

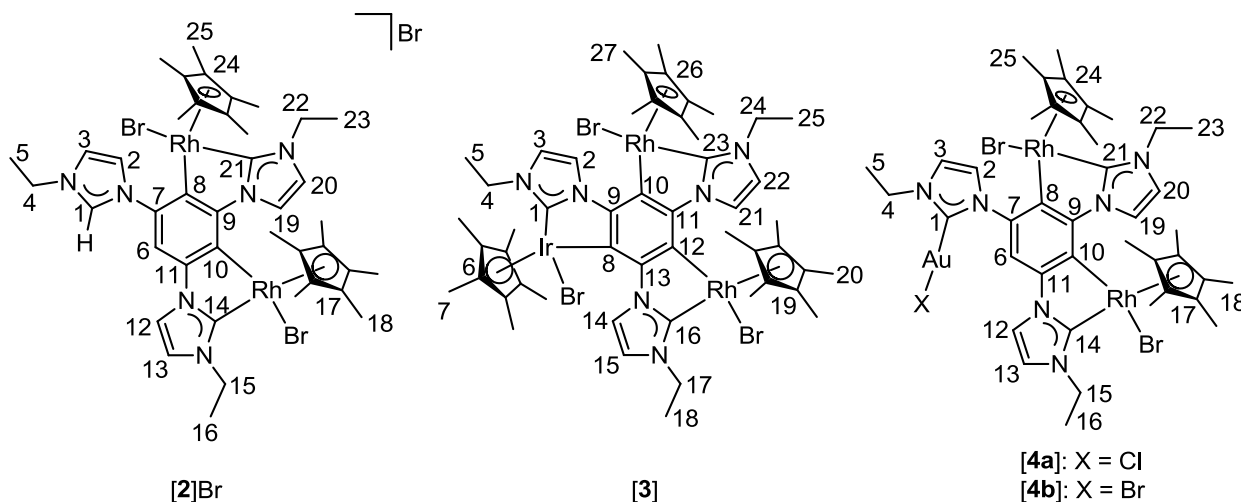
## Heterobimetallic complexes of a phenylene-bridged tricarbene ligand

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### Supporting Information

**General Procedures.** All reactions were carried out under an argon atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C. Solvents were distilled by standard procedures prior to use.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts ( $\delta$ ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz and only given for  $^1\text{H}, ^1\text{H}$  couplings unless mentioned otherwise. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen), Quattro LCZ (Waters-Micromass, Manchester, UK), Bruker Reflex IV or Varian MAT 212 spectrometers. Compounds  $\text{H}_3\text{-1}(\text{Br})_3^1$  and  $[\text{Rh}(\text{Cp}^*)(\text{Cl})_2]_2^2$  were prepared as described in the literature.  $\text{Cs}_2\text{CO}_3$ ,  $[\text{AuCl}(\text{SMe}_2)]$ ,  $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  and  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  were purchased from commercial sources and were used as received without further purification. For assignment of NMR resonances see Figure S1.



