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Supporting Information

Heterobimetallic Rhodium-Gold Halide and Hydride Complexes

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Experimental Methods

General Considerations. All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox using solvents previously dried by passage through an alumina column under argon. The starting materials bis(dicyclohexylphosphino)methane (dcpm), bis(diphenylphosphino)methane (dppm) and $[Rh^{I}(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) were obtained from Strem Chemicals. Bromine, $LiHBEt_3$ (1 M in THF), 2,6-lutidine, 2 M HCl/Et_2O solution, ammonium hexafluorphosphate and sodium trifluoromethanesulfonate (NaOTf) were obtained from Sigma-Aldrich, whereas CO was purchased from BOC (Grade 2.3). Chlorine was delivered as the iodobenzene adduct $PhICl_2$.[1] $[Rh^{I}(COD)Br]_2$ was prepared according to the literature.[2] The gold(I) starting materials $Au^{I}(tht)Cl$ (tht = tetrahydrothiophene) and $Au^{I}(tht)Br$ were synthesised as previously described.[3] For additions of Br_2 to reactions, a stock solution was prepared using a weighed amount of bromine, and then an appropriate aliquot was added using an autopipet. 2,6-Lutidinium hydrochloride ($LutH^{+}Cl^{-}$) was synthesised by reacting 2,6-lutidine with HCl (2 M Et_2O solution).

Physical Methods. All NMR spectra were recorded at the MIT Department of Chemistry Instrumentation Facility on a Varian Mercury 300 NMR Spectrometer, a Varian Inova-500 NMR Spectrometer or a Bruker Avance-400 Spectrometer. $^{31}P\{^{1}H\}$ NMR spectra were referenced to an external standard of 85% D_3PO_4 and ^{1}H spectra were referenced to the residual proteo solvent resonances. UV-vis spectra were recorded at 293 K in CH_2Cl_2 solutions in quartz cuvettes on a Varian Cary 5000 UV-vis-NIR spectrophotometer. Extinction coefficients were determined over a concentration range of ~2 – 50 μM, for which all compounds obeyed Beer's Law. Steady state emission spectra were recorded on an automated Photon Technology International (PTI) QM 4 fluorimeter equipped with a 150-W Xe arc lamp and a Hamamatsu R928 photomultiplier tube. Excitation light was excluded with appropriate glass filters. Samples were housed in custom quartz EPR tubes with a ground-glass joint and Teflon plug. Solution samples were prepared in 1:1 CH_2Cl_2/toluene and freeze pump thaw degassed (4 cycles, 1×10^{-5} torr). Spectra were recorded at 77 K by immersion of the sealed EPR tubes into a liquid nitrogen filled quartz dewar. IR spectra of powdered samples were recorded on a PerkinElmer Spectrum 400 FT-IR/FT-FIR Spectrometer outfitted with a Pike Technologies GladiATR attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp.

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1 A. Zielinska and and L. Skulski, *Tetrahedron Lett.,* 2004, **45**, 1087.

2 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1990, **28**, 88.

3 R. Usón, A. Laguna, and M. Laguna, *Inorg. Synth.,* 1989, **26**, 85.

Photochemistry. Photochemical reactions were performed using a 1000 W high-pressure Hg/Xe arc lamp (Oriel). The beam was passed through a water-jacketed filter holder containing appropriate long pass filters, an iris and collimating lens. Samples for all photolysis experiments were prepared in a nitrogen-filled glovebox in quartz cuvettes equipped with a magnetic stir bar and a threaded screw-cap and kept rigorously excluded from light until the start of irradiation. Monochromatic light was generated by combining the output from a long-pass filter with a Hg line filter of the appropriate wavelength. For quantum yield measurements, potassium ferrioxalate was synthesised via a published procedure and used as a chemical actinometer.[4] The photon flux was determined from the average of the actinometric measurements collected before and after irradiation of a set of three samples. UV-vis spectra for steady-state photolysis experiments and quantum yield measurements were recorded on a Spectral Instruments 400 diode array spectrophotometer and were blanked to the appropriate solvent.

GC Measurements. Gas quantification measurements were performed on an Agilent 7890A GC System equipped with an Agilent G3432A EPC Thermal Conductivity Detector. The oven temperature was 150 °C, the rate of the N_2 makeup flow set to 3 ml/min, and the N_2 reference flow adjusted to 5 ml/min (N_2 was supplied by Airgas, UHP grade). A calibration curve was generated using gas mixtures of N_2/H_2 with known ratios.

Preparation of $[Rh^IAu^I(dcpm)_2(CO)Cl](PF_6)$ [1-(PF_6)]. A solution of $[Rh^I(COD)Cl]_2$ (186 mg, 0.377 mmol, 1.00 eq) in 10 mL of CH_2Cl_2 was prepared in the glovebox and contained in a 100 mL Schlenk flask. A solution of dcpm (616 mg, 1.51 mmol, 4.00 eq) in 10 mL of CH_2Cl_2 was added dropwise to afford a bright orange solution. The solution was bubbled with CO gas for 10 min (oil bubbler pressure) with no noticeable colour change. At this time, Au^I(tht)Cl (242 mg, 0.754 mmol, 2.00 eq) dissolved in 10 mL of CH_2Cl_2 was added, resulting in a lighter yellow-orange solution. The solution was stirred at room temperature for 30 min and then filtered through a plug of glass wool in open air. A solution of NH_4PF_6 (307 mg, 1.89 mmol, 5.00 eq) in 20 mL of MeOH was added with stirring. The resulting solution was concentrated by rotary evaporation to <10 mL, resulting in the formation of a yellow-orange solid which was collected by filtration, washed with 10 mL of MeOH and dried in vacuo. Yield: 831 mg (83.1%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm: 2.53 – 2.64 (m, 2H), 2.45 – 2.53 (br, m, 4H), 2.21 – 2.30 (m, 4H), 2.14 – 2.20 (br, d, 2H), 1.13 – 2.12 (br, m, 80H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ / ppm: 52.9 (m, 2P), 34.8 (dm, $^1J_{Rh–P}$ = 114 Hz, 2P), –144.1 (sept., $^1J_{P–F}$ = 711 Hz, 1P). UV-vis (CH_2Cl_2): λ / nm (ε / M^{-1} cm^{-1}) 263 (9700), 291 (sh) (5100), 418 (14000). IR (solid): $\tilde{\nu}_{CO}$ = 1953 cm^{-1}. Anal. Calcd. for $C_{51}H_{92}AuClF_6RhOP_5$: C, 46.21; H, 7.00. Found: C, 46.28; H, 6.83.

4 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry*, 3rd ed.; Taylor and Francis: Boca Raton, 2006.

