Supporting Information for

A Rh^{II}–Au^{II} Bimetallic Core with a Direct Metal–Metal Bond

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Experimental Methods

General Considerations. All manipulations were carried out in an N_2-filled glovebox or under an inert atmosphere provided by a Schlenk line unless otherwise noted. All solvents were reagent grade (Aldrich) or better and were dried and degassed by standard methods.[1] $[Rh^{I}(COD)Cl]_2$, (Strem), *tert*-butylisonitrile (Aldrich), and $KAu^{III}Cl_4$ (Aldrich) were purchased from the commercial sources indicated and used as received. $Au^{I}(tht)Cl$[2] and tfepma[3,4] were prepared by literature procedures.

Methods. NMR data were collected at the MIT Department of Chemistry Instrument Facility (DCIF) on a Varian Mercury 300 spectrometer. NMR solvents (CD_3CN) were purchased from Cambridge Isotope labs and purified by standard procedures prior to use.[1] ^1H NMR spectra (300 MHz) were referenced to the residual proteo impurities of the given solvent. $^{31}P\{^1H\}$ NMR (121.4 MHz) spectra were referenced to an external 85% H_3PO_4 standard. All chemical shifts are reported in the standard δ notation in parts per million; positive chemical shifts are to higher frequency from the given reference. Elemental analyses were performed by Robertson Microlit Laboratories, Madison NJ. UV-vis spectra were recorded on a Spectral Instruments 400 series diode array spectrometer and referenced against the appropriate solvent.

X-Ray Crystallographic Details. Single crystals were immersed in a drop of Paratone N oil on a clean microscope slide, affixed to either a glass fiber or a human hair coated in epoxy resin and then cooled to –173 °C. The crystals were then mounted on a Bruker three circle goniometer platform equipped with an APEX detector. A graphite monochromator was employed for wavelength selection of the Mo K_α radiation (λ = 0.71073 Å). The data were processed and refined using the program SAINT supplied by Siemens Industrial Automation Inc. Structures were solved by a Patterson heavy atom map and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation Inc., 2000). Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all other atoms were refined anisotropically. Unit cell parameters, morphology, and solution statistics for complexes **1**, **2**, **3** and **4** are summarized in Table S1. Selected bond lengths and angles are summarized in Tables S2-S4. All thermal ellipsoid plots are drawn at the 50% probability level, with $–CH_2CF_3$ groups, –N–Me groups, and solvents of crystallization and non-coordinating anions omitted for clarity.

Emission Spectroscopy Details. Steady state emission spectra were recorded on an automated Photon Technology International (PTI) QM 4 fluorimeter equipped with a 150-W Xe

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[1] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth–Heinmann: Oxford, 1996.

[2] Uson, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85-91.

[3] Ganesan, M; Krishnamurthy, S. S.; Nethaji, M. *J. Organomet. Chem.* **1998**, *570*, 247-254.

[4] Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S.; Siriwardane, U; Hosmane, N. S. *J. Organomet. Chem.* **1990**, *390*, 203-216.

arc lamp and a Hamamatsu R928 photomultiplier tube. Exclusion of excitation light was provided by using the appropriate glass filters. Sample solutions were added to a custom resealable quartz EPR tube and freeze pump thaw degassed (4 cycles, 1×10^{-5} Torr). Low temperature emission spectra were recorded in a rigid solvent glass at 77 K by immersion of the sealed EPR tubes into a liquid nitrogen filled dewer. Time resolved phosphorescence lifetimes were recorded on a nanosecond laser system described previously.[5]

Preparation of $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (1). In a scintillation vial equipped with a stirbar, 154 mg $[Rh^{I}(COD)Cl]_2$ (0.312 mmol, 2 equiv rhodium) was dissolved in 2 mL of CH_2Cl_2 with stirring to give an orange solution. 608 mg of tfepma (1.25 mmol, 2 equiv per rhodium) was then added dropwise to cause the solution to turn green and subsequently gradually fade to yellow. The solution was stirred for 5 min at which time 145 μL of *tert*-butylisonitrile (0.735 g/mL, 1.31 mmol, 2.1 equiv per rhodium) was added. The solution immediately turned orange. 201 mg $Au^{I}(tht)Cl$ (0.625 mmol, 1 equiv per rhodium) was added as a solid to give an orange solution. The vial was wrapped in tin foil and allowed to stir for 2 hrs during which time an orange precipitate formed. The yellow supernatant was decanted and the solid washed with pentane (2 × 5 mL) to give 781 mg of $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**) (83% based on rhodium) as an orange solid. ^{1}H NMR (CD_3CN) δ / ppm: 1.454 (s, 18H), 2.983 (pseudotriplet, $^{3}J_{P-H}$ = 3.0 Hz, 6 H), 4.86 (bs, 16 H). $^{31}P\{^{1}H\}$ NMR (CD_3CN) δ / ppm: 136.9 (dm, $^{1}J_{Rh-P}$ = 172.3 Hz), 151.3 (m). Anal. Calc. for $C_{28}H_{40}N_4O_8F_{24}Cl_2P_4RhAu$: C, 22.25; H, 2.67; N, 3.71. Found: C, 22.29; H, 2.67; N, 3.68. λ_{max}/nm (ε/$M^{-1}cm^{-1}$) in CH_3CN: 307 (30800); 380 (9700); 419 (12400). Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/pentane liquid layers as orange blocks.

