74 min for (E)-n-butyl cinnamate, 3.24 min for iodobenzene, 5.12 min for 4-acetylbiphenyl, 4.03 min for 1-(4-bromophenyl)ethanone, 3.67 min for naphthalene (an internal standard) and 4.54 min for hexadecane (an internal standard).

Energy Dispersive X-Ray Fluorescence analyses (EDXRF) of metal concentrations were performed using an ARL Quant’X (Thermo Scientific) EDXRF spectrometer (Cu anode X-ray tube; excitation at 50 kV and 0.6 mA; Si/Li dispersive detector in a coplanar, right angle geometry to the X-ray source) with appropriate filter for 180 s acquisition period (50% dead time).

HPLC analyses were performed using an Agilent 1260 Infinity LC system (reversed-phase Zorbax SB-C18 column 50×4.6 mm thermostated at 35 °C; detection wavelength 280 nm; a flow rate of gradient elution was 1 mL/min). The mobile phase A contained 10 % aqueous MeCN, the phase B was neat MeCN, the phase C was 0.02 M NaClO₄ aqueous solution. The gradient modes were as follows: ramp over 3 min from 80% A and 20% C to 80% B and 20% C; then hold for 5 min.

UV-spectra were recorded using a Shimadzu UV-1800 spectrometer.

FE-SEM studies were performed using a Hitachi SU8000 field-emission scanning electron microscope. The measurements were carried out with accelerating voltage 2–10 kV and a working distance of 2.5–9 mm. Before measurements the samples were placed on a 25 mm aluminum specimen stub and fixed by conductive carbon tape. Images were obtained in secondary electron mode at 10 kV
accelerating voltage. SEM/EDS studies were carried out using Oxford Instruments X-max 80 EDS system at 20 kV accelerating voltage and at working distance 15 mm. Powder X-ray diffraction (XRD) experiments were performed using a Thermo Scientific ARL XTRA diffractometer employing CuKα (λ = 0.154056 nm) radiation source operating at 40 kV and 40 mA. The scanning speed was 1.2°/min in 2θ range from 10° to 80° using a step size of 0.02°. Thin-layer chromatography (TLC) was performed using Sorbfil (50×75 mm) precoated sheets. Column chromatography was performed on Merck silica gel 60 (230–400 mesh). Glassware was dried at 120 °C in an oven for at least 3 h.
S2. Synthetic Procedures

Reaction of \( \text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 \) with metallic mercury.

\[
\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 + \text{Hg}^0 \xrightarrow{\text{THF} \quad 50 \ ^\circ\text{C}} \text{dba} + \text{Pd/Hg}
\]

dba = dibenzylideneacetonate

A solution of \( \text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 \) (31.1 mg, 0.03 mmol) in degassed dry THF (6 mL) and metallic mercury (6 g, 30 mmol) were stirred in a sealed tube at 50 °C within 2 h then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~5 mm). The filtrate was evaporated to dryness by a rotary evaporator. The residue obtained was recrystallized from ethanol and dried at 20 °C to give 17 mg (81% yield) of pure dba. Mp 112 °C (lit. \(^4\) mp 110–112 °C). \(^1\)H NMR (500 MHz, THF-\(d_8\)): \( \delta \) 7.21 (d, \( J = 16.0 \) Hz, 2H, \( 2\text{CH} \)), 7.37–7.41 (m, 6H, Ar), 7.70–7.66 (m, 4H), 7.73 (d, \( J = 16.0 \) Hz, 2H, \( 2\text{CH} \)).

Reaction of \( \text{Pt}_2(\text{dba})_3 \cdot \text{CHCl}_3 \) with metallic mercury.

\[
\text{Pt}_2(\text{dba})_3 \cdot \text{CHCl}_3 + \text{Hg}^0 \xrightarrow{\text{THF} \quad 50 \ ^\circ\text{C}} \text{dba} + \text{Pt/Hg}
\]

dba = dibenzylideneacetonate

A solution of \( \text{Pt}_2(\text{dba})_3 \cdot \text{CHCl}_3 \) (36.4 mg, 0.03 mmol) in degassed dry THF (6 mL) and metallic mercury (6 g, 30 mmol) were stirred in a sealed tube at 50 °C within 5 h then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~5 mm). The filtrate was evaporated to dryness by a rotary evaporator. The residue obtained was recrystallized from ethanol and dried at 20 °C to give 18 mg (86% yield) of pure dba. NMR, GC-MS and mp of the obtained substance were identical with the authentic sample of dba.

Reaction of \( \text{Pd}[\text{PPh}_3]_4 \) with metallic mercury.

\[
\left[ \begin{array}{c} \text{Ph} \\ \text{Ph} \\ \text{Ph} \\ \text{Ph} \end{array} \right] \text{Pd}^0 + \text{Hg}^0 \xrightarrow{\text{THF} \quad 50 \ ^\circ\text{C}} \left[ \begin{array}{c} \text{Ph} \\ \text{Ph} \\ \text{Ph} \\ \text{Ph} \end{array} \right] \text{Pd}^0 + \text{Pd/Hg}
\]

A solution of \( \text{Pd}[\text{PPh}_3]_4 \) (34.7 mg, 0.03 mmol) in degassed dry THF (6 mL) and metallic mercury (6 g, 30 mmol) were stirred in a sealed tube at 50 °C under magnetic stirring within 5 h. Then the suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~5 mm). The filtrate was evaporated to dryness by a rotary evaporator. The residue obtained was recrystallized from MeOH and dried at 20 °C to give 29.1 mg (93% yield) of pure PPh\(_3\), mp 80 °C (lit.\(^5\) mp 79–81 °C). \(^1\)H NMR (500 MHz, THF-\(d_8\)): \( \delta \) 7.25–7.32 (m, 15H, Ar). GC-MS data were identical with the authentic sample of PPh\(_3\).
Reaction of Pt[PPh$_3$]$_4$ with metallic mercury.

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\begin{array}{c}
\text{Pt}
\end{array}
+ \begin{array}{c}
\text{Hg}
\end{array}
\xrightarrow{\text{THF}, 50^\circ\text{C}}
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\begin{array}{c}
\text{Pt}
\end{array}
+ \begin{array}{c}
\text{Pt/Hg}
\end{array}
\]

A solution of Pt[PPh$_3$]$_4$ (37.3 mg, 0.03 mmol) in degassed dry THF (6 mL) and metallic mercury (6 g, 30 mmol) were stirred in a sealed tube at 50 °C under magnetic stirring within 5 h. Then the suspension was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~5 mm). The filtrate was evaporated to dryness by a rotary evaporator. The residue obtained was recrystallized from MeOH and dried at 20 °C to give 28 mg (89%) of pure PPh$_3$. NMR, GC-MS and mp of the obtained substance were identical with the authentic sample of PPh$_3$.