Preparation of [$Rh^IAu^I(dcpm)_2(CO)Br](PF_6)$ [2-(PF_6)]. [$Rh^I(COD)Br]_2$ (212 mg ,0.365 mmol, 1.00 eq) was dissolved in 10 mL of CH_2Cl_2. With stirring, dcpm (596 mg, 1.46 mmol, 4.00 eq) in 10 mL of CH_2Cl_2 was added dropwise to give a bright orange solution. CO was bubbled through the solution for 15 min with no colour change. Addition of Au^I(tht)Br (266 mg 0.730 mmol, 2.00 eq) dissolved in 10 mL CH_2Cl_2 effects a colour change to yellow. The solution was stirred under a CO atmosphere for 60 min and afterwards filtered through a plug of glass wool. A solution of NH_4PF_6 (300 mg, 1.82 mmol, 5.00 eq) in 20 mL of MeOH was added, stirred for 5 min and concentrated to <10 mL by rotary evaporation. A light orange solid was collected by filtration, washed with MeOH and dried in vacuo. Yield: 832 mg (83.2%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm: 2.55 – 2.73 (m, 6H), 2.12 – 2.36 (m, 6H), 1.10 – 2.12 (m, 80H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ / ppm: 52.5 (m, 2P), 33.7 (dm, $^1J_{Rh–P}$ = 113 Hz, 2P), –144.1 (sept., $^1J_{P–F}$ = 711 Hz, 1P). UV-vis (CH_2Cl_2): λ / nm (ε / (M^{-1} cm^{-1}) 263 (9300), 305 (6000), 423 (14000). IR (solid): $\tilde{\nu}_{CO}$ = 1955 cm^{-1}. Anal. Calcd. for $C_{51}H_{92}AuBrF_6RhOP_5$: C, 44.71; H, 6.77; Found: C, 44.56; H, 6.65.

Preparation of [$Rh^IAu^I(dppm)_2(CO)Cl](PF_6)$ [3-(PF_6)]. In a scintillation vial equipped with a stir bar, [$Rh^I(COD)Cl]_2$ (186 mg, 0.377 mmol, 1.00 eq) was dissolved in 10 mL of CH_2Cl_2 with stirring giving a dark yellow solution. A sample of dppm (580 mg, 1.51 mmol, 4.00 eq) was dissolved in 10 mL of CH_2Cl_2 and added dropwise, causing a colour change to orange. After stirring the solution at RT for 10 min, CO was bubbled through it for 15 min. Au^I(tht)Cl (242 mg, 0.754 mmol, 2.00 eq) dissolved in 10 mL CH_2Cl_2 was added and the solution stirred for 30 min. Addition of NH_4PF_6 (308 mg, 1.89 mmol, 5.00 eq) that was dissolved in 20 mL of MeOH gave an orange solution. Upon concentrating the solution to <10 mL by rotary evaporation, an orange solid precipitated. The solid was collected by filtration, washed with methanol and dried in vacuo. Yield: 779 mg (80.9%). ^{1}H NMR (500 MHz, CD_3CN) δ / ppm: 7.89 – 7.91 (m, 4H), 7.79 – 7.86 (m, 4H), 7.64 – 7.71 (m, 4H), 7.39 – 7.60 (m, 22H), 7.21 – 7.27 (m, 2H), 7.05 – 7.12 (m, 4H), 4.15 – 4.30 (m, 4H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN) δ / ppm: 36.9 (m, 2P), 28.3 (dm, $^1J_{Rh–P}$ = 120 Hz, 2P), –143.4 (sept., $^1J_{P–F}$ = 706 Hz, 1P). UV-vis (CH_2Cl_2): λ / nm (ε / (M^{-1} cm^{-1}) 424 (15000). IR (solid): $\tilde{\nu}_{CO}$ = 1966 cm^{-1}. Anal. Calcd. for $C_{51}H_{44}AuClF_6RhOP_5$: C, 47.96; H, 3.47; Found: C, 47.58; H, 3.45.

Preparation of [$Rh^IAu^I(dppm)_2COBr](SO_3CF_3)$ [4-(OTf)]. In a scintillation vial equipped with a stir bar, [$Rh^I(COD)Br]_2$ (146 mg, 0.250 mmol, 1.00 eq) was dissolved in 6 mL of CH_2Cl_2 with stirring to afford a dark yellow solution. To this solution was added dppm (384 mg, 1 mmol, 4.00 eq) dissolved in 5 mL of CH_2Cl_2, resulting in a colour change to orange. After stirring the solution at RT for 10 min, CO was bubbled through it for 15 min. Au^I(tht)Br (183 mg, 0.500 mmol, 2.00 eq) dissolved in 5 mL CH_2Cl_2 was added and the solution stirred for 30 min.

Addition of NaOTf (430 mg, 2.50 mmol, 10.0 eq) that was dissolved in 10 mL MeOH produced an orange solution. Concentrating the solution to <10 mL by rotary evaporation caused an orange solid to precipitate. The solid was collected by filtration, washed with methanol and dried in vacuo. Yield: 490 mg (73.9%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm: 7.80 – 7.91 (m, 4H), 7.65 – 7.75 (m, 4H), 7.36 – 7.63 (m, 22H), 7.25 – 7.34 (m, 4H), 7.18 – 7.24 (m, 2H), 7.00 – 7.07 (m, 4H), 4.35 – 4.48 (m, 2H), 4.02 – 4.12 (m, 2H). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ / ppm: 32.4 (m, 2P), 24.2 (dm, $^1J_{Rh–P}$ = 119 Hz, 2P). UV-vis (CH_2Cl_2): λ / nm (ε / (M^{-1} cm^{-1}) 430 (12000). IR (solid): $\tilde{\nu}_{CO}$ = 1966 cm^{-1}. Anal. Calcd. for $C_{52}H_{44}AuBrF_3RhO_4P_4S$: C, 47.11; H, 3.35; Found: C, 46.86; H, 3.29.

Preparation of [Rh^{II}Au^{II}(dcpm)$_2$COCl$_3$](PF$_6$) [5-(PF$_6$)]. A sample of **1** (100 mg, 0.0750 mmol, 1.00 eq) was dissolved in 10 mL of CH_2Cl_2 and frozen in the coldwell of the glovebox. Upon thawing a cold solution of $PhICl_2$ (22.0 mg 0.0800 mmol, 1.05 eq), dissolved in 10 mL of CH_2Cl_2, was added dropwise, giving a dark red solution that was stirred at RT for 30 min. Addition of 18 mL of pentane affords a red solid which was isolated by decantation and washed with 10 mL of pentane twice. Yield: 102 mg (96.9%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm: 3.40 – 3.55 (m, 2H), 3.19 – 3.32 (m, 2H), 2.83 – 3.02 (m, 4H), 2.68 – 2.80 (m, 2H), 2.49 – 2.63 (m, 4H), 1.20 – 2.40 (m, 78H). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ / ppm: 37.8 (pseudotriplet, 2P), 20.2 (doublet of pseudotriplets, $^1J_{Rh–P}$ = 74 Hz, 2P), –144.1 (sept., $^1J_{P–F}$ = 711 Hz, 1P). UV-vis (CH_2Cl_2): λ / nm (ε / (M^{-1} cm^{-1}) 306 (26000), 372 (20000), 450 (6200). IR (solid): $\tilde{\nu}_{CO}$ = 2030 cm^{-1}. Anal. Calcd. for $C_{51}H_{92}AuCl_3F_6RhOP_5$: C, 43.87; H, 6.64; Found: C, 44.51; H, 6.60.