Preparation of $[Rh^{II}Au^{II}(tfepma)_2(CN^{t}Bu)_2Cl_3]^{+}[Au^{I}Cl_2]^{-}$ (2) To a scintillation vial equipped with a stirbar, 57 mg of $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**) (0.0377 mmol, 1 equiv) was dissolved in 2 mL of CH_3CN and frozen in a coldwell. In a separate vial, 14.3 mg of $KAu^{III}Cl_4$ (0.0377 mmol, 1 equiv) was dissolved in 2 mL of CH_3CN and the solution was frozen in a coldwell. Both vials were brought out of the coldwell and, upon thawing, the $KAu^{III}Cl_4$ solution was added dropwise to the solution of **1** with stirring; the solution color turned from orange to red. The vial was covered in tin foil and the CH_3CN was stripped away to leave a solid, which was suspended in Et_2O (5 mL), filtered, washed with Et_2O (2 x 2 mL). The solid was washed from the filter with CH_2Cl_2 (2 mL), and the solvent was removed in vacuo to give 30 mg (44%) of $[Rh^{II}Au^{II}(tfepma)_2(CN^{t}Bu)_2Cl_3]^{+}$ $[Au^{I}Cl_2]^{-}$ (**2**) as a dark orange. ^{1}H NMR (CD_3CN) δ / ppm: 1.609 (s, 18H), 3.050 (pseudotriplet, 4.4 Hz, 6H), 4.61-4.72 (m, 8H), 4.99 (m, 4H), 5.79 (m, 4H). $^{31}P\{^{1}H\}$ NMR (CD_3CN) δ / ppm: 95.6-100.5 (ovm). Anal. Calc. for $C_{28}H_{40}N_4O_8F_{24}Cl_5P_4RhAu_2$: C, 18.53; H, 2.22; N, 3.09. Found: C, 18.68; H, 2.02; N, 3.06. λ_{max}/nm (ε/$M^{-1}cm^{-1}$) in CH_3CN: 329 (33000); 460 (4000). Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/pentane layers as red blocks.

[5] Loh, Z.-H.; Miller, S. E.; Chang, C. J.; Carpenter, S. D.; Nocera, D. G. *J. Phys. Chem. A* **2002**, *106*, 11700-11708.

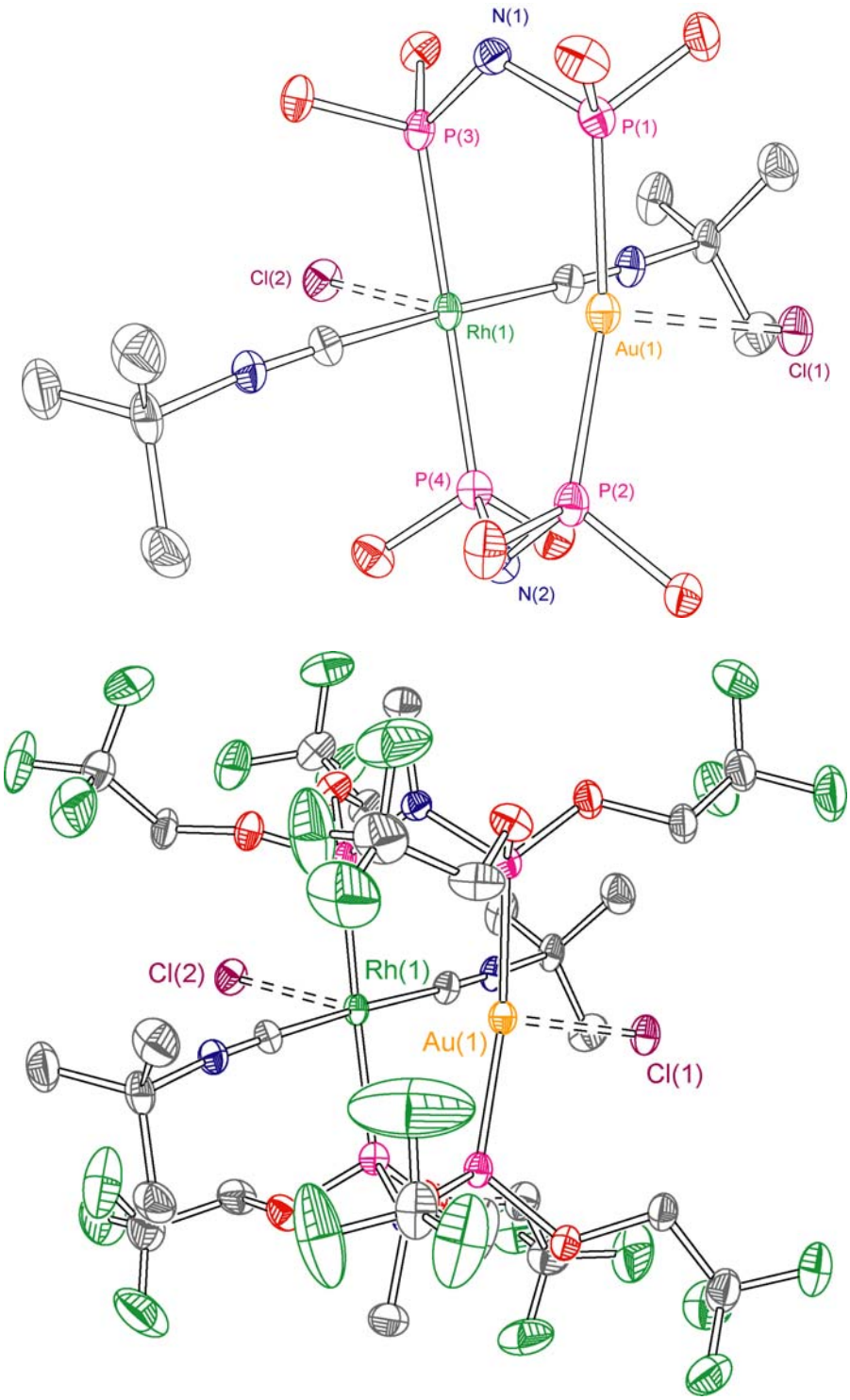

Figure S1. Thermal ellipsoid plot of $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level with $–CH_2CF_3$, –N–Me groups (top) and hydrogens (top and bottom) omitted for clarity.