**Figure S1.** Assignment of NMR resonances for [2]Br, [3], [4a] and [4b].

**Synthesis of [2]Br.** Acetonitrile (20 mL) was added to a mixture of H<sub>3</sub>-**1**(Br)<sub>3</sub> (0.050 g, 0.083 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.057 g, 0.175 mmol), [Rh(Cp\*)(Cl)<sub>2</sub>]<sub>2</sub> (0.051 g, 0.083 mmol), NaOAc (0.014 g, 0.017 mmol) and NaBr (excess). The resulting suspension was heated to 65 °C for 18 h. The reaction mixture was cooled to ambient temperature and then filtered through Celite to get a clear solution. The filtrate was concentrated *in vacuo* to give an orange coloured compound. The compound was further purified by column chromatography (silica gel) using a dichloromethane:methanol (95:5, v:v) solvent mixture. Yield: 0.062 g (0.058 mmol, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.51 (s br, 1H, H1), 9.09 (s br, 1H, H19), 8.90 (s br, 1H, H2), 8.35 (s br, 1H, H12), 7.82 (s, 1H, H6), 7.39 (s br, 1H, H3), 7.10 (s br, 1H, H13), 7.04 (s br, 1H, H20), 4.42–4.21 (m, 4H, H4, HH15, HH22), 4.19–4.09 (m, 2H, HH15, HH22), 1.54 (s, 15H, H18), 1.53 (s br, 3H, H5), 1.51 (s br, 3H, H16), 1.49 (s br, 3H, H23), 1.47 (s 15H, H25) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 179.2 (d, <sup>1</sup>J<sub>C,Rh</sub> = 53.2 Hz, C14), 178.4 (d, <sup>1</sup>J<sub>C,Rh</sub> = 52.0 Hz, C21), 155.5 (C9), 145.8 (C11), 142.8 (d, <sup>1</sup>J<sub>C,Rh</sub> = 39.6 Hz, C8), 139.6 (d, <sup>1</sup>J<sub>C,Rh</sub> = 40.1 Hz, C10), 138.6 (C7), 136.3 (C1), 125.7 (C2), 122.7 (C19), 120.6 (C13), 120.1 (C3), 118.5 (C12), 118.0 (C20), 106.9 (C6), 98.1 (d, <sup>1</sup>J<sub>C,Rh</sub> = 4.9 Hz, C17), 97.9 (d, <sup>1</sup>J<sub>C,Rh</sub> = 4.9 Hz, C24), 45.1 (C22, C15), 44.9 (C4), 16.4 (C16), 15.9 (C23), 15.5 (C5), 9.7 (C25), 9.4 (C18) ppm. MS (ESI, positive ions): *m/z* = 995.0763 (calcd for [[2]Br–Br]<sup>+</sup> 995.0793). Anal. Calcd (%) for [2]Br·CH<sub>2</sub>Cl<sub>2</sub>: C, 43.47; H, 4.78; N, 7.24. Found: C, 43.03; H, 4.91; N, 7.14.

**Synthesis of [3].** To a mixture of Ag<sub>2</sub>O (0.013 g, 0.056 mmol) and [2]Br (0.050 g, 0.046 mmol) was added acetonitrile (15 mL). The resulting suspension was stirred for 48 h at 65 °C under exclusion of light. A mixture of [Ir(Cp\*)(Cl)<sub>2</sub>] (0.020 g, 0.025 mmol), NaOAc (0.005 g, 0.061 mmol) and NaBr (0.029 g, 0.282 mmol) was subsequently added to this suspension. The reaction mixture was heated for an additional 18 h to 60 °C. After cooling to room temperature the resulted suspension was filtered through a pad of Celite to get a clear solution. The solvent was removed *in vacuo* to give the crude product as a reddish orange solid. Analytically pure compound [3] was obtained by column chromatography using a dichloromethane:acetone solvent mixture (8:2, v:v). Yield: 0.025 g (0.018 mmol, 39%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.14 (s br, 1H, H21), 9.09 (s br, 1H, H2), 9.02 (s br, 1H, H14), 6.93 (s br, 1H, H22), 6.91 (s br, 1H, H15), 6.89 (s br, 1H, H3), 4.42–4.31 (m, 3H, HH4, HH17, HH24), 4.19–4.08 (m, 3H, HH4, HH17, HH24), 1.67 (s, 15H, H7), 1.62 (s, 15H, H20), 1.60 (s, 15H, H27), 1.54 (s br, 6H, H18,