Reaction of PdCl$_2$Py$_2$ with metallic mercury.

\[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{Pd}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
+ \begin{array}{c}
\text{Hg}
\end{array}
\xrightarrow{\text{THF}, 50^\circ\text{C}}
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{Hg}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
+ \begin{array}{c}
\text{Pd/Hg}
\end{array}
\]

A mixture of PdPy$_2$Cl$_2$ (10.1 mg, 0.03 mmol), metallic mercury (6 g, 30 mmol) and degassed dry THF (6 mL) was heated in a sealed tube at 50 °C under magnetic stirring within 5 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot THF (10 mL). The filtrate and washings were combined and evaporated to dryness. The obtained residue was recrystallized from methanol and dried in vacuo to give 9 mg (70% yield) of HgPy$_2$Cl$_2$, mp 182-184 °C. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.51–7.54 (m, 4H, Ar), 7.91-7.95 (m, 2H, Ar), 8.61-8.62 (m, 4H, Ar). $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ 124.6, 137.9, 148.6. Found: C, 27.91; H, 2.39; N, 6.61. C$_{10}$H$_{10}$Cl$_2$HgN$_2$. Calculated: C, 27.95; H, 2.35; N, 6.52.

Reaction of PtCl$_2$Py$_2$ with metallic mercury.

\[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{Pt}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
+ \begin{array}{c}
\text{Hg}
\end{array}
\xrightarrow{\text{THF}, 50^\circ\text{C}}
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{Hg}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
+ \begin{array}{c}
\text{Pt/Hg}
\end{array}
\]

A mixture of PtPy$_2$Cl$_2$ (12.7 mg, 0.03 mmol), metallic mercury (6 g, 30 mmol) and degassed dry THF (6 mL) was heated in a sealed tube at 50 °C under magnetic stirring within 5 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot THF (10 mL). The filtrate and washings were combined and evaporated to dryness. The obtained residue was recrystallized from methanol three times and dried in vacuo to give 1.3 mg (10% yield) of HgPy$_2$Cl$_2$. Physical properties of the obtained substance were identical with the sample of HgPy$_2$Cl$_2$ described above.
Reaction of Pd(PPh₃)₂Cl₂ with metallic mercury.

\[
\text{PhPdPPh}_3 - \text{Cl} + \text{Hg}^0 \xrightarrow{50 \degree \text{C}} \text{PhHgPPh}_3 - \text{Cl} + \text{Pd/Hg}
\]

A mixture of Pd(PPh₃)₂Cl₂ (21.1 mg, 0.03 mmol), metallic mercury (6 g, 30 mmol) and degassed dry THF (6 mL) was heated in a sealed tube at 50 °C under magnetic stirring within 5 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot THF (10 mL). The filtrate and washings were combined and evaporated to dryness. The obtained residue was crystallized from EtOH and dried in vacuo to give 17 mg (71% yield) of Hg(PPh₃)₂Cl₂, mp 272–273 °C with decomposition (lit. mp 273 °C). ¹H NMR (500 MHz, DMSO-d₆): δ 7.46–7.52 (m, 24 H, Ar), 7.61–7.64 (m, 6H, Ar). ¹³C NMR (125 MHz, DMSO-d₆): δ 127.5, 127.8, 129.5, 129.6, 132.1, 133.4, 133.5. ESI-MS calcd for C₃₆H₃₀ClHgP₂⁺ [M – Cl]⁺ 761.1208, found 761.1206.

Reaction of Pt(PPh₃)₂Cl₂ and metallic mercury.

\[
\text{PhPtPPh}_3 - \text{Cl} + \text{Hg}^0 \xrightarrow{50 \degree \text{C}} \text{PhHgPPh}_3 - \text{Cl} + \text{Pt/Hg}
\]

A mixture of Pt(PPh₃)₂Cl₂ (23.7 mg, 0.03 mmol), metallic mercury (6 g, 30 mmol) and degassed dry THF (6 mL) was heated in a sealed tube at 50 °C under magnetic stirring within 5 h, then cooled to room temperature. The suspension was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot THF (10 mL). The filtrate and washings were combined and evaporated to dryness. The obtained residue was crystallized three times from EtOH and dried in vacuo to give 4 mg (17% yield) of Hg(PPh₃)₂Cl₂. Physical properties of the obtained substance were identical with the sample of Hg(PPh₃)₂Cl₂ described above.

Reaction of compound 2a with metallic mercury.

\[
\text{2a} \xrightarrow{\text{Hg}^0} \text{4a} + \text{Hgl}_4^{2-} + \text{Pa/Hg}
\]

A magnetically stirred mixture of compound 2a (32.6 mg, 0.05 mmol), metallic mercury (10 g, 50 mmol), and degassed dry 1,4-dioxane (16 mL) was heated in a sealed tube at 80 °C within 160 h, then cooled to room temperature. A formed dioxane suspension was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot 1,4-dioxane (20 mL). The filtrate and washings were combined and evaporated to dryness. The obtained residue was dissolved in DMSO (1 mL) at 90-95 °C. The DMSO solution was cooled and stored at room temperature overnight. Yellow crystals precipitated were collected by filtration, washed with CH₂Cl₂ and dried to give starting compound 2a (17 mg, 52% recovery). After separation of 2a, the DMSO solution was diluted with CH₂Cl₂ (1:1) and stored at 5 °C overnight. The solid precipitated was collected by filtration and recrystallized twice from DMSO-CH₂Cl₂ (1:1) mixture to give bis(1,3-dimethyl-1,3-dihydro-2H-imidazol-2-ylidene)mercury(II) tetraiodomercurate (4a), yield 3.3 mg (11%). ¹H NMR (DMSO-d₆): δ 4.31 s (12H, 4CH₃), 7.71 (dd, 3J = 6.1 Hz, 4J = 3.1 Hz, 4H, 4CH), 8.0 (dd, 3J = 6.1 Hz, 4J = 3.0 Hz, 4H, 4CH), 8.0 (dd, 3J = 6.1 Hz, 4J = 3.0 Hz, 4H, 4CH).
4CH). The spectrum contains small impurity signals (see Figure S26) which could not be removed after additional recrystallization of the 4a sample. Intensities of the impurity NMR signals increased with time of the NMR solution storage. Additional NMR experiments at 80 °C revealed that the substance 4a suffered dynamic transformations in DMSO solution (see Figure S27). We were unable to obtain reasonable 13C NMR spectrum of compound 4a due to its low solubility and instability in DMSO and other common NMR solvents. 1H NMR and ESI-MS spectra of the compound were identical with the properties of the sample of compound 4a which structure was confirmed by single crystal X-Ray analysis (see procedure for preparation of 4a from 1a described below).