Preparation of [Rh^{II}Au^{II}(dcpm)$_2$COBr$_3$](PF$_6$) [6-(PF$_6$)]. In 4 mL of CH_3CN **2** (100 mg, 0.073 mmol, 1.00 eq) was dissolved. Br_2 (12.2 mg, 0.0763 mmol, 1.05 eq) that was dissolved in 157 µL of CH_3CN was added and the solution stirred at RT for 15 min during which time a solid started to precipitate. The solution was concentrated at the rotary evaporator and the resulting dark solid dried in vacuo. The solid was redissolved in 2 mL of CH_2Cl_2 and precipitated with Et_2O. The solvent was removed via pipet and the red solid dried in vacuo. Yield: 103 mg (92.2%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm: 3.65 – 3.76 (m, 2H), 3.41 – 3.54 (m, 2H), 3.13 – 3.27 (m, 2H), 2.87 – 3.00 (m, 2H), 2.70 – 2.87 (m, 2H), 2.52 – 2.71 (m, 4H), 2.37 (br, d, 2H), 2.28 (br, d, 2H), 1.20 – 2.17 (m, 74H). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ / ppm: 32.8 (pseudotriplet, 2P), 14.3 (doublet of pseudotriplets, $^1J_{Rh–P}$ = 74 Hz, 2P), –144.1 (sept., $^1J_{P–F}$ = 711 Hz, 1P). UV-vis (CH_2Cl_2): λ / nm (ε / (M^{-1} cm^{-1}) 335 (26000), 426 (13000). IR (solid): $\tilde{\nu}_{CO}$ = 2028 cm^{-1}. Anal. Calcd. for $C_{51}H_{92}AuBr_3F_6RhOP_5$: C, 40.04; H, 6.06; Found: C, 40.17; H, 6.06.

Preparation of [Rh^{II}Au^{II}(dppm)$_2$COCl$_3$](PF$_6$) [7-(PF$_6$)]. $PhICl_2$ (11.3 mg, 0.0411 mmol, 1.05 eq) was dissolved in 1 mL of CH_2Cl_2 and frozen in the coldwell of the glovebox. **3**-(PF_6) (50.0 mg, 0.0392 mmol, 1.00 eq) was dissolved in 5 mL of CH_2Cl_2 and likewise frozen. Upon thawing

the solution of $PhICl_2$ was added dropwise, effecting a colour change from yellow to deep red. The resulting solution was frozen in the coldwell again to avoid decomposition of the product which is stable below –20 °C but decomposes rapidly at RT. The instability of the product precluded determination of the isolated yield and further characterisation, though NMR indicates a clean conversion. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ / ppm: 27.7 (pseudotriplet, 2P), 11.3 (doublet of pseudotriplets, $^1J_{Rh–P}$ = 78 Hz, 2P), –143.4 (sept., $^1J_{P–F}$ = 708 Hz, 1P).

Preparation of $[Rh^{II}Au^{II}(dppm)_2COBr_3](SO_3CF_3)$ [8-(OTf)]. **4**-(OTf) (25.0 mg, 0.0188 mmol, 1.00 eq) was dissolved in 5 mL of CH_2Cl_2 and cooled to –78 °C with a dry ice/acetone bath. Br_2 (3.15 mg, 0.0197 mmol, 1.05 eq) in 0.167 mL of CH_2Cl_2 was added to the cold solution of **4** resulting in an immediate colour change to dark red. The solution was kept in the cold to avoid decomposition of the product. Due to the thermal instability of the product it was not possible to determine the yield or perform further characterisation. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ / ppm: 20.5 (pseudotriplet, 2P), 3.4 (doublet of pseudotriplets, $^1J_{Rh–P}$ = 79 Hz, 2P).

Preparation of $[Rh^IAu^I(dcpm)_2COH](PF_6)$ [9]. **1**-(PF_6) (300 mg, 0.226 mmol, 1.00 eq) was dissolved in 10 mL of THF and the solution frozen in the coldwell of the glovebox. Upon thawing a 1 M $LiHBEt_3$ solution in THF (0.238 mL, 0.238 mmol, 1.05 eq) was added. The solution was allowed to warm to RT and stirred for 1 h, giving a dark red solution. The solvent was removed in vacuo to afford a red-orange residue. The residue was triturated with 4 mL of Et_2O to afford an orange solid, and subsequently the Et_2O was removed in vacuo. The resulting solid was taken up in 6 mL of benzene and filtered through celite. Evaporation of the benzene yielded a red-orange solid, which was washed with 2 × 5 mL of Et_2O to remove a dark red impurity. The resulting orange solid was dried in vacuo. Yield: 250 mg (85.5%). ^1H NMR (500 MHz, C_6D_6) δ / ppm: 2.63 – 2.77 (m, 4H), 2.33 – 2.48 (m, 4H), 1.98 – 2.33 (m, 20H), 1.00 – 1.96 (m, 64H), –4.40 (nonet,, 1H, $^1J_{H–Rh}$ = $^2J_{H–P}$ = 12 Hz, $^3J_{H–P}$ = 6 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6) δ / ppm: 54.6 (m, 2P), 50.4 (dm, $^1J_{Rh-P}$ = 137 Hz, 2P), -144.1 (sept., $^1J_{P-F}$ = 711 Hz, 1P). UV-vis (C_6H_6): λ / nm (ε/(M^{-1} cm^{-1}) 359 (5000), 472 (16000). IR (solid): $\tilde{\nu}_{CO}$ = 1948 cm^{-1}. Anal. Calcd. for $C_{51}H_{93}AuF_6RhOP_5$: C, 47.45; H, 7.26; Found: C, 47.49; H, 7.31.

Reactions of 9 with $LutH^+Cl^-$ and $PhICl_2$. Samples for all experiments were prepared in a nitrogen-filled glovebox. In a typical experiment **9** (25 mg, 0.019 mmol, 1.0 eq) was weighed into a scintillation vial, dissolved in 2 mL of CH_3CN and sealed with a septum. Lutidinium hydrochloride (3.0 mg 0.021 mmol, 1.1 eq) or $PhICl_2$ (2.9 mg, 0.010 mmol, 0.55 eq), dissolved in CH_3CN, were added via syringe from stock solutions prepared previously in the glovebox. The reaction was stirred for 5 min at RT before a 10 μL sample of the headspace gas was removed by syringe and injected directly into the GC.

X-Ray Crystallographic Details. Single crystals of **1** and **5** were obtained by layering a CH_2Cl_2 solution with diethyl ether, crystals of **2** were grown by vapor diffusion of diethyl ether into an acetonitrile solution, crystals of **3** and **4** were grown by layering CH_2Cl_2 solutions with pentane, crystals of **6** were obtained by layering a CH_2Cl_2 solution with methanol/diethyl ether, and crystals of **9** were obtained from a C_6D_6 NMR sample layered with diethyl ether. The crystals were mounted on a Bruker three circle goniometer platform equipped with an APEX detector. A graphite monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and refined using the program SAINT supplied by Siemens Industrial Automation. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms bonded to carbon were placed in calculated positions using the standard riding model and refined isotropically; all other atoms were refined anisotropically. The rhodium-bound hydrogen atom in **9** was located in the difference map and refined semi-freely. A positional disorder of the CO ligand and the halide *trans* to it was present in the structures of **2**, **5**, and **6**. The thermal displacement parameters of the CO ligand in the minor disordered component were constrained to be identical to those of the CO ligand in the major component. The structures of **1**, **4**, **5**, and **6** all contained one dichloromethane solvate molecule that was modeled as a two-part disorder. In **1**, **2**, and **9**, one of the cyclohexyl groups was found to be disordered over two sites, and an analogous 2-part disorder was observed for one phenyl ring in **4**. In **9**, the Rh···Au core was found to be disordered over two sites. The (1,2) and (1,3) distances of all disordered parts were restrained to be similar using the SADI command; the rigid-bond restraints SIMU and DELU were also used on disordered parts. The structures of **1** and **4** had one and two A-level checkcif alerts respectively. These alerts are attributed to close contacts between disordered parts and were not deemed to be serious errors. Unit cell parameters, morphology, and solution statistics for the structures of **1**, **2**, **3**, **4**, **5**, **6** and **9** are summarised in Tables S1 and S2. All thermal ellipsoid plots are drawn at 50% probability level, with hydrogen atoms, counterions, and solvent molecules omitted.