Table S1.1. Crystal data and structure refinement for $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**).

Identification code	C05036t	
Empirical formula	$C_{28}H_{40}N_4O_8F_{24}P_4Cl_2RhAu$	
Formula weight	1511.30	
Temperature	–173(2)°C	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*2(1)/*c*	
Unit cell dimensions	a = 23.5341(13) Å	α = 90°
	b = 10.8576(6) Å	β = 116.4540(10)°
	c = 22.7690(12) Å	γ = 90°
Volume	5208.8(5) Å^3	
Z	4	
Density (calculated)	1.927 Mg/m^3	
Absorption coefficient	3.487 mm^{-1}	
F(000)	2936	
Crystal size	0.20 × 0.15 × 0.12 mm^3	
Θ range for data collection	0.97 to 28.27°	
Index ranges	$-29 \le h \le 31$, $-12 \le k \le 14$, $-29 \le \ell \le 30$	
Reflections collected	36938	
Independent reflections	12896 [R_{int} = 0.0382]	
Completeness to Θ = 28.29°	99.7 %	
Absorption correction	Empirical SADABS	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	12896 / 0 / 657	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2σ(I)]	R_1 = 0.0334 wR_2 = 0.0757	
R indices (all data)	R_1 = 0.0445, wR_2 = 0.0827	
Largest diff. peak and hole	1.606 and –1.302 e/Å^3	

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. Refinement on F_o^2 for all reflections (having $F_o^2 \ge -3\sigma(F_o^2)$). wR_2 and GOF based on F_o^2, R_1 based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. [b] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data, p = number of parameters varied; $w = [\sigma^2 F_o^2 + (0.0638P)^2]^{-1}$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table S1.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au(1)	2825(1)	–1165(1)	7644(1)	19(1)
Rh(1)	2504(1)	1321(1)	7302(1)	17(1)
Cl(1)	3890(1)	–1500(1)	7526(1)	26(1)
Cl(2)	2276(1)	3677(1)	7180(1)	27(1)
P(1)	3212(1)	–882(1)	8744(1)	20(1)
P(2)	2092(1)	–1943(1)	6675(1)	20(1)
P(3)	2781(1)	1653(1)	8401(1)	19(1)
P(4)	2130(1)	589(1)	6268(1)	20(1)
O(1)	3959(1)	–979(2)	9217(1)	27(1)
O(2)	2964(1)	–1788(2)	9144(1)	28(1)
O(3)	2299(1)	–2981(2)	6302(1)	26(1)
O(4)	1416(1)	–2480(2)	6590(1)	27(1)
O(5)	3227(1)	2814(2)	8779(1)	24(1)
O(6)	2193(1)	1996(2)	8554(1)	24(1)
O(7)	2546(1)	676(2)	5866(1)	27(1)
O(8)	1508(1)	1291(2)	5741(1)	28(1)
C(1)	3232(2)	779(4)	9652(2)	28(1)
C(2)	1374(2)	–1179(4)	5411(2)	31(1)
C(3)	3384(2)	1533(3)	7411(2)	20(1)
C(4)	4552(2)	1943(3)	7603(2)	25(1)
C(5)	4681(2)	3316(4)	7729(3)	37(1)
C(6)	4980(2)	1192(4)	8198(2)	37(1)
C(7)	4612(2)	1554(4)	6991(2)	38(1)
C(8)	1636(2)	968(3)	7185(2)	20(1)
C(9)	452(2)	540(4)	6901(2)	27(1)
C(10)	428(2)	–317(5)	7418(2)	40(1)
C(11)	183(2)	–53(4)	6222(2)	36(1)
C(12)	134(2)	1771(5)	6890(3)	43(1)
C(13)	4276(2)	–2087(4)	9197(2)	27(1)
C(14)	4980(2)	–1823(4)	9564(2)	34(1)
C(15)	2369(2)	–2407(4)	8823(2)	35(1)