Reaction of compound 1a with metallic mercury.

\[
\begin{align*}
\text{1a} & \rightarrow \text{2a} + \text{4a} + \text{Pd/Hg} \\
\text{Hg}^2+ & \rightarrow \text{Hg}^0
\end{align*}
\]

**Conditions (i).** A mixture of compound 1a (17.6 mg, 0.03 mmol), metallic mercury (6 g, 30 mmol) and degassed dry THF (6 mL) was heated in a sealed tube at 50 °C under magnetic stirring within 5 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot THF (40 mL). The filtrate and washings were combined. A small part (~ 2.5 mL) of the combined solution was evaporated to dryness and the residue obtained was analyzed by 1H NMR [HgPy2I2, 2a and 4a (traces) were detected as the reaction products]. Other part of the combined solution was evaporated to dryness *in vacuo*. The obtained residue was treated with hot methanol (5 mL). The insoluble residue was collected by filtration and recrystallized twice from DMSO-MeOH (1:1) mixture to give 3.6 mg (37% yield) of bis(1,3-dimethyl-1,3-dihydro-2H-benzimidazol-2-ylidene)diiodopalladium (2a). 1H and 13C NMR spectra of the substance were identical with the authentic sample of 2a.

After separation of 2a, the methanol solution was evaporated to dryness. The obtained residue was recrystallized twice from acetone and dried at room temperature to give 5.4 mg (59% yield) of HgPy2I2. 1H NMR (500 MHz, DMSO-\(d_6\)): \(\delta 7.41–7.44\) (m, 4H, Ar), 7.80-7.83 (m, 2H, Ar), 8.58-8.59 (m, 4H, Ar). 13C NMR (125 MHz, DMSO-\(d_6\)): \(\delta 123.9, 136.2, 149.5\). Found: C, 19.54; H, 1.59; N, 4.53. C\(_{10}\)H\(_{10}\)HgI\(_2\)N\(_2\). Calculated: C, 19.61; H, 1.65; N, 4.57.

**Conditions (ii).** A magnetically stirred mixture of compound 1a (29.3 mg, 0.05 mmol), metallic mercury (10 g, 50 mmol), and degassed dry 1,4-dioxane (10 mL) was heated in a sealed tube at 80 °C within 160 h, then cooled to room temperature. A suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which then was washed with hot 1,4-dioxane (40 mL). The filtrate and washings were combined. A small part (2.5 mL) of the combined solution was evaporated to dryness and the residue obtained was analyzed by 1H NMR [HgPy2I2 (traces), 2a and 4a were detected as the reaction products]. Other part of the combined solution was evaporated to dryness *in vacuo*. The obtained residue was dissolved in DMSO (0.5 mL) at 90-95 °C. The DMSO solution was cooled and stored at room temperature overnight. Yellow crystals precipitated were collected by filtration, washed with CH\(_2\)Cl\(_2\) and dried to give bis(1,3-dimethyl-1,3-dihydro-2H-benzimidazol-2-ylidene)diiodopalladium (2a), yield 7.3 mg (45%). Structure of the compound 2a was confirmed by single crystal X-ray analysis (Section S6). 1H and 13C NMR spectra were similar to the described in the literature.2

After separation of 2a, the DMSO solution was diluted with CH\(_2\)Cl\(_2\) (1:1) and stored at 5 °C overnight. The solid precipitated was collected by filtration and recrystallized twice from DMSO-CH\(_2\)Cl\(_2\) (1:1) mixture to give bis(1,3-dimethyl-1,3-dihydro-2H-imidazol-2-ylidene)mercury(II)
tetraiodomercurate (4a), yield 4.8 mg (16%). Structure of the compound 4a was confirmed by single crystal X-ray analysis (Section S6).

**Reaction of compound 1b with metallic mercury.**

A magnetically stirred mixture of compound 1b (109.5 mg, 0.2 mmol), metallic mercury (40 g, 200 mmol), and degassed dry 1,4-dioxane (40 mL) was heated in a sealed tube at 80 °C within 160 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot 1,4-dioxane (2×40 mL). The filtrate and washings were combined. A small part (2.5 mL) of the combined solution was evaporated to dryness and the residue obtained was analyzed by ¹H NMR [HgPy₂Br₂ (traces), 2b (~ 50% NMR yield) and 4b were detected as the reaction products]. Other part of the combined solution was evaporated to dryness in vacuo. The residue obtained was recrystallized three times from DMSO-CH₂Cl₂ (1:3) mixture to give bis[1,3-diisopropyl-1,3-dihydro-2H-benzo[d]imidazol-2-ylidene]mercury(II) tetrabromomercurate (4b), yield 8 mg (7%). ¹H NMR spectra showed dynamic nature of the compound 4b in DMSO solution (see Figure S28). Structure of compound 4b was unambiguously confirmed by a single crystal X-ray analysis (Section S6).

**Reaction of compound 1c with metallic mercury.**

_A magnetically stirred mixture of compound 1c (56.1 mg, 0.1 mmol), metallic mercury (20.1 g, 100 mmol) and degassed dry 1,4-dioxane (20 mL) was heated in a sealed tube at 80 °C under magnetic stirring within 160 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which then was washed with hot 1,4-dioxane (40 mL). The filtrate and washings were combined. A small part (2.5 mL) of the combined solution was evaporated to dryness and the residue obtained was analyzed by ¹H NMR [HgPy₂Cl₂ (traces), 2c (traces), 4c and 4c' (traces) were detected as the reaction products]. Other part of the combined solution was evaporated to dryness in vacuo. The obtained residue was recrystallized from CH₂Cl₂-MeOH (1:3) and dried in vacuo to give bis[1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene]mercury(2+) tetrachloromercurate(2-) (4c). Yield 32 mg (56%). ¹H NMR (300 MHz, DMSO- d₆): δ 2.05 (s, 24H, Me), 2.33 (s, 12H, Me), 7.10 (s, 8H, Ar), 8.04 (s, 4H, CH of imidazole cycle). ¹³C NMR (125 MHz, DMSO-d₆): δ 17.0, 20.7, 125.4, 129.0, 133.6, 134.8, 139.3, 178.2. ESI-MS calcd for C₄₂H₄₈ClHgN₄⁺ [M – HgCl₃]⁺ 845.3265, found 845.3269._

_Conditions (iii). A mixture of compound 1c (16.8 mg, 0.03 mmol), metallic mercury (6 g, 30 mmol) and degassed dry THF (6 mL) was heated in a sealed tube at 100 °C under magnetic stirring within 5 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a_
syringe and filtered through a thin layer of Celite (~2 mm) which then was washed with hot THF (10 mL). The filtrate and washings were combined. A small part (1 mL) of the combined solution was evaporated to dryness and the residue obtained was analyzed by $^1$H NMR and ESI-MS [HgPy$_2$Cl$_2$, 2c (traces), 4c (traces) and 4c' (traces) were detected as the reaction products]. Other part of the combined solution was evaporated to dryness in vacuo. The obtained residue was recrystallized twice from methanol and dried in vacuo to give 3.1 mg (48% yield) of HgPy$_2$Cl$_2$. Physical properties of the obtained substance were identical with the sample of HgPy$_2$Cl$_2$ described previously.