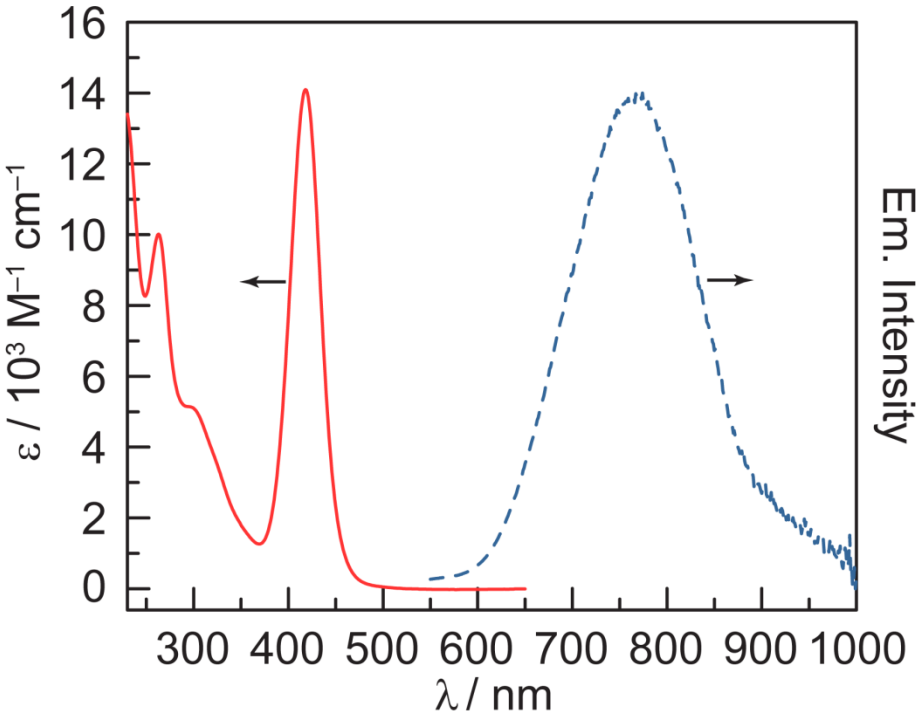

Figure S1. Absorption (—, red) and glass emission (– – –, blue) spectra of $[Rh^{I}Au^{I}(dcpm)_2(CO)Cl](PF_6)$ (**1**-(PF_6)). The absorption spectrum was recorded at 293 K in CH_2Cl_2 solution. The emission spectrum (λ_{exc} = 418 nm) was recorded at 77 K; the frozen glass was of a 1:1 CH_2Cl_2/toluene solvent mixture.

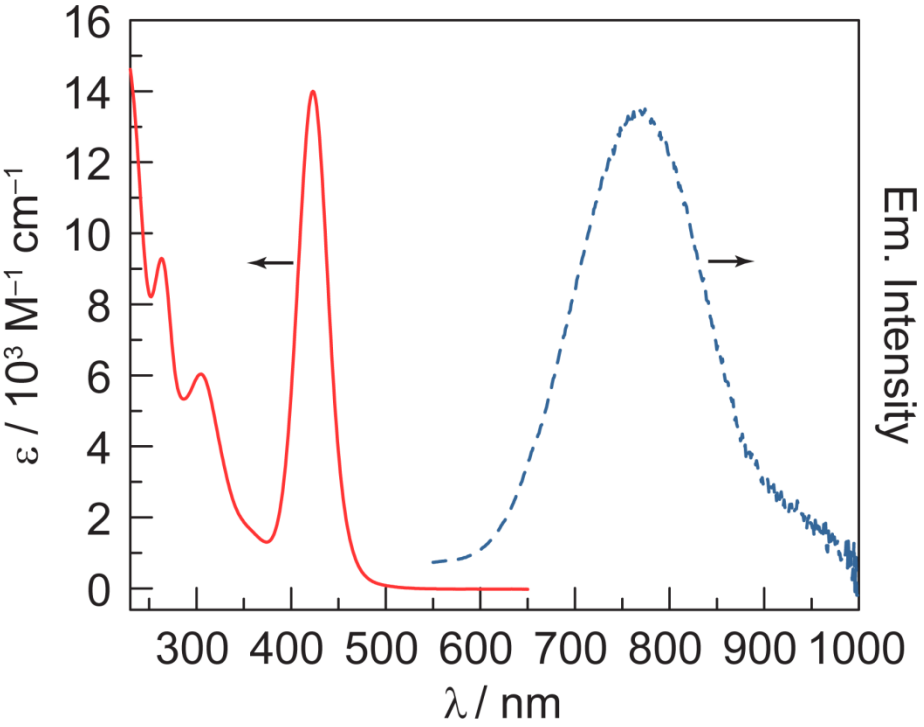

Figure S2. Absorption (—, red) and glass emission (— — —, blue) spectra of $[Rh^{I}Au^{I}(dcpm)_2(CO)Br](PF_6)$ (**2**-(PF_6)). The absorption spectrum was recorded at 293 K in CH_2Cl_2 solution. The emission spectrum (λ_{exc} = 423 nm) was recorded at 77 K; the frozen glass was of a 1:1 CH_2Cl_2/toluene solvent mixture.

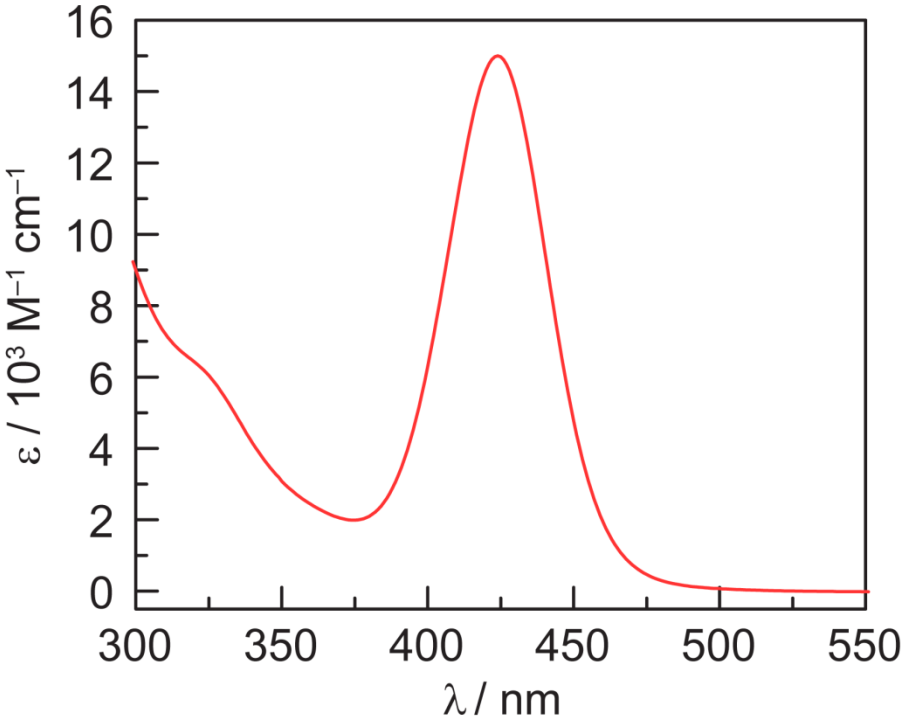

Figure S3. Electronic absorption spectrum of $[Rh^{I}Au^{I}(dppm)_2(CO)Cl](PF_6)$ (**3**-(PF_6)) recorded at 293 K in CH_2Cl_2.