C(16)	1906(2)	–1872(5)	9036(3)	47(1)
C(17)	2835(2)	–3784(3)	6652(2)	25(1)
C(18)	2987(2)	–4380(4)	6150(2)	35(1)
C(19)	1298(3)	–3735(4)	6611(4)	62(2)
C(20)	859(2)	–3961(4)	6887(3)	36(1)
C(21)	3654(2)	3378(3)	8575(2)	25(1)
C(22)	3771(2)	4668(4)	8851(2)	34(1)
C(23)	1899(2)	3184(4)	8404(2)	30(1)
C(24)	1543(2)	3318(4)	8800(2)	36(1)
C(25)	3050(2)	–170(4)	5988(2)	32(1)
C(26)	3261(2)	26(4)	5462(2)	38(1)
C(27)	1540(2)	2575(4)	5610(2)	33(1)
C(28)	874(3)	3035(4)	5318(3)	47(1)
N(1)	3087(2)	528(3)	8954(2)	20(1)
N(2)	1820(2)	–841(3)	6103(2)	21(1)
N(3)	3891(2)	1715(3)	7481(2)	22(1)
N(4)	1124(2)	788(3)	7087(2)	23(1)
F(1)	5158(1)	–900(3)	9311(2)	50(1)
F(2)	5166(1)	–1578(3)	10195(1)	48(1)
F(3)	5301(1)	–2827(3)	9534(2)	54(1)
F(4)	2102(2)	–2012(4)	9679(2)	71(1)
F(5)	1813(2)	–674(3)	8907(2)	84(1)
F(6)	1355(2)	–2442(4)	8742(2)	73(1)
F(7)	3456(2)	–5193(3)	6438(2)	58(1)
F(8)	3180(1)	–3571(3)	5835(2)	49(1)
F(9)	2492(1)	–4984(2)	5691(1)	44(1)
F(10)	1113(3)	–3588(5)	7507(2)	136(2)
F(11)	730(2)	–5118(2)	6926(2)	73(1)
F(12)	340(2)	–3336(3)	6633(2)	90(2)
F(13)	4045(2)	4714(3)	9496(1)	49(1)
F(14)	4162(2)	5242(2)	8647(2)	55(1)
F(15)	3240(1)	5338(2)	8639(2)	49(1)
F(16)	1287(2)	4456(3)	8712(2)	61(1)
F(17)	1905(2)	3180(3)	9437(1)	59(1)
F(18)	1070(1)	2512(3)	8636(2)	59(1)
F(19)	3428(2)	1182(3)	5429(2)	50(1)

F(20)	3763(2)	–689(3)	5581(2)	63(1)
F(21)	2808(2)	–250(3)	4869(1)	57(1)
F(22)	866(2)	4232(3)	5165(2)	68(1)
F(23)	621(2)	2961(3)	5733(2)	78(1)
F(24)	501(2)	2452(3)	4772(2)	79(1)

Table S1.3. Bond lengths (Å) for $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**).

Au(1)–P(1)	2.2713(10)	C(9)–N(4)	1.469(5)
Au(1)–P(2)	2.2741(10)	C(9)–C(10)	1.521(6)
Au(1)–Cl(1)	2.6632(9)	C(9)–C(12)	1.526(6)
Au(1)–Rh(1)	2.8181(3)	C(9)–C(11)	1.528(6)
Rh(1)–C(8)	1.975(4)	C(13)–C(14)	1.513(6)
Rh(1)–C(3)	1.988(4)	C(14)–F(1)	1.314(5)
Rh(1)–P(4)	2.2603(10)	C(14)–F(2)	1.329(5)
Rh(1)–P(3)	2.3147(10)	C(14)–F(3)	1.345(5)
Rh(1)–Cl(2)	2.6027(9)	C(15)–C(16)	1.492(7)
P(1)–O(1)	1.605(3)	C(16)–F(6)	1.319(5)
P(1)–O(2)	1.616(3)	C(16)–F(5)	1.331(6)
P(1)–N(1)	1.669(3)	C(16)–F(4)	1.333(6)
P(2)–O(3)	1.611(3)	C(17)–C(18)	1.490(6)
P(2)–O(4)	1.623(3)	C(18)–F(7)	1.334(5)
P(2)–N(2)	1.671(3)	C(18)–F(8)	1.334(5)
P(3)–O(6)	1.615(3)	C(18)–F(9)	1.340(5)
P(3)–O(5)	1.621(3)	C(19)–C(20)	1.451(6)
P(3)–N(1)	1.670(3)	C(20)–F(12)	1.286(5)
P(4)–O(8)	1.611(3)	C(20)–F(11)	1.304(5)
P(4)–O(7)	1.613(3)	C(20)–F(10)	1.328(6)
P(4)–N(2)	1.685(3)	C(21)–C(22)	1.510(5)
O(1)–C(13)	1.428(4)	C(22)–F(13)	1.316(5)
O(2)–C(15)	1.426(5)	C(22)–F(15)	1.337(5)
O(3)–C(17)	1.446(4)	C(22)–F(14)	1.352(5)
O(4)–C(19)	1.395(5)	C(23)–C(24)	1.487(5)
O(5)–C(21)	1.420(4)	C(24)–F(17)	1.323(5)
O(6)–C(23)	1.431(4)	C(24)–F(18)	1.331(5)
O(7)–C(25)	1.426(5)	C(24)–F(16)	1.350(5)
O(8)–C(27)	1.435(5)	C(25)–C(26)	1.503(6)
C(1)–N(1)	1.494(5)	C(26)–F(19)	1.327(5)
C(2)–N(2)	1.498(5)	C(26)–F(21)	1.330(5)
C(3)–N(3)	1.149(5)	C(26)–F(20)	1.335(6)
C(4)–N(3)	1.474(5)	C(27)–C(28)	1.490(7)
C(4)–C(6)	1.516(6)	C(28)–F(24)	1.320(6)

C(4)–C(7)	1.522(6)	C(28)–F(23)	1.326(6)
C(4)–C(5)	1.523(5)	C(28)–F(22)	1.344(5)
C(8)–N(4)	1.141(5)		

Table S1.4. Bond angles (°) for $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**).