**Reaction of compound 1d with metallic mercury.**

**Conditions (ii).** A mixture of compound 1d (32 mg, 0.05 mmol), metallic mercury (10 g, 0.05 mol) and degassed dry 1,4-dioxane (10 mL) was heated in a sealed tube at 80 °C under magnetic stirring within 160 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which was then washed with hot 1,4-dioxane (40 mL). The filtrate and washings were combined. A small part (2.5 mL) of the combined solution was evaporated to dryness and the residue obtained was analyzed by $^1$H NMR and ESI-MS [HgPy$_2$Cl$_2$ (traces), 2d (traces), 4d (traces) and 4d' were detected as the reaction products]. Other part of the combined solution was evaporated to dryness in vacuo to give {1,3-bis[2,6-di(propan-2-yl)phenyl]-1,3-dihydro-2H-imidazol-2-ylidene}(dichloro)mercury (4d'). Yield 20 mg (61%). The $^1$H and $^{13}$C NMR spectra of the obtained compound 4d' were identical to those described in the literature. ESI-MS calcd for C$_{27}$H$_{36}$ClHgN$_2$ $^+$ [M – Cl]$^+$ 625.2262, found 625.2267.

**Conditions (iii).** A mixture of compound 1d (19.4 mg, 0.03 mmol), metallic mercury (6 g, 30 mmol) and degassed dry THF (6 mL) was heated in a sealed tube at 100 °C under magnetic stirring within 5 h, then cooled to room temperature. The suspension formed was separated from metallic mercury by a syringe and filtered through a thin layer of Celite (~2 mm) which then was washed with hot THF (10 mL). The filtrate and washings were combined. A small part (1 mL) of the combined solution was evaporated to dryness and the residue obtained was analyzed by $^1$H NMR and ESI-MS [HgPy$_2$Cl$_2$, 2d (traces), 4d (traces) and 4d' (traces) were detected as the reaction products]. Other part of the combined solution was evaporated to dryness in vacuo. The obtained residue was recrystallized twice from methanol and dried in vacuo to give 1.6 mg (25% yield) of HgPy$_2$Cl$_2$. Physical properties of the obtained substance were identical with the sample of HgPy$_2$Cl$_2$ described previously.
S3. Effect of the operational conditions on the mercury test results

Effect of Hg(0) loadings on the mercury test results in the Mizoroki-Heck reaction.

The experiments were carried out under an argon atmosphere in the identical 7 mL screw capped glass tubes equipped with identical ball-shaped magnetic stir bars. A solution of corresponding Pd catalyst (2.5 μmol, 0.5 mol%) in DMF (20 μL) and appropriate amount of metallic mercury (Table 2 in the article) were added successively to the solution of triethylamine (101 mg, 1 mmol), tetra-N-butylammonium bromide (161 mg, 0.5 mmol), iodobenzene (102 mg, 0.5 mmol), n-butyl acrylate (96 mg, 0.75 mmol), and naphthalene (internal GC standard, 32 mg, 0.25 mmol) in DMF (1.0 mL). The mixture was placed into thermostated oil bath preheated to 100 ºC, and that instant was taken as the starting time of the reaction. After 2 h stirring (300 rpm) at 100 ºC the reaction mixture was analyzed by GC-MS to determine the yield of n-butyl acrylate and the conversion of the iodobenzene (see Table 2 in the article).

Effect of agitation intensity on the mercury test results in the Mizoroki-Heck reaction.

The experiments were carried out under an argon atmosphere in the identical 7 mL screw capped glass tubes equipped with identical ball-shaped magnetic stir bars. A solution of corresponding Pd catalyst (2.5 μmol, 0.5 mol%) in DMF (2 μL) and 300 eq. of metallic mercury (1.5 g, 7.5 mmol) were added successively to the solution of triethylamine (101 mg, 1 mmol), tetra-N-butylammonium bromide (161 mg, 0.5 mmol), iodobenzene (102 mg, 0.5 mmol), n-butyl acrylate (96 mg, 0.75 mmol), and naphthalene (32 mg, 0.25 mmol) in DMF (1.0 mL). The mixture was placed into thermostated oil bath preheated to 100 ºC, and that instant was taken as the starting time of the reaction. After 2 h stirring at appropriate rate (0–1000 rpm) the reaction mixture was analyzed by GC-MS to determine the yield of n-butyl acrylate and conversion of the starting iodobenzene (Table S1, Figures S1, S2).

Table S1. Effect of the magnetic stirrer rotation rate on the yields of (E)-n-butyl cinnamate (8) in the Mizoroki-Heck reaction

| Entry | Magnetic stirrer rotation rate (rpm) | Yield\(^b\) of 8 (%) in the presence of a [Pd] catalyst Pd(OAc)_2 | 1d |
|-------|------------------------------------|-------------------------------------------------|-----|
| 1     | 0                                  | 100                                            | 100 |
| 2     | 100                                | 93                                             | 87  |
| 3     | 200                                | 87                                             | 79  |
| 4     | 300                                | 87                                             | 73  |
| 5     | 500                                | 81                                             | 30  |
| 6     | 700                                | 50                                             | 2   |
| 7     | 1000                               | 8                                              | 0   |

\(^a\) 300 equiv of Hg(0) was loaded for each entry.
\(^b\) An average of three runs is reported. The experimental errors were found to be no more than ±5%.
**Figure S1.** Effect of the magnetic stirrer rotation rate on the yields of \((E)\)-n-butyl cinnamate (8) in the Mizoroki-Heck reaction catalyzed by 1d at various Hg(0) loadings.

**Figure S2.** Approximated rotation rate required to attain 90% inhibition of the Mizoroki-Heck reaction catalyzed by 1d at various loaded quantity of Hg(0). The plot was obtained from the data presented on the Figure S1.
Effect of Hg(0) loading on the yield of \( p \)-phenylacetophenone (11) in the Suzuki–Miyaura reaction.

The experiments were carried out under an argon atmosphere in the identical 7 mL screw capped glass tubes equipped with identical ball-shaped magnetic stir bars. A solution of corresponding Pd catalyst (0.125 \( \mu \)mol, 0.05 mol\%) in DMF (20 \( \mu \)L), potassium tert-butoxide (79 mg, 0.7 mmol) and appropriate amount of metallic mercury (Table S2) were added successively to the solution of 1-(4-bromophenyl)ethanone (50 mg, 0.25 mmol), phenylboronic acid (42 mg, 0.35 mmol), tetra-N-butylammonium bromide (81 mg, 0.25 mmol) and hexadecane (internal GC standard, 28 mg, 0.125 mmol) in propan-2-ol (1 mL). The mixture was placed into thermostated oil bath preheated to 80 \( ^\circ \)C, and that instant was taken as the starting time of the reaction. After 2 h stirring at 80 \( ^\circ \)C the reaction mixture was analyzed by GC-MS to determine the yield of 4-acetylbiphenyl and the conversion of 1-(4-bromophenyl)ethanone (see Table S2).