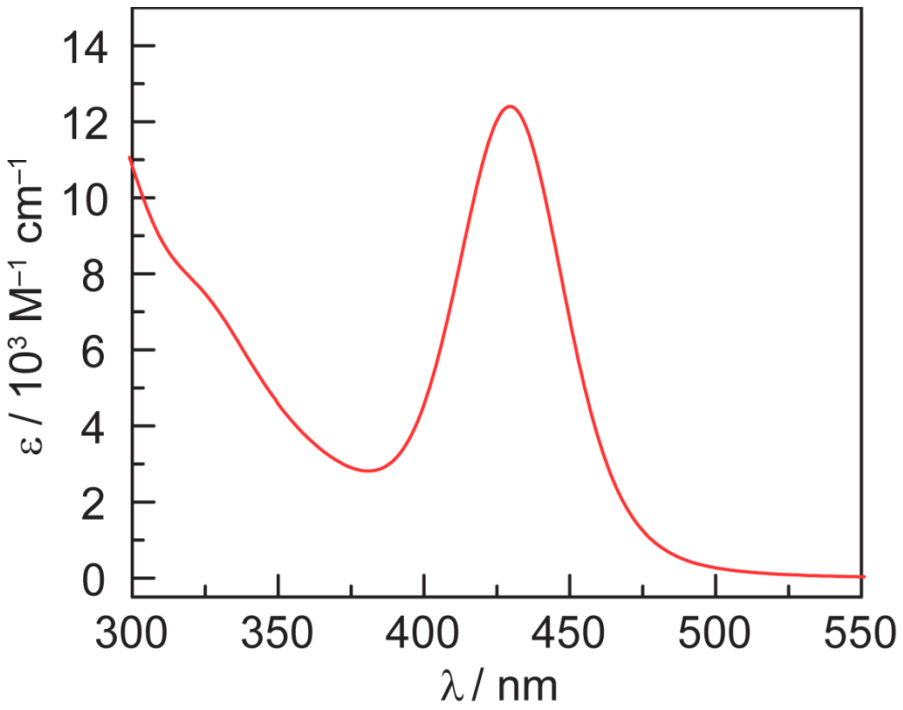

Figure S4. Electronic absorption spectrum of $[Rh^{I}Au^{I}(dppm)_2(CO)Br](OTf)$ (**4**-(OTf)) recorded at 293 K in CH_2Cl_2.

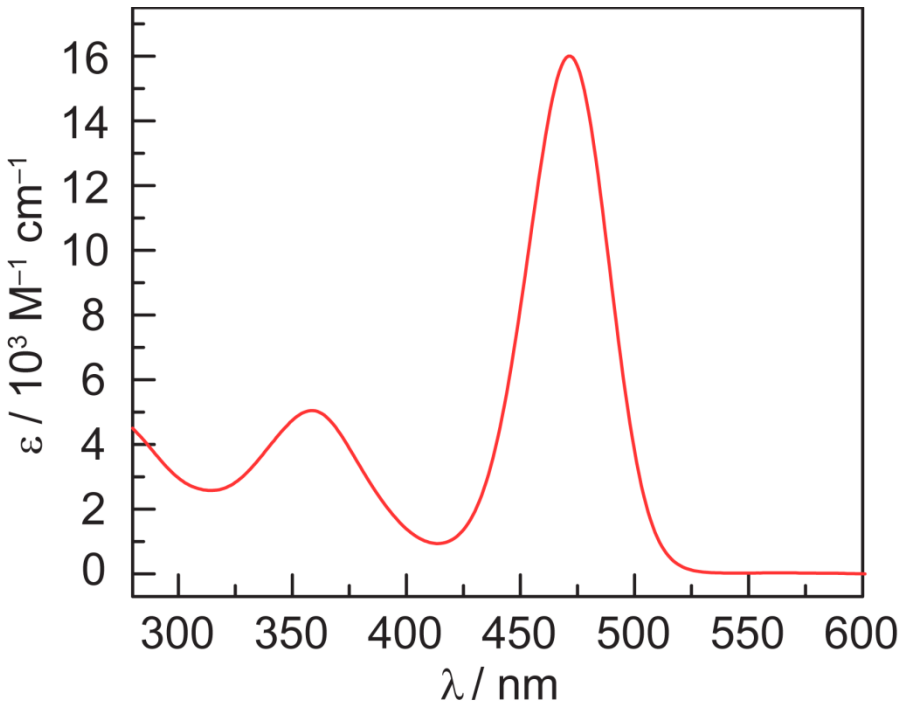

Figure S5. Electronic absorption spectrum of $[Rh^{I}Au^{I}(dcpm)_2(CO)H](PF_6)$ (**9**) recorded at 293 K in C_6H_6.

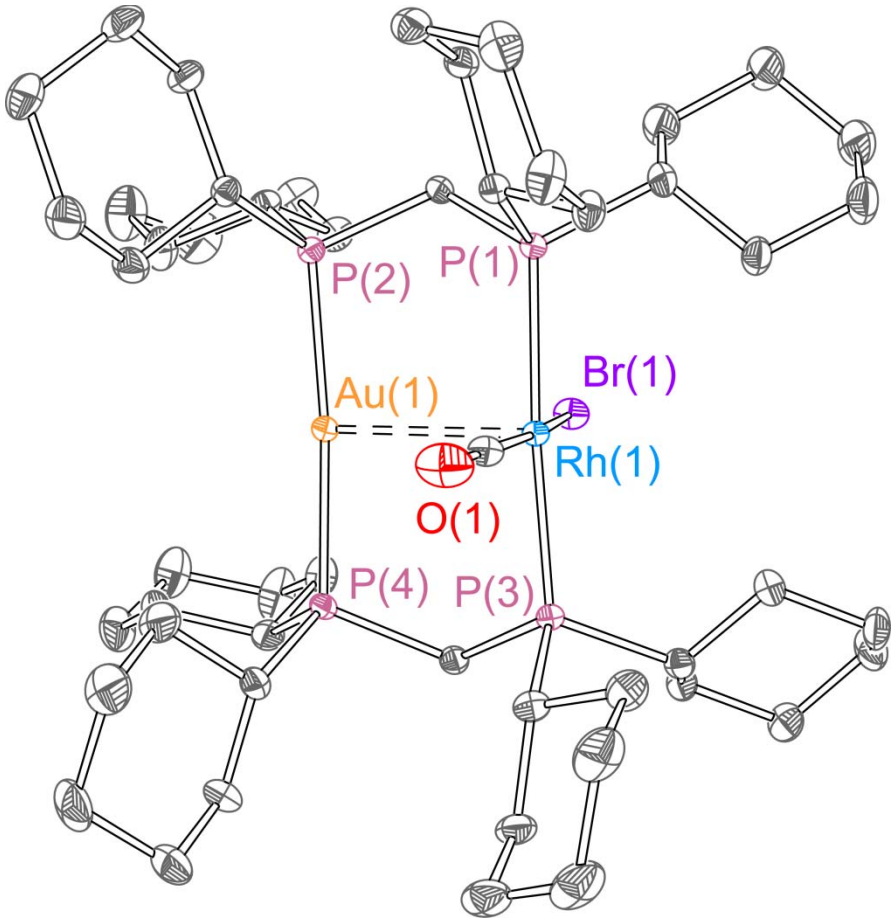

Figure S6. Thermal ellipsoid plot for **2**. Ellipsoids are shown at 50% probability level with counterions, solvent molecules and hydrogen atoms omitted for clarity. Data was collected at 100 ± 2 K. The metal-metal distance is d(Rh···Au) = 2.9187(2) Å.