H25), 1.53 (s br, 3H, H5) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.7 (d,  $^1J_{\text{C,Rh}} = 52.9$  Hz, C23), 177.6 (d,  $^1J_{\text{C,Rh}} = 52.7$  Hz, C16), 159.9 (C1), 150.6/149.3/148.7 (C9, C11, C13), 134.3 (d,  $^1J_{\text{C,Rh}} = 38.0$  Hz, C12), 133.6 (d,  $^1J_{\text{C,Rh}} = 38.2$  Hz, C10), 123.6 (C14), 123.1 (C21), 122.7 (C2), 119.9 (C8), 116.7 (C22), 116.6 (C15), 116.0 (C3), 97.3 (d,  $^1J_{\text{C,Rh}} = 4.9$  Hz, C19), 97.3 (d,  $^1J_{\text{C,Rh}} = 4.9$  Hz, C26), 90.6 (C6), 44.6 (C17, C24), 44.2 (C4), 16.4 (C5), 16.0 (C18, C25), 9.7 (C20), 9.6 (C27), 9.3 (C7) ppm. MS (ESI, positive ions):  $m/z = 1401.0688$  (calcd for  $[[\mathbf{3}]+\text{H}]^+$  1401.0687) and 1423.0504 (calcd for  $[[\mathbf{3}]+\text{Na}]^+$  1423.0507). Anal. Calcd (%) for  $[\mathbf{3}]\cdot\text{CH}_3\text{CN}$ : C, 44.15; H, 4.82; N, 6.80. Found: C, 43.07; H, 4.78; N, 6.81.

**Synthesis of [4].**  $\text{Ag}_2\text{O}$  (0.009 g, 0.039 mmol) was added to a solution of  $[\mathbf{2}]\text{Br}$  (0.060 g, 0.056 mmol) and NaBr (excess) in acetonitrile (15 mL). The resulting suspension was heated to 65 °C for 48 h under exclusion of light. The suspension was cooled to ambient temperature. Subsequently, a mixture of  $[\text{AuCl}(\text{SMe}_2)]$  (0.018 g, 0.061 mmol) and NaBr (0.046 g, 0.447 mmol) was added to the suspension. The reaction mixture was stirred at ambient temperature for an additional 18 h. The obtained suspension was filtered through a pad of Celite to get a clear orange solution. The solvent was removed *in vacuo* and the residue was loaded onto a silica gel column and eluted with a dichloromethane:acetone mixture (9:1, v:v) to give compounds **[4a]** and **[4b]** as reddish orange solids. Yield: 0.036 g (0.028 mmol, 50%) of a mixture of **[4a]** and **[4b]**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): (major product, **[4a]**)  $\delta$  = 9.0 (s br, 1H, H2), 8.26 (s br, 1H, H19), 7.66 (s 1H, H6), 7.52 (s br, 1H, H12), 7.06–7.02 (m, 2H, H13, H20), 6.96 (s br, 1H, H3), 4.51–4.15 (m, 6H, H4, H15, H22), 1.62 (s, 15H, H18), 1.60–1.55 (m, 9H, H5, H16, H23), 1.54 (s, 15H, H25) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ): (major product, **[4a]**)  $\delta$  = 182.3 (d,  $^1J_{\text{C,Rh}} = 54.1$  Hz, C14), 180.2 (d,  $^1J_{\text{C,Rh}} = 52.0$  Hz, C21), 173.5 (C1), 155.2 (C9), 144.4 (d,  $^1J_{\text{C,Rh}} = 39.6$  Hz, C8), 143.7 (C11), 142.6 (C7), 139.4 (d,  $^1J_{\text{C,Rh}} = 40.8$  Hz, C10), 127.6 (C2), 119.8 (C13), 119.7 (C19), 117.4 (C3), 117.3 (C20), 115.9 (C12), 108.6 (C6), 98.0 (d,  $^1J_{\text{C,Rh}} = 5.1$  Hz, C17), 97.0 (d,  $^1J_{\text{C,Rh}} = 4.1$  Hz, C24), 46.5 (C4), 45.1 (C15), 44.5 (C22), 16.7 (C5), 16.6 (C23), 16.1 (C16), 9.9 (C25), 9.1 (C18) ppm.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): (minor product, **[4b]**)  $\delta$  = 9.21 (d,  $^3J = 1.9$  Hz, 1H, H19), 8.89 (d,  $^3J = 1.8$  Hz, 1H, H2), 7.56 (s, 1H, H6), 7.48 (d,  $^3J = 1.9$  Hz, 1H, H12), 7.06 (d,  $^3J = 1.9$  Hz, 1H, H13), 7.01 (d,  $^3J = 1.9$  Hz, 1H, H20), 6.95 (d,  $^3J = 1.8$  Hz, 1H, H3), 4.47–4.15 (m, 6H, H4, H15, H22), 1.58 (s, 15H, H18), 1.55 (s, 15H, H25), 1.53–1.49 (m, 9H, H5, H16, H23) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ): (minor product, **[4b]**)  $\delta$  = 180.1 (d,