Table S2. Effect of Hg(0) loading on the yield of \( p \)-phenylacetophenone (11) in the Suzuki–Miyaura reaction catalyzed by various Pd compounds

| Entry | Hg(0) loaded (equiv.) | Yield\(^a\) of 11 (%) in the presence of a [Pd] catalyst |
|-------|----------------------|-------------------------------------------------------|
|       |                      | \( \text{Pd(PPh}_3)_2\text{Cl}_2 \) | \( \text{1d} \) | Pd/C 5\% |
| 1     | 0\(^b\)              | 100 | 100 | 100 |
| 3     | 100\(^b\)            | 69  | 89  | 54  |
| 4     | 300\(^b\)            | 52  | 82  | 17  |
| 5     | 500\(^b\)            | 34  | 70  | 16  |
| 6     | 1000\(^b\)           | 25  | 64  | 13  |
| 8     | 2000\(^c\)           | 10  | 33  | 5   |

\(^a\) An average of three runs is reported. The experimental errors were found to be no more than ±8\%.

\(^b\) Magnetic stirrer rotation rate was 300 rpm.

\(^c\) Magnetic stirrer rotation rate was 1000 rpm.
S4. ESI-MS Experiments

1. **ESI-MS study of the reaction between PdCl$_2$Py$_2$ and Hg$^0$.** A mixture of PdCl$_2$Py$_2$ (1.7 mg, 5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated at 50 °C under magnetic stirring within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS.

$$\text{PdCl}_2\text{Py}_2 + \text{Hg}^0 \xrightarrow{\text{THF}} \text{HgCl}_2\text{Py}_2$$

**Figure S3.** ESI-(+)MS spectrum of the reaction mixture (THF solution) after heating PdCl$_2$Py$_2$ with metallic mercury at 50 °C.
2. ESI-MS study of the reaction between Pd(PPh₃)₂Cl₂ and Hg⁰. A mixture of Pd(PPh₃)₂Cl₂ (3.5 mg, 5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated at 50 °C under magnetic stirring within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS.

Figure S4. ESI-(+)MS spectra of mercury complexes in the reaction mixture (THF solution) after heating Pd(PPh₃)₂Cl₂ with metallic mercury at 50 °C.
3. ESI-MS study of the reaction between PdCl$_2$ and Hg$^0$. A mixture of PdCl$_2$ (0.9 mg, 5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated at 50 °C under magnetic stirring within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS. No ions of PdCl$_2$ were detected by ESI-MS.

\[
PdCl_2 + Hg^0 \xrightarrow{THF} Hg(II) \text{- products or/and Hg(II)-products}
\]

4. ESI-MS study of the reaction between Pd(OAc)$_2$ and Hg$^0$. A mixture of Pd(OAc)$_2$ (1.1 mg, 5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated at 50 °C under magnetic stirring within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS. No ions of Pd(OAc)$_2$ were detected by ESI-MS.

\[
Pd(OAc)_2 + Hg^0 \xrightarrow{THF} Pd \text{- products}
\]

5. Stability control experiment for compound 1a in THF at 50 °C. A solution of compound 1a (2.9 mg, 5 µmol) in THF (3 mL) was heated under stirring at 50 °C for 5 h. Then 10 µL of the solution was diluted with MeCN (1.0 mL) and analyzed by ESI-MS. No any transformations were detected by ESI-MS.

\[
\text{transformations were not detected by HRMS}
\]
6. **Stability control experiment for compound 2a in THF at 50 °C.** A solution of compound 2a (3.2 mg, 5 µmol) in THF (3 mL) was heated under stirring at 50 °C for 5 h. Then 10 µL of the solution was diluted with MeCN (1.0 mL) and analyzed by ESI-MS. No any transformations were detected by ESI-MS.

![Diagram](image)

**Figure S5.** ESI-(+)-MS spectrum of the solution of compound 2a in THF after heating at 50 °C within 5 h. The spectrum is identical with the spectrum of fresh solution of compound 2a.
7. ESI-MS study of the reaction between compound 1a and Hg\textsuperscript{0}. A mixture of compound 1a (2.9 mg, 5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated with stirring at 50 °C under argon atmosphere within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS.

Figure S6. ESI-(+)MS spectra of the reaction mixture (THF solution) after heating compound 1a with metallic mercury at 50 °C.
ESI-MS study of the reaction between compound 2a and Hg⁰. A mixture of compound 2a (1.6 mg, 2.5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated with stirring at 50 °C under argon atmosphere within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS.

Figure S7. ESI-(+)

Figure S7. ESI-(+)MS spectrum of the reaction mixture (THF solution) after heating compound 2a with metallic mercury at 50 °C.
9. ESI-MS study of the reaction between compound 1c and Hg\(^0\). A mixture of compound 1c (1.4 mg, 2.5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated with stirring at 100 °C under argon atmosphere within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS.
Figure S8. ESI-(+)MS spectra of the reaction mixture (THF solution) after heating compound 1c with metallic mercury at 50 °C.
10. ESI-MS study of the reaction between compound 1d and Hg⁰.

A mixture of compound 1d (1.6 mg, 2.5 µmol), metallic mercury (0.95 g, 5 mmol) and THF (3 mL) was heated with stirring at 100 °C under argon atmosphere within 2 h. Then 10 µL of the solution formed was diluted with MeCN (1.0 mL) and analyzed by ESI-MS.

![Diagram](image)

**Figure S9.** ESI-(+)MS spectra of the reaction mixture (THF solution) after heating compound 1d with metallic mercury at 50 °C.
11. **ESI-MS online monitoring of the reaction between compound 1a and Hg\(^0\).**

Online monitoring of ions during the reaction between compound 1a and Hg\(^0\) was performed according to the following procedure. A two-necked flask equipped with a magnetic stir bar was flushed with argon and filled under argon backflush with a degassed THF solution (2 mL) containing compound 1a (5.9·10\(^{-7}\) g, 0.1 µmol). One neck of the flask was closed with a septum, and the second neck was attached to the “double” argon balloon.\(^8\) The flask was placed into a hot (60 °C) glycerol bath. A red PEEK capillary (72 cm) was pulled into the flask through the septum and immersed into the THF solution. After heating for 2 min, metallic mercury (0.95 g, 5 mmol) was injected into the flask via a syringe through the septum, and the reaction was monitored for 150 min. Structures of the main reaction products proposed on the basis of the observed ion signals are outlined in the scheme:

![Chemical Structures](image_url)
Figure S10. Real-time records of abundances of ions in the reaction of complex 1a with Hg\(^0\) in THF.