P(1)–Au(1)–P(2)	151.41(3)	C(12)–C(9)–C(11)	111.9(4)
P(1)–Au(1)–Cl(1)	101.39(3)	O(1)–C(13)–C(14)	106.4(3)
P(2)–Au(1)–Cl(1)	101.10(3)	F(1)–C(14)–F(2)	107.8(4)
P(1)–Au(1)–Rh(1)	95.84(2)	F(1)–C(14)–F(3)	107.4(4)
P(2)–Au(1)–Rh(1)	95.35(2)	F(2)–C(14)–F(3)	107.2(4)
Cl(1)–Au(1)–Rh(1)	104.58(2)	F(1)–C(14)–C(13)	112.8(4)
C(8)–Rh(1)–C(3)	175.39(14)	F(2)–C(14)–C(13)	112.8(4)
C(8)–Rh(1)–P(4)	83.77(11)	F(3)–C(14)–C(13)	108.6(4)
C(3)–Rh(1)–P(4)	94.08(11)	O(2)–C(15)–C(16)	110.0(4)
C(8)–Rh(1)–P(3)	87.32(11)	F(6)–C(16)–F(5)	108.5(5)
C(3)–Rh(1)–P(3)	94.06(11)	F(6)–C(16)–F(4)	106.4(4)
P(4)–Rh(1)–P(3)	166.48(3)	F(5)–C(16)–F(4)	107.2(5)
C(8)–Rh(1)–Cl(2)	91.45(10)	F(6)–C(16)–C(15)	110.4(4)
C(3)–Rh(1)–Cl(2)	93.05(10)	F(5)–C(16)–C(15)	112.5(4)
P(4)–Rh(1)–Cl(2)	105.59(3)	F(4)–C(16)–C(15)	111.6(4)
P(3)–Rh(1)–Cl(2)	84.72(3)	O(3)–C(17)–C(18)	106.7(3)
C(8)–Rh(1)–Au(1)	89.17(10)	F(7)–C(18)–F(8)	107.2(4)
C(3)–Rh(1)–Au(1)	86.52(10)	F(7)–C(18)–F(9)	107.5(4)
P(4)–Rh(1)–Au(1)	83.27(3)	F(8)–C(18)–F(9)	106.8(4)
P(3)–Rh(1)–Au(1)	86.47(2)	F(7)–C(18)–C(17)	109.8(4)
Cl(2)–Rh(1)–Au(1)	171.13(3)	F(8)–C(18)–C(17)	112.4(4)
O(1)–P(1)–O(2)	98.32(15)	F(9)–C(18)–C(17)	112.8(4)
O(1)–P(1)–N(1)	98.46(15)	O(4)–C(19)–C(20)	111.8(4)
O(2)–P(1)–N(1)	104.06(15)	F(12)–C(20)–F(11)	109.7(4)
O(1)–P(1)–Au(1)	120.78(11)	F(12)–C(20)–F(10)	101.9(5)
O(2)–P(1)–Au(1)	118.13(11)	F(11)–C(20)–F(10)	103.4(4)
N(1)–P(1)–Au(1)	113.89(11)	F(12)–C(20)–C(19)	115.6(5)
O(3)–P(2)–O(4)	101.30(14)	F(11)–C(20)–C(19)	115.1(4)
O(3)–P(2)–N(2)	101.00(15)	F(10)–C(20)–C(19)	109.7(5)
O(4)–P(2)–N(2)	98.64(16)	O(5)–C(21)–C(22)	106.8(3)
O(3)–P(2)–Au(1)	119.62(11)	F(13)–C(22)–F(15)	107.3(4)
O(4)–P(2)–Au(1)	121.94(11)	F(13)–C(22)–F(14)	107.3(4)
N(2)–P(2)–Au(1)	110.59(12)	F(15)–C(22)–F(14)	107.1(4)
O(6)–P(3)–O(5)	96.88(14)	F(13)–C(22)–C(21)	114.0(4)