$^1J_{C,Rh} = 53.4$  Hz, C14), 179.2 (d,  $^1J_{C,Rh} = 52.2$  Hz, C21), 173.6 (C1), 155.3 (C9), 144.4 (d,  $^1J_{C,Rh} = 39.3$  Hz, C8), 143.8 (C11), 143.0 (C7), 137.9 (d,  $^1J_{C,Rh} = 40.2$  Hz, C10), 127.7 (C2), 122.6 (C19), 120.1 (C13), 117.4 (C3), 117.9 (C20), 116.2 (C12), 109.2 (C6), 98.0 (d,  $^1J_{C,Rh} = 5.0$  Hz, C17), 97.8 (d,  $^1J_{C,Rh} = 5.1$  Hz, C24), 46.3 (C4), 45.1 (C15), 45.0 (C22), 16.7 (C5), 16.3 (C16), 16.1 (C23), 10.0 (C25), 9.3 (C18) ppm. MS (ESI, positive ions):  $m/z = 1191.0389$  (calcd for  $[[\mathbf{4b}]-Br]^+$  1191.0380) and 1147.0894 (calcd for  $[[\mathbf{4a}]-Br]^+$  1147.0885). Satisfactory microanalytical data could not be obtained due to halide scrambling.

**X-ray Crystallography:** X-ray diffraction data were collected at  $T = 153(2)$  K with a Bruker APEX-II CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97 package<sup>3</sup> using direct methods and were refined with SHELXL-97 against  $|F^2|$  of all data using first isotropic and later anisotropic thermal parameters (for exceptions see description of the individual molecular structures). Hydrogen atoms were added to the structure models on calculated positions.

**[3]:** Crystals of  $[\mathbf{3}] \cdot 0.75C_6H_5Br \cdot CH_3CN$  suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a saturated acetonitrile/bromobenzene solution of  $[\mathbf{3}]$ .  $C_{57.50}H_{72.75}Br_{3.75}N_7IrRh_2$ ,  $M = 1559.66$  g·mol<sup>-1</sup>, orange crystal, 0.32 x 0.32 x 0.25 mm<sup>3</sup>, orthorhombic, space group  $Pbca$ ,  $Z = 8$ ,  $a = 22.4122(4)$  Å,  $b = 22.5470(4)$  Å,  $c = 22.8436(4)$  Å,  $V = 11543.5(4)$  Å<sup>3</sup>,  $\rho_{calc} = 1.795$  g·cm<sup>-3</sup>,  $\mu = 5.504$  mm<sup>-1</sup>,  $\omega$ - and  $\varphi$ -scans, 202471 measured intensities ( $5.40^\circ \leq 2\theta \leq 61.02^\circ$ ), semiempirical absorption correction ( $0.2718 \leq T \leq 0.3399$ ), 17599 independent ( $R_{int} = 0.0789$ ) and 14811 observed intensities ( $I \geq 2\sigma(I)$ ), refinement of 698 parameters against  $|F^2|$  of all measured intensities with hydrogen atoms on calculated positions.  $R = 0.0238$ ,  $wR = 0.0658$ ,  $R_{all} = 0.0313$ ,  $wR_{all} = 0.0675$ . The three metal centers are disordered over three positions and each position contains 1/3 of iridium atom and 2/3 of a rhodium atom. The asymmetric unit contains, apart from  $[\mathbf{3}]$ ,  $\frac{3}{4}$  of a bromobenzene molecule and one acetonitrile molecule.

**[4b]:** Crystals of  $[\mathbf{4b}] \cdot CH_3CN$  suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a saturated acetonitrile solution of  $[\mathbf{4b}]$ .  $C_{43}H_{55}N_7AuBr_3Rh_2$ ,  $M =$