12. **ESI-MS online monitoring of the reaction between compound 1a and Hg\(^0\).**

Online monitoring of ions during the reaction between compound 3 and Hg\(^0\) in THF at 60 °C was performed analogously to the procedure used for the online monitoring of the reaction between 1a and Hg (see the previous section). Metallic mercury (0.95 g, 5 mmol) was injected to the preheated within 2 min THF solution (2 mL) containing compound 3 (6.7·10\(^{-7}\) g, 0.1 µmol). Structures of the main reaction products proposed on the basis of the observed ion signals are outlined in the scheme:
Figure S11. Real-time records of abundances of ions in the reaction of complex 3 with Hg\(^0\) in THF.
12. Observation of mercury complexes forming in the course of mercury test trials of the Mizoroki-Heck reaction.

\[
\begin{align*}
\text{Pd(PPh}_3\text{)}_2\text{Cl}_2 \text{ (5 mol %)} & \quad \text{DMF, Et}_3\text{N, TBAB, Hg(0) (2000 eq.), 100 °C, 2 h} \\
6 + 7 & \quad \text{Pd(PPh}_3\text{)}_2\text{Cl}_2 \text{ (5 mol %)} \\
 & \quad \text{Hg(0) (2000 eq.), 100 °C, 2 h} \\
8 & \quad \text{Pd/Pd amalgam}
\end{align*}
\]

The experiment was carried out under argon atmosphere in 7 mL screw capped glass tube equipped with ball-shaped magnetic stir bar. A solution of Pd catalyst Pd(PPh$_3$)$_2$Cl$_2$ (17.5 mg, 25 μmol, 5 mol%) in DMF (100 μL) and metallic mercury (10.03 g, 50 mmol, 2000 eq.) were added successively to the solution of triethylamine (101 mg, 1 mmol), iodobenzene (102 mg, 0.5 mmol), and $n$-butyl acrylate (96 mg, 0.75 mmol) in DMF (0.9 mL). The mixture was placed into thermostated oil bath preheated to 100 °C, and that instant was taken as the starting time of the reaction. After 2 hours of stirring (1000 rpm) at 100 °C the reaction mixture was diluted with DMF (5 mL), decanted from mercury and evaporated in vacuo. The oily organic residue was dissolved in CHCl$_3$ (20 mL), filtered via paper filter, washed with water (3×5 mL), dried with Na$_2$SO$_4$ and evaporated to dryness. The residue obtained was dissolved in acetonitrile (5 mL) and analyzed by ESI-MS. ESI-MS spectra of mercury complexes formed in the course of the mercury test trials are presented below (Figures S12 - S14).
Figure S12. ESI-(+)MS spectra of Hg(PPh$_3$)$_2$X$_2$ complexes formed in the course of mercury test trial of the Mizoroki-Heck reaction catalyzed by Pd(PPh$_3$)$_2$Cl$_2$. Regions corresponding to the [Hg(PPh$_3$)Cl]$^+$ and [Hg(PPh$_3$)$_2$Cl]$^+$ ions are presented.
Figure S13. ESI-(+)-MS spectra of Hg(PPh$_3$)$_2$X$_2$ complexes formed in the course of mercury test trial of the Mizoroki-Heck reaction catalyzed by Pd(PPh$_3$)$_2$Cl$_2$. Regions corresponding to the [Hg(PPh$_3$)Br]$^+$ and [Hg(PPh$_3$)$_2$Br]$^+$ ions are presented. These ions are formed due to the presence of [Bu$_4$N]Br in the reaction mixture.
Figure S14. ESI-(+)-MS spectra of Hg(PPh$_3$)$_2$X$_2$ complexes formed in the course of mercury test trial of the Mizoroki-Heck reaction catalyzed by Pd(PPh$_3$)$_2$Cl$_2$. Regions corresponding to the [Hg(PPh$_3$)$_2$I]$^+$ and [Hg(PPh$_3$)$_2$II]$^+$ ions are presented. These ions are formed due to the presence of iodide anions released from PhI in the course of the Mizoroki-Heck reaction.
The experiment was carried out under argon atmosphere in 7 mL screw capped glass tube equipped with ball-shaped magnetic stir bar. A solution of Pd catalyst 1d (16.1 mg, 25 μmol, 5 mol%) in DMF (100 μL) and metallic mercury (10.03 g, 50 mmol, 2000 eq.) were added successively to the solution of triethylamine (101 mg, 1 mmol), iodobenzene (102 mg, 0.5 mmol), and n-butyl acrylate (96 mg, 0.75 mmol) in DMF (0.9 mL). The mixture was placed into thermostated oil bath preheated to 100 ºС, and that instant was taken as the starting time of the reaction. After 2 hours of stirring (1000 rpm) at 100 ºС the reaction mixture was diluted with DMF (5 mL), decanted from mercury and evaporated in vacuo. The oily organic residue was dissolved in CHCl₃ (20 mL), filtered via paper filter, washed with water (3×5 mL), dried with Na₂SO₄ and evaporated to dryness. The residue obtained was dissolved in acetonitrile (5 mL) and analyzed by ESI-MS. ESI-MS spectra of mercury complexes formed in the course of the mercury test trials are presented below (Figures S15 - S17).

Figure S15. ESI-(+)MS spectrum of Hg(NHC)X₂ complexes formed in the course of mercury test trial of the Mizoroki-Heck reaction catalyzed by complex 1d. Region corresponding to the [Hg(NHC)Cl]⁺ is presented.
Figure S16. ESI-(+)MS spectrum of Hg(NHC)X₂ complexes formed in the course of mercury test trial of the Mizoroki-Heck reaction catalyzed by complex 1d. Region corresponding to the [Hg(NHC)Br]⁺ is presented. This ion is formed due to the presence of [Bu₄N]Br in the reaction mixture.

Figure S17. ESI-(+)MS spectrum of Hg(NHC)X₂ complexes formed in the course of mercury test trial of the Mizoroki-Heck reaction catalyzed by complex 1d. Region corresponding to the [Hg(NHC)I]⁺ is presented. This ion is formed due to the presence of iodide anions released from PhI in the course of the Mizoroki-Heck reaction.
S5. $^1$H and $^{13}$C NMR Spectra