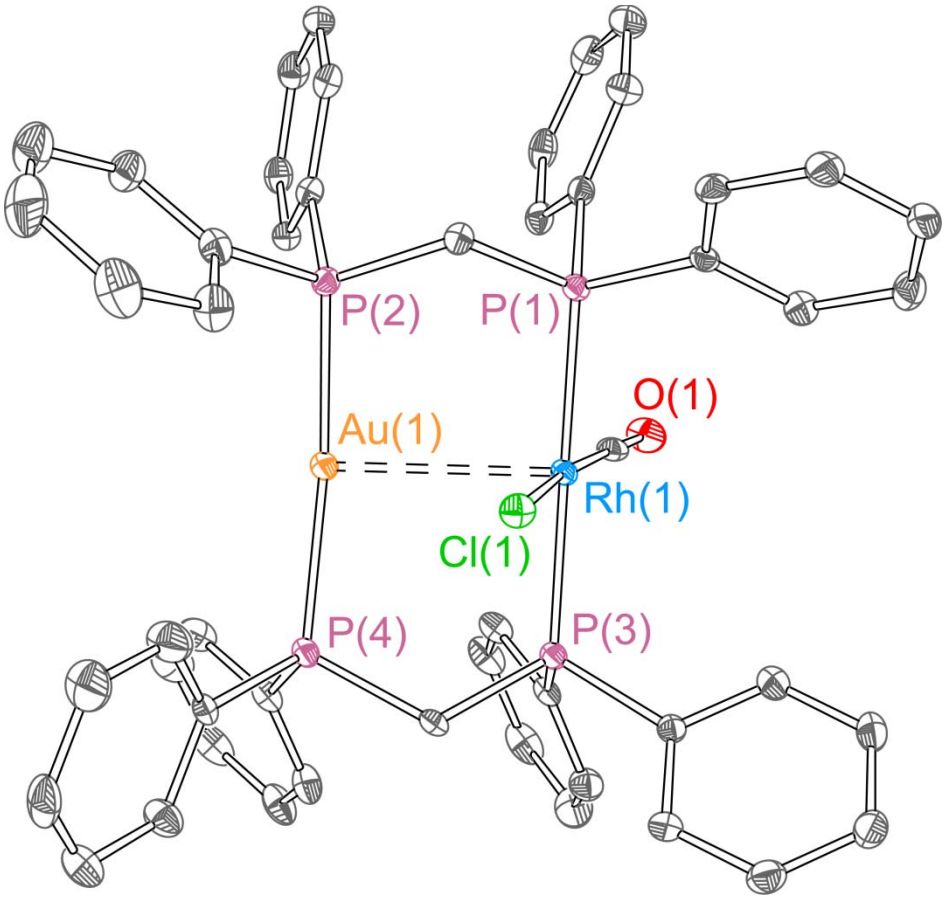

Figure S7. Thermal ellipsoid plot for **3**. Ellipsoids are shown at 50% probability level with counterions, solvent molecules and hydrogen atoms omitted for clarity. Data was collected at 100 ± 2 K. The metal-metal distance is d(Rh···Au) = 2.9551(3) Å.

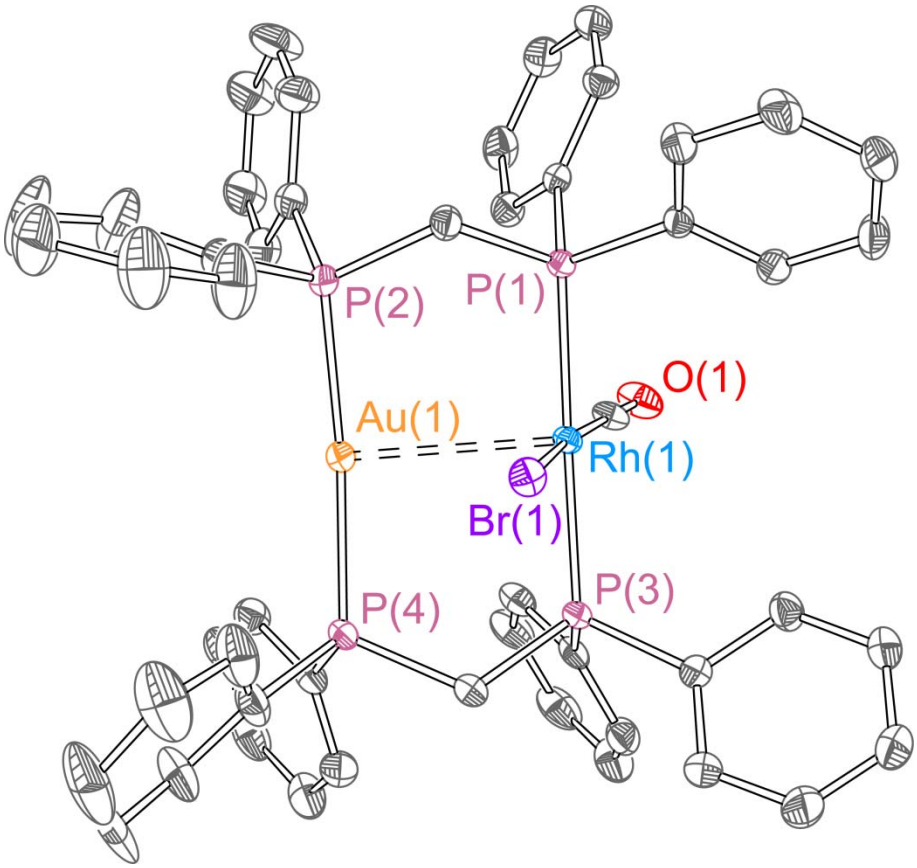

Figure S8. Thermal ellipsoid plot for **4**. Ellipsoids are shown at 50% probability level with counterions, solvent molecules and hydrogen atoms omitted for clarity. Data was collected at 100 ± 2 K. The metal-metal distance is d(Rh···Au) = 2.9537(5) Å.