O(6)–P(3)–N(1)	97.42(15)	F(15)–C(22)–C(21)	112.7(4)
O(5)–P(3)–N(1)	102.00(15)	F(14)–C(22)–C(21)	108.1(3)
O(6)–P(3)–Rh(1)	114.44(11)	O(6)–C(23)–C(24)	106.6(3)
O(5)–P(3)–Rh(1)	119.96(10)	F(17)–C(24)–F(18)	106.5(4)
N(1)–P(3)–Rh(1)	121.38(11)	F(17)–C(24)–F(16)	107.1(4)
O(8)–P(4)–O(7)	97.40(15)	F(18)–C(24)–F(16)	107.4(4)
O(8)–P(4)–N(2)	96.37(15)	F(17)–C(24)–C(23)	113.0(4)
O(7)–P(4)–N(2)	103.91(15)	F(18)–C(24)–C(23)	113.1(4)
O(8)–P(4)–Rh(1)	114.35(11)	F(16)–C(24)–C(23)	109.5(4)
O(7)–P(4)–Rh(1)	121.13(12)	O(7)–C(25)–C(26)	107.2(3)
N(2)–P(4)–Rh(1)	119.02(12)	F(19)–C(26)–F(21)	106.2(4)
C(13)–O(1)–P(1)	117.8(2)	F(19)–C(26)–F(20)	107.8(4)
C(15)–O(2)–P(1)	121.1(3)	F(21)–C(26)–F(20)	108.2(4)
C(17)–O(3)–P(2)	121.7(2)	F(19)–C(26)–C(25)	112.9(4)
C(19)–O(4)–P(2)	123.1(3)	F(21)–C(26)–C(25)	112.1(4)
C(21)–O(5)–P(3)	123.1(2)	F(20)–C(26)–C(25)	109.4(4)
C(23)–O(6)–P(3)	121.7(2)	O(8)–C(27)–C(28)	106.1(4)
C(25)–O(7)–P(4)	120.9(2)	F(24)–C(28)–F(23)	108.7(5)
C(27)–O(8)–P(4)	120.0(3)	F(24)–C(28)–F(22)	107.0(4)
N(3)–C(3)–Rh(1)	176.6(3)	F(23)–C(28)–F(22)	106.5(4)
N(3)–C(4)–C(6)	107.6(3)	F(24)–C(28)–C(27)	112.7(4)
N(3)–C(4)–C(7)	107.5(3)	F(23)–C(28)–C(27)	112.2(4)
C(6)–C(4)–C(7)	112.0(3)	F(22)–C(28)–C(27)	109.3(4)
N(3)–C(4)–C(5)	107.8(3)	C(1)–N(1)–P(1)	119.1(2)
C(6)–C(4)–C(5)	111.2(4)	C(1)–N(1)–P(3)	119.1(2)
C(7)–C(4)–C(5)	110.7(4)	P(1)–N(1)–P(3)	121.76(18)
N(4)–C(8)–Rh(1)	176.7(3)	C(2)–N(2)–P(2)	119.3(2)
N(4)–C(9)–C(10)	107.2(3)	C(2)–N(2)–P(4)	119.4(2)
N(4)–C(9)–C(12)	107.5(3)	P(2)–N(2)–P(4)	120.59(19)
C(10)–C(9)–C(12)	111.2(4)	C(3)–N(3)–C(4)	177.4(4)
N(4)–C(9)–C(11)	106.1(3)	C(8)–N(4)–C(9)	175.0(4)
C(10)–C(9)–C(11)	112.6(4)		

Table S1.5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Rh^IAu^I(tfepma)_2(CN^tBu)_2Cl_2$ (**1**). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	18(1)	18(1)	23(1)	2(1)	11(1)	1(1)
Rh(1)	14(1)	17(1)	23(1)	2(1)	11(1)	0(1)
Cl(1)	20(1)	26(1)	38(1)	1(1)	17(1)	1(1)
Cl(2)	34(1)	18(1)	32(1)	4(1)	16(1)	3(1)
P(1)	17(1)	21(1)	23(1)	3(1)	8(1)	1(1)
P(2)	17(1)	18(1)	26(1)	1(1)	12(1)	0(1)
P(3)	17(1)	19(1)	26(1)	0(1)	12(1)	0(1)
P(4)	21(1)	19(1)	23(1)	3(1)	12(1)	0(1)
O(1)	19(1)	24(1)	33(2)	–3(1)	6(1)	4(1)
O(2)	28(2)	26(1)	26(1)	4(1)	9(1)	–6(1)
O(3)	24(1)	23(1)	29(2)	–4(1)	10(1)	4(1)
O(4)	23(1)	17(1)	46(2)	0(1)	19(1)	–3(1)
O(5)	27(1)	23(1)	28(1)	–3(1)	17(1)	–6(1)
O(6)	21(1)	25(1)	33(2)	1(1)	18(1)	1(1)
O(7)	34(2)	28(1)	28(2)	4(1)	21(1)	0(1)
O(8)	27(2)	21(1)	29(2)	6(1)	7(1)	1(1)
C(1)	30(2)	30(2)	24(2)	1(2)	12(2)	0(2)
C(2)	36(2)	26(2)	25(2)	–1(2)	7(2)	–1(2)
C(3)	21(2)	16(2)	27(2)	0(1)	13(2)	–1(1)
C(4)	15(2)	25(2)	41(2)	–2(2)	17(2)	–1(2)
C(5)	27(2)	29(2)	63(3)	–4(2)	29(2)	–7(2)
C(6)	24(2)	38(2)	46(3)	–2(2)	12(2)	–1(2)
C(7)	27(2)	50(3)	46(3)	–13(2)	24(2)	–10(2)
C(8)	16(2)	19(2)	23(2)	3(1)	7(1)	1(1)
C(9)	13(2)	32(2)	39(2)	1(2)	13(2)	–1(2)
C(10)	30(2)	52(3)	41(3)	6(2)	19(2)	–4(2)
C(11)	21(2)	46(3)	36(2)	–3(2)	10(2)	–7(2)
C(12)	24(2)	46(3)	55(3)	–3(2)	15(2)	8(2)
C(13)	21(2)	24(2)	34(2)	–1(2)	9(2)	5(2)
C(14)	26(2)	33(2)	38(2)	3(2)	10(2)	8(2)
C(15)	38(3)	42(2)	27(2)	–3(2)	15(2)	–18(2)