Figure S18. $^1$H NMR spectrum of HgPy$_2$Cl$_2$ (DMSO-$d_6$, 300 MHz).
**Figure S19.** $^{13}$C NMR spectrum of HgPy$_2$Cl$_2$ (DMSO-$d_6$, 125 MHz).
Figure S20. $^1$H NMR spectrum of HgPy$_2$I$_2$ (DMSO-$d_6$, 500 MHz).
Figure S21. $^{13}$C NMR spectrum of $\text{HgPy}_2\text{I}_2$ (DMSO-$d_6$, 125 MHz).
Figure S22. $^1$H NMR spectrum of $\text{HgCl}_2(\text{PPh}_3)_2$ (DMSO-$d_6$, 300 MHz).
Figure S23. $^{13}$C NMR spectrum of $\text{HgCl}_2(\text{PPh}_3)_2$ (DMSO-$d_6$, 125 MHz).
**Figure S24.** $^1$H NMR spectrum of compound 2a (DMSO-$d_6$, 400 MHz).
Figure S25. $^{13}$C NMR spectrum of compound 2a (CDCl$_3$, 125 MHz).
Figure S26. $^1$H NMR spectrum of compound 4a (DMSO-$d_6$, 300 MHz).
Figure S27. Time-dependent $^1$H NMR spectra of compound 4a in DMSO-$d_6$ at 80 °C. Proposed equilibrium transformation between the isomers 4a and 4a' is depicted on the scheme above the NMR plots.
Figure S28. $^1$H NMR spectrum of compound 4b (DMSO-$d_6$, 300 MHz). The spectrum contains signals of two isomers, probably due to equilibrium similar to the reaction depicted on the Figure S27.
Figure S29. $^1$H NMR spectrum of compound 4c (DMSO-$d_6$, 300 MHz).
Figure S30. $^{13}$C NMR spectrum of compound 4c (DMSO-$_d$6, 125 MHz).
Figure S31. $^1$H NMR spectrum compound of 4d' (DMSO-$d_6$, 300 MHz).
S6. Single Crystal X-Ray Diffraction Data

Experimental

X-ray diffraction data were collected at the «Belok» beamline of the National Research Center «Kurchatov Institute» (Moscow, Russian Federation) using a Rayonix SX165 CCD detector. All images were collected using an oscillation range of 1.0° and corrected for absorption using the Scala program.9 The data were indexed, integrated and scaled using the utility iMOSFLM in CCP4 program.10 The structures were determined by direct method and refined by full-matrix least squares technique on $F^2$ with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters ($U_{iso}(H) = 1.5U_{eq}(C)$ for the CH3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other groups). All calculations were carried out using the SHELXTL program.11 Crystallographic data for 2a, 4a, 4b have been deposited in the Cambridge Crystallographic Data Center. CCDC 1861069 (2a), CCDC 1861070 (4a), and CCDC 1861071 (4b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).
Compound 2a

Figure S32. The molecular structure of compound 2a according to single-crystal X-ray diffraction data. Thermal ellipsoids are shown at 50% probability.

Table S3. Crystal data for compound 2a

| C_{18}H_{20}I_{2}N_{4}Pd | F(000) = 616 |
|-------------------------|--------------|
| M_r = 625.58            | D_x = 2.123 Mg m$^{-3}$ |
| Monoclinic, P2_1/c      | Synchrotron radiation, $\lambda = 0.96990$ Å |
| a = 8.3065(17) Å        | Cell parameters from 600 reflections |
| b = 16.337(3) Å        | $\theta = 3.8$–36.0° |
| c = 7.6187(15) Å        | $\mu = 8.98$ mm$^{-1}$ |
| $\beta = 99.14(3)$°     | $T = 100$ K |
| $V = 1020.8(4)$ Å$^3$   | Prism, yellow |
| Z = 2                   | 0.12 x 0.10 x 0.10 mm$^3$ |

Table S4. Data collection for compound 2a

| Rayonix SX165 CCD diffractometer | 1643 reflections with $I > 2\sigma(I)$ |
|----------------------------------|--------------------------------------|
| $\varphi$ scan                   | $R_{int} = 0.085$ |
| Absorption correction: multi-scan SCALA (Evans, 2006) | $\theta_{\text{max}} = 38.4^\circ$, $\theta_{\text{min}} = 3.8^\circ$ |
| $T_{\text{min}} = 0.340$, $T_{\text{max}} = 0.400$ | $h = -10$–7 |
| 9763 measured reflections        | $k = -20$–20 |
| 2055 independent reflections     | $l = -9$–9 |
### Table S5. Refinement for compound 2a

| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
|---------------------|----------------------------------------------------------|
| Least-squares matrix: full | H-atom parameters constrained |
| $R_1[F^2 > 2\sigma(F^2)] = 0.052$ | $w = 1/\sigma^2(F_o^2) + (0.0461P)^2$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR_2(F^2) = 0.128$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| $S = 1.07$ | $\Delta\rho_{\text{max}} = 1.58\ \text{e}\ \text{Å}^{-3}$ |
| 2055 reflections | $\Delta\rho_{\text{min}} = -1.59\ \text{e}\ \text{Å}^{-3}$ |
| 118 parameters | Extinction correction: SHELXL, $F_c^\sigma = kF_c[1 + 0.001xF_c^2\lambda^2/\sin(2\theta)]^{-\frac{1}{4}}$ |
| 0 restraint | Extinction coefficient: 0.0026(2) |
| Primary atom site location: difference Fourier map | |

**Special details (Geometry):**

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.’s in distances, angles and torsion angles; correlations between e.s.d.’s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.’s is used for estimating e.s.d.’s involving l.s. planes.
Figure S33. The molecular structure of compound 4a according to single-crystal X-ray diffraction data. Thermal ellipsoids are shown at 50 % probability.

Table S6. Crystal data for compound 4a

| Compound | Formula | Moles | Density |
|----------|---------|-------|---------|
| 4a       | C_{18}H_{20}Hg_{2}I_{4}N_{4} | F(000) = 2112 | Density = 3.099 Mg m^{-3} |

| Crystal System | Space Group | Synchrotron Radiation, λ = 0.96990 Å |
|----------------|-------------|-------------------------------------|
| Monoclinic, P2 \_1/n | | |

| Parameters | Value |
|-----------|-------|
| a         | 10.648(2) Å |
| b         | 20.021(4) Å |
| c         | 12.134(2) Å |
| β         | 95.49(3)° |
| T         | 100 K |
| V         | 2574.9(8) Å^3 |
| Z         | 4 |

| Density       | 0.12 × 0.07 × 0.02 mm^3 |

Table S7. Data collection for compound 4a

| Instrument | Data collected | |
|------------|----------------|---|
| Rayonix SX165 CCD diffractometer | 4312 reflections with I > 2σ(I) | |

| Technique | Description | |
|-----------|-------------|---|
| φ scan    | Resolved | |
| Absorption correction | Multi-scan SCALA (Evans, 2006) | |
| θ_{max} | 38.5° | |
| θ_{min} | 3.3° | |
| T_{min} | 0.050 | |
| T_{max} | 0.500 | |
| h         | -13→8   | |
| k         | -25→24  | |
| l         | -14→13  | |
Table S8. Refinement for compound 4a

| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
|---------------------|------------------------------------------------------|
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R_1[F^2 > 2 \sigma(F^2)] = 0.081$ | H-atom parameters constrained |
| $wR_2(F^2) = 0.189$ | $w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 1.7631P]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.86$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 5252 reflections | $\Delta\rho_{\text{max}} = 4.15 \text{ e Å}^{-3}$ |
| 210 parameters | $\Delta\rho_{\text{min}} = -3.77 \text{ e Å}^{-3}$ |
| 0 restraints | Extinction correction: SHELXL, $F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: difference Fourier map | Extinction coefficient: 0.00151(14) |

**Special details (Geometry):**

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
Compound 4b

Figure S34. The molecular structure of compound 4b according to single-crystal X-ray diffraction data. Thermal ellipsoids are shown at 50% probability.