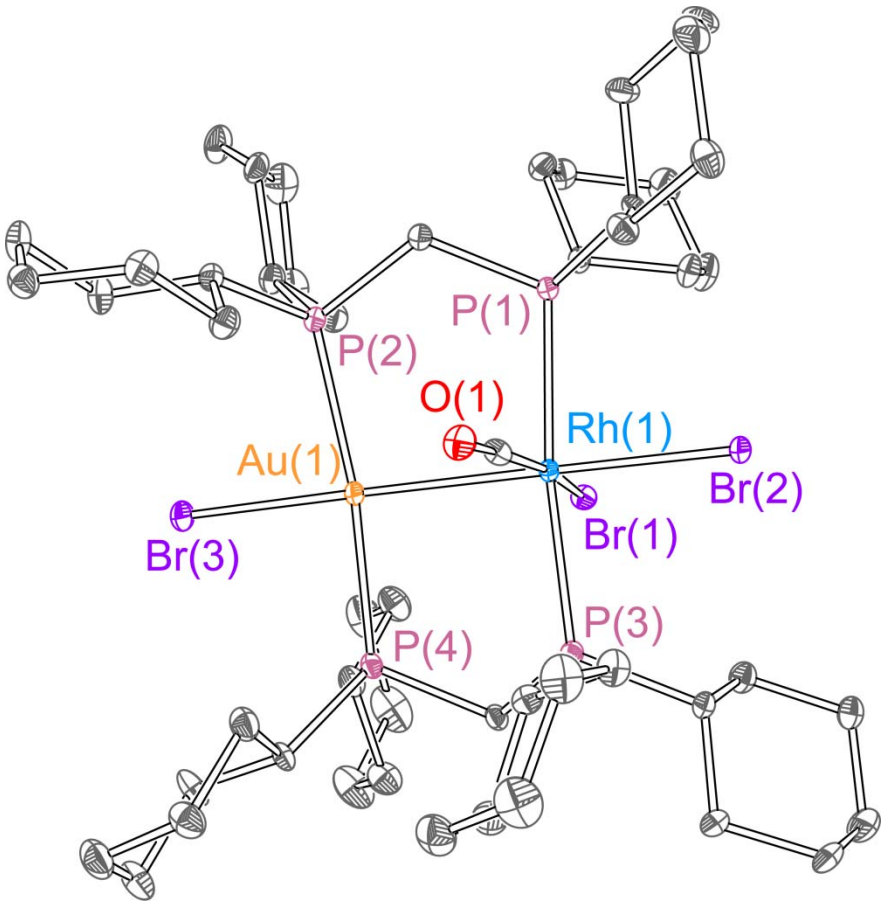

Figure S9. Thermal ellipsoid plot for **6**. Ellipsoids are shown at 50% probability level with counterions, solvent molecules and hydrogen atoms omitted for clarity. Data was collected at 100 ± 2 K. The metal-metal distance is d(Rh—Au) = 2.6960(3) Å.

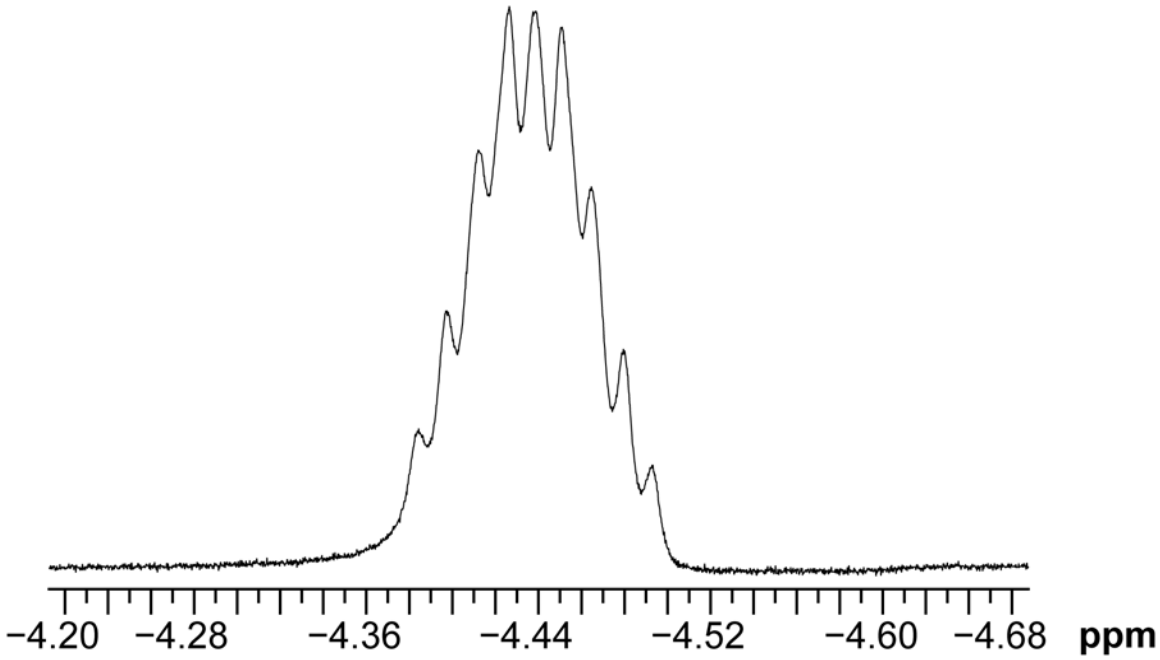

Figure S10. Low-frequency region of the ^{1}H NMR spectrum of $[Rh^{I}Au^{I}(dcpm)_2(CO)H](PF_6)$ (**9**), showing the characteristic nine-line pattern of the Rh–*H* resonance. Spectrum was recorded at 293 K in C_6D_6.

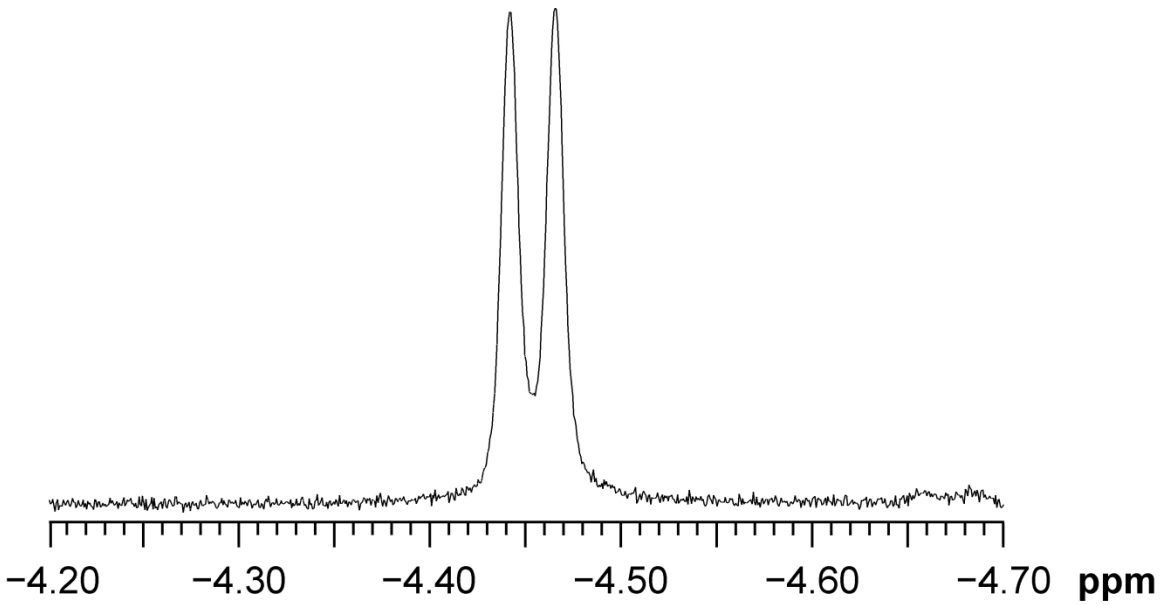

Figure S11. Low-frequency region of the $^{1}H\{^{31}P\}$ NMR spectrum of $[Rh^{I}Au^{I}(dcpm)_2(CO)H](PF_6)$ (**9**), showing only the $^{1}J_{H-Rh}$ coupling of the Rh–*H* resonance. Spectrum was recorded at 293 K in C_6D_6.