C(16)	31(3)	55(3)	52(3)	–8(3)	16(2)	–16(2)
C(17)	23(2)	20(2)	31(2)	0(2)	12(2)	3(2)
C(18)	30(2)	32(2)	46(3)	–4(2)	19(2)	5(2)
C(19)	78(4)	26(2)	119(5)	–3(3)	78(4)	–12(3)
C(20)	33(2)	27(2)	56(3)	8(2)	27(2)	0(2)
C(21)	26(2)	23(2)	33(2)	–6(2)	19(2)	–6(2)
C(22)	39(3)	27(2)	43(3)	–5(2)	27(2)	–8(2)
C(23)	30(2)	32(2)	35(2)	6(2)	21(2)	12(2)
C(24)	30(2)	47(3)	38(3)	–3(2)	21(2)	4(2)
C(25)	34(2)	33(2)	35(2)	2(2)	22(2)	2(2)
C(26)	38(3)	51(3)	36(2)	0(2)	25(2)	–5(2)
C(27)	42(3)	26(2)	26(2)	7(2)	10(2)	3(2)
C(28)	50(3)	28(2)	53(3)	6(2)	13(3)	13(2)
N(1)	22(2)	20(2)	19(2)	0(1)	10(1)	1(1)
N(2)	21(2)	19(1)	23(2)	1(1)	9(1)	–1(1)
N(3)	20(2)	20(2)	31(2)	1(1)	15(1)	1(1)
N(4)	17(2)	28(2)	26(2)	–2(1)	10(1)	1(1)
F(1)	29(2)	53(2)	65(2)	10(2)	19(1)	–3(1)
F(2)	36(2)	58(2)	33(2)	–7(1)	–1(1)	4(1)
F(3)	33(2)	49(2)	70(2)	–3(2)	14(2)	17(1)
F(4)	64(2)	112(3)	51(2)	–24(2)	39(2)	–28(2)
F(5)	38(2)	56(2)	152(4)	8(2)	36(2)	4(2)
F(6)	36(2)	97(3)	80(2)	–12(2)	20(2)	–35(2)
F(7)	51(2)	58(2)	63(2)	–5(2)	24(2)	29(2)
F(8)	45(2)	64(2)	52(2)	–1(1)	34(2)	–5(1)
F(9)	49(2)	38(2)	46(2)	–16(1)	20(1)	–2(1)
F(10)	164(5)	198(5)	64(3)	–27(3)	68(3)	–108(4)
F(11)	75(2)	30(2)	151(3)	12(2)	84(3)	–4(2)
F(12)	38(2)	67(2)	171(4)	58(3)	51(2)	11(2)
F(13)	62(2)	49(2)	39(2)	–18(1)	24(1)	–21(2)
F(14)	77(2)	36(1)	82(2)	–22(2)	63(2)	–29(2)
F(15)	55(2)	29(1)	70(2)	–5(1)	33(2)	6(1)
F(16)	58(2)	58(2)	86(2)	2(2)	49(2)	28(2)
F(17)	59(2)	89(2)	34(2)	–6(2)	28(2)	12(2)
F(18)	35(2)	78(2)	78(2)	–8(2)	39(2)	–6(2)
F(19)	55(2)	55(2)	56(2)	6(1)	38(2)	–14(1)

F(20)	66(2)	80(2)	74(2)	17(2)	58(2)	23(2)
F(21)	68(2)	75(2)	37(2)	–16(2)	30(2)	–13(2)
F(22)	81(3)	30(2)	76(2)	17(2)	19(2)	22(2)
F(23)	77(3)	67(2)	113(3)	17(2)	62(3)	32(2)
F(24)	63(2)	52(2)	66(2)	2(2)	–21(2)	11(2)

Table S1.6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**).

	x	y	z	U(eq)
H(1A)	3393	1622	9767	42
H(1B)	3555	197	9939	42
H(1C)	2845	684	9708	42
H(2A)	1391	–2070	5352	47
H(2B)	1498	–746	5109	47
H(2C)	941	–941	5321	47
H(5A)	4365	3783	7360	55
H(5B)	5106	3505	7776	55
H(5C)	4655	3544	8133	55
H(6A)	4930	1474	8582	56
H(6B)	5422	1297	8280	56
H(6C)	4863	320	8118	56
H(7A)	4503	680	6903	57
H(7B)	5049	1685	7059	57
H(7C)	4321	2046	6616	57
H(10A)	657	–1079	7433	59
H(10B)	–15	–512	7307	59
H(10C)	626	87	7848	59
H(11A)	258	489	5920	53
H(11B)	–275	–183	6059	53
H(11C)	392	–847	6251	53
H(12A)	355	2171	7319	65
H(12B)	–311	1632	6791	65
H(12C)	155	2302	6552	65
H(13A)	4161	–2322	8738	33
H(13B)	4158	–2769	9410	33
H(15A)	2427	–3295	8932	42
H(15B)	2203	–2320	8342	42
H(17A)	2726	–4415	6900	30
H(17B)	3203	–3304	6965	30
H(19A)	1703	–4164	6879	74
H(19B)	1120	–4077	6161	74

H(21A)	3467	3401	8090	30
H(21B)	4057	2911	8744	30
H(23A)	1606	3245	7930	36
H(23B)	2224	3838	8518	36
H(25A)	2900	–1027	5973	38
H(25B)	3406	–19	6426	38
H(27A)	1726	2690	5300	40
H(27B)	1804	3023	6021	40

Table S1.7. Selected torsion angles (°) for $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (**1**).