Table S9. Crystal data for compound 4b

| Compound | Formula | Space Group | Color | Z | Dimensions | Monoclinic, C2/c | Synchrotron radiation, λ = 0.96260 Å | a = 18.486(4) Å | b = 9.2309(19) Å | c = 20.682(4) Å | β = 106.80(3)° | T = 100 K | V = 3378.6(13) Å³ | Z = 4 | Data collection for compound 4b |
|----------|---------|-------------|------|---|------------|-----------------|-----------------------------------|----------------|----------------|----------------|----------------|---------|----------------|----------------|-----|-----------------|
| C_{26}H_{36}HgN_{4}Br_{4}Hg | F(000) = 2080 | D_x = 2.212 Mg m^{-3} | | | | | | | | | | | | | | | 2181 reflections with I > 2σ(I) |
| | | | | | | | | | | | | | | | | | R_{int} = 0.111 |
| | | | | | | | | | | | | | | | | | θ_{max} = 38.5°, θ_{min} = 3.4° |
| | | | | | | | | | | | | | | | | | h = -23→23 |
| | | | | | | | | | | | | | | | | | k = -10→10 |
| | | | | | | | | | | | | | | | | | l = -26→26 |
Table S11. Refinement for compound 4b

| Refinement on $F^2$       | Secondary atom site location: difference Fourier map |
|---------------------------|------------------------------------------------------|
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R_1[F^2 > 2\sigma(F^2)] = 0.098$ | H-atom parameters constrained |
| $wR_2(F^2) = 0.253$ | $w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.95$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3444 reflections | $\Delta\rho_{max} = 3.12 \text{ e Å}^{-3}$ |
| 127 parameters | $\Delta\rho_{min} = -2.63 \text{ e Å}^{-3}$ |
| 0 restraints | Extinction correction: SHELXL, $Fc^2 = kFc[1 + 0.001xFc^2\lambda^2/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: difference Fourier map | Extinction coefficient: 0.00043 (8) |

**Special details (Geometry):**

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
**Figure S35.** XRD patterns of the inorganic precipitate from the Pt(II) complex (3) (black line), inorganic precipitate from the Pt(0) complex (Pd$_2$dba$_3$) (purple line).
Figure S36. FE-SEM image and EDS spectrum of Pd/Hg precipitate isolated from the reaction mixture after heating Pd(II) complex (1a) with Hg in THF at 50 ºC within 5 h.
**Figure S37.** FE-SEM image and EDS spectrum of Pt/Hg precipitate isolated from the reaction mixture after heating Pt(II) complex (3) with Hg in THF at 50 °C within 5 h.
Figure S38. FE-SEM image and EDS spectrum of Pd/Hg precipitate isolated from the reaction mixture after heating Pd$_2$(dba)$_3$ with Hg in THF at 50 ºC within 2 h.
Figure S39. FE-SEM image and EDS spectrum of Pt/Hg precipitate isolated from the reaction mixture after heating Pt$_2$(dba)$_3$ with Hg in THF at 50 °C within 5 h.
S9. Photos of Reaction Mixtures

Figure S40. Visual changes of the Pd$_2$(dba)$_3$·CHCl$_3$ solution samples taken from the reaction mixture at defined times.

Figure S41. Visual changes of the Pt$_2$(dba)$_3$·CHCl$_3$ solution samples taken from the reaction mixture at defined times.
Figure S42. Visual changes of the solution samples of complex 1a taken from the reaction mixtures at defined times.

Figure S43. Visual changes of the solution samples of complex 3 taken from the reaction mixtures at defined times.
S10. Analysis of the Literature Relating to the “Mercury test”

The literature search was performed by means of the Google Scholar search engine. Totally 4822 publications (experimental research articles and reviews, books and book chapters, patents, etc.) were found from 1985 up to 2018. Obtained distribution is shown on Figure S44.

![Figure S44. Number of publications per year in the time period 1985 – 2018 (4822 in total).](image)

It should be noted that in many cases rather simplified description of experimental implementation of mercury test is provided in the published articles (sometimes even without specification of exact amount of mercury, conditions, etc.). Detailed analysis of publications published from 2015 to 2018 allowed to select 474 research articles containing clearly described experimental procedures and relevant for analysis.

Among the 474 articles, 322 articles include the mercury test as the only method for distinguishing between “homogeneous” and “heterogeneous” catalysis mechanisms. Remaining 152 articles contain, together with the mercury test, additional methods for the distinguishing catalysis mechanisms. The circular diagrams on Figures S45 and S46 demonstrate relative distribution of the articles and distribution of additional methods used in combination with the mercury test in the 152 articles.
Relative share of articles using mercury test and additional methods in catalytic studies (2015-2018)

- Mercury test was used the only method for distinguishing catalysis mechanism
- Mercury test was used in combination with additional methods

**Figure S45.** Relative share between articles using the mercury test only and the mercury test in combination with additional methods in catalytic studies. The data were obtained from the 474 articles containing clearly described experimental procedures and published within 2015 – 2018.
It appears from the data analysis that approximately two-thirds of experimental articles make conclusions concerning reaction mechanism on the basis of mercury test only without verification of its validity for the conditions under study.

Concerning the analyzed articles published in the period of 2015-2018 in should be noted that validity of mercury test for the study of specific catalysts was reliably verified only in small number of the articles, for example: Bayram et al., *ACS Catal.*, 2015, 5, P. 3876-3886. DOI: 10.1021/acscatal.5b00315 ; Gorunova et al., *Organometallics*. 2018, 37, P. 2842-2858. DOI: 10.1021/acs.organomet.8b00363).\textsuperscript{12-13} In the last article mercury test has been recognized a misleading method.\textsuperscript{13} Just in a few articles (for example: Olsen et al., doi: 10.1021/acs.inorgchem.7b00029 ; Pandiri et al., doi: 10.1039/C7NJ00452D) provision of sufficient amount of mercury and agitation level was ascertained.\textsuperscript{14-15} In a few articles, results of mercury test were considered ambiguous and were

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**Figure S46.** Relative share of methods used in combination with mercury test for distinguishing reaction mechanisms in the 152 articles published within 2015 – 2018.
disregarded on the basis of alternative experimental methods (for example: Manojveer et al., doi: 10.1002/chem.201705208; Ortiz et al., doi: 10.1021/acs.organomet.8b00295; Pušavec et al., doi: 10.1021/acs.joc.6b00945).
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