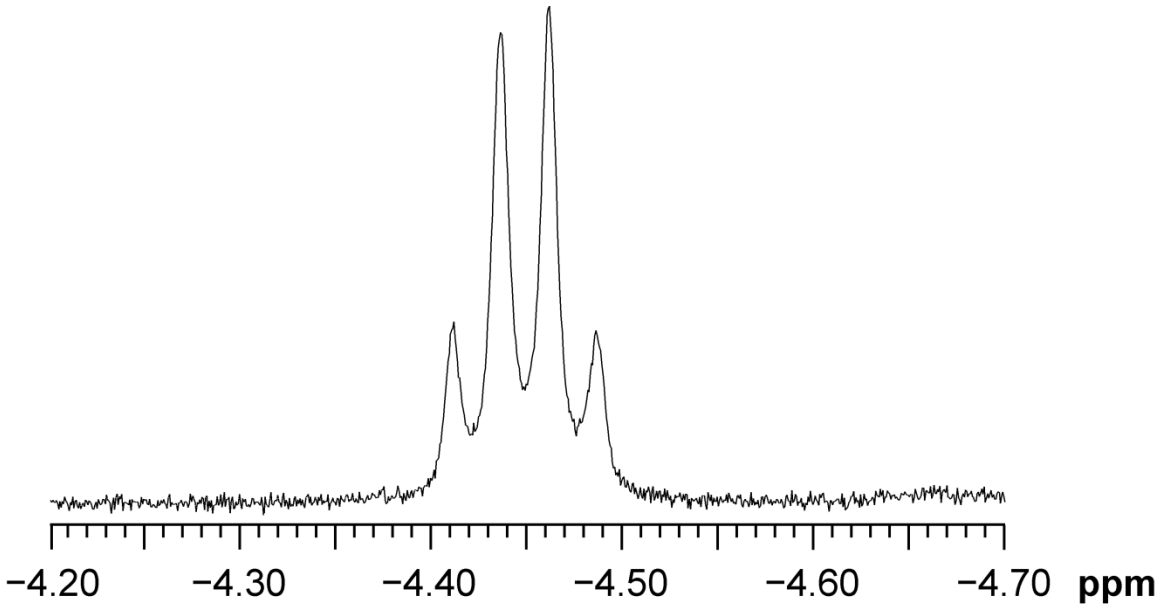

Figure S12. Low-frequency region of the $^{1}H\{^{31}P\}$ NMR spectrum of $[Rh^{I}Au^{I}(dcpm)_2(CO)H](PF_6)$ (**9**), with partial ^{31}P decoupling. Only the $^{1}J_{H–Rh}$ and $^{2}J_{H–P}$ coupling of the Rh–*H* resonance are observed. Spectrum was recorded at 293 K in C_6D_6.

Table S1. Crystallographic Summary for Complexes **1, 2, 3, 4**.

	1-(PF_6)•CH_2Cl_2	**2**-(PF_6)•Et_2O	**3**-(OTf)•CH_2Cl_2	**4**-(OTf)•$2CH_2Cl_2$
Formula	$C_{52}H_{94}AuCl_3F_6OP_5Rh$	$C_{55}H_{102}AuBrF_6O_2P_5Rh$	$C_{53}H_{46}AuCl_3F_3O_4P_4RhS$	$C_{54}H_{48}AuBrCl_4F_3O_4P_4RhS$
fw, g/mol	1410.35	1444.00	1366.06	1495.45
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
cryst. syst.	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
colour	orange	Orange	orange	orange
a (Å)	15.031(2)	15.0137(12)	10.4553(11)	19.5635(17)
b (Å)	21.469(3)	21.2486(17)	19.2177(19)	10.8423(10)
c (Å)	20.325(3)	20.3833(16)	26.395(3)	28.356(3)
α (°)	90	90	90	90
β (°)	102.251(2)	102.5770(10)	90	100.659(2)
γ (°)	90	90	90	90
V ($Å^3$)	6409.6(16)	6346.6(9)	5303.4(9)	5910.9(9)
Z	4	4	4	4
no. refl.	145895	147939	120893	122157
no. unique refl.	18727	19764	16512	17969
R_{int}	0.0514	0.0492	0.0440	0.0523
$R1^a$ (all data)	0.0401	0.0390	0.0287	0.0698
$wR2^b$ (all data)	0.0978	0.0640	0.0591	0.1681
$R1$ [(I > 2σ)]	0.0329	0.0279	0.0258	0.0572
$wR2$ [(I > 2σ)]	0.0930	0.0597	0.0583	0.1599
GOF^c	1.071	1.034	1.041	1.074
Flack param.	—	—	0.0089(21)	—

Table S2. Crystallographic Summary for Complexes **5, 6, 9.**

	5-$(PF_6)\bullet CH_2Cl_2$	**6**-$(PF_6)\bullet CH_2Cl_2$	**9**$\bullet 2.5(C_6H_6)$
Formula	$C_{52}H_{94}AuCl_5F_6OP_5Rh$	$C_{52}H_{94}AuBr_3Cl_2F_6OP_5Rh$	$C_{66}H_{108}AuF_6OP_5Rh$
fw, g/mol	1481.25	1614.63	1486.25
Temperature	100(2) K	100(2) K	100(2) K
cryst. syst.	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
colour	orange	red	orange
a (Å)	14.6050(13)	14.6332(13)	13.5672(15)
b (Å)	20.5013(17)	20.6673(18)	14.0811(15)
c (Å)	20.6567(18)	20.6771(18)	19.974(2)
α (°)	90	90	76.123(2)
β (°)	95.374(2)	95.422(2)	82.666(2)
γ (°)	90	90	66.756(2)
V (Å^3)	6157.9(9)	6225.4(9)	3401.4(6)
Z	4	4	2
no. refl.	122466	143038	78297
no. unique refl.	16655	18943	19683
R_{int}	0.0552	0.0525	0.0395
$R1^a$ (all data)	0.0552	0.0461	0.0394
$wR2^b$ (all data)	0.0899	0.0829	0.0723
$R1$ [(I > 2σ)]	0.0377	0.0335	0.0325
$wR2$ [(I> 2σ)]	0.0814	0.0772	0.0698
GOF^c	1.060	1.041	1.117

^{a} $R1 = \Sigma||F_o - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2}$. ^{c} $GOF = (\Sigma\, w(F_o^2 - F_c^2)^2/(n - p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

Table S3. Summary of the quantum yields for the photoreductions of $[Rh^{II}Au^{II}(dcpm)_2(CO)X_3](PF_6)$ (**5**, X = Cl; **6**, X = Br) [a]

[DMBD] / M	Quantum Yield (%)	
	5	**6**
0.055	–	3.1 (0.2)
0.55	6.9 (0.3)	6.7 (1.0)
1.1	8.5 (0.3)	9.5 (0.6)
2.2	9.4 (0.8)	13.0 (1.6)
3.3	–	15.3 (0.5)
4.4	10.1 (0.4)	18.2 (0.5)

[a] in acetonitrile, λ_{exc} = 320 nm.