P(1)–Au(1)–Rh(1)–P(3)	–6.05(3)
P(2)–Au(1)–Rh(1)–P(4)	–23.59(3)

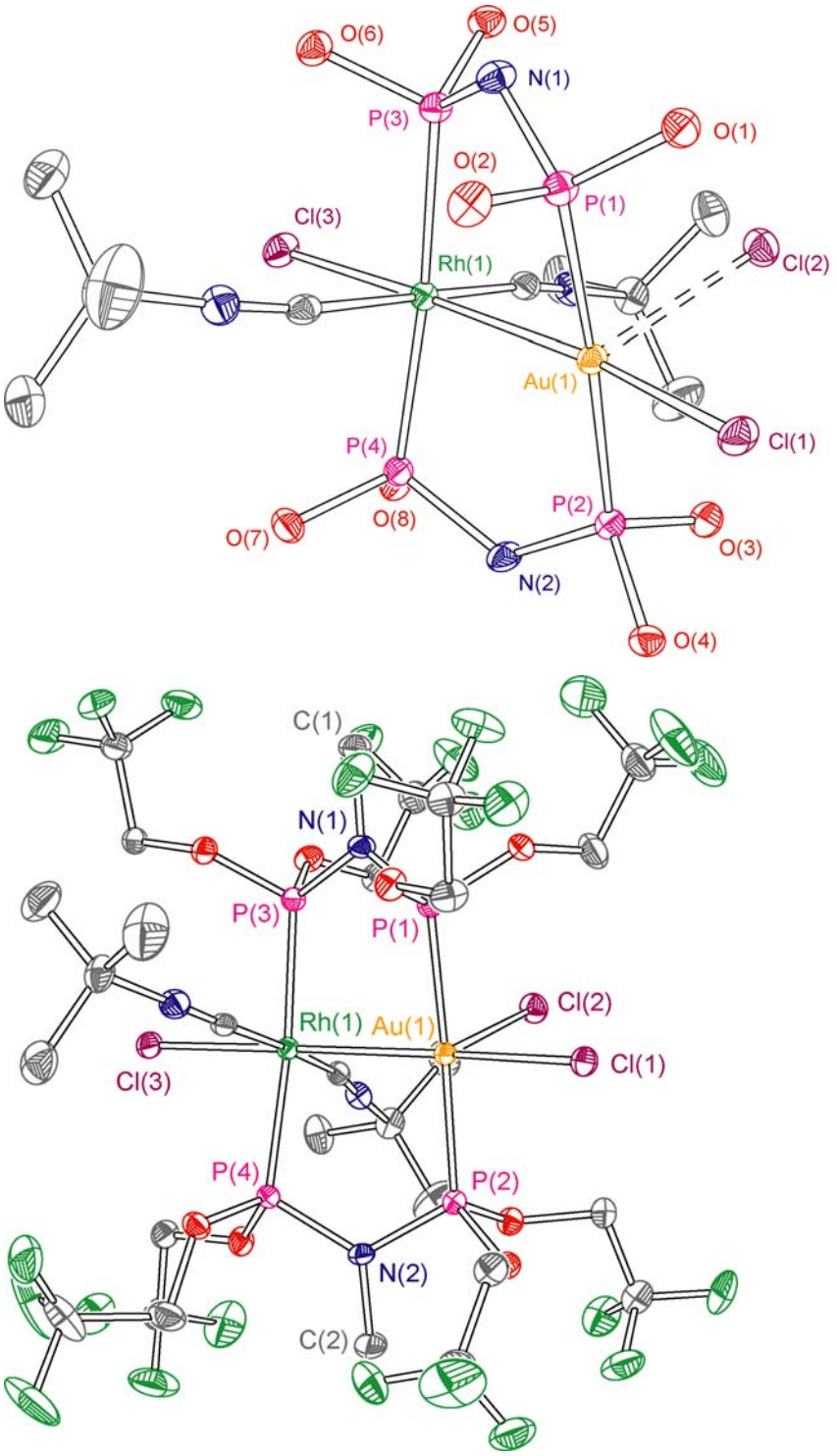

Figure S2. Thermal ellipsoid plot of $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+[Au^ICl_2]^-$ (**2**). Thermal ellipsoids are drawn at the 50% probability level with $–OCH_2CF_3$ groups (top) and hydrogens (top and bottom) omitted for clarity.

Table S2.1. Crystal data and structure refinement for $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+$ $[Au^ICl_2]^-$ (**2**).

Identification code	06010_p21n	
Empirical formula	$C_{28}H_{40}N_4O_8F_{24}P_4Cl_5RhAu_2$	
Formula weight	1814.61	
Temperature	–173(2)°C	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*2(1)/*n*	
Unit cell dimensions	a = 16.111(3) Å	α = 90°
	b = 20.119(3) Å	β = 92.803(3)°
	c = 17.299(3) Å	γ = 90°
Volume	5600.5(16) Å^3	
Z	4	
Density (calculated)	2.152 Mg/m^3	
Absorption coefficient	5.995 mm^{-1}	
F(000)	3456	
Crystal size	0.25 × 0.20 × 0.18 mm^3	
Θ range for data collection	1.55 to 28.26°	
Index ranges	$-21 \le h \le 14$, $-26 \le k \le 26$, $-23 \le \ell \le 20$	
Reflections collected	31787	
Independent reflections	13291 [R_{int} = 0.0372]	
Completeness to Θ = 28.29°	95.7 %	
Absorption correction	Empirical SADABS	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	13291 / 0 / 693	
Goodness–of–fit on F^2	1.010	
Final R indices [I>2σ(I)]	R_1 = 0.0299, wR_2 = 0.0751	
R indices (all data)	R_1 = 0.0347, wR_2 = 0.0773	
Largest diff. peak and hole	2.183 and –1.961 e/Å^3	

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. Refinement on F_o^2 for all reflections (having $F_o^2 \ge -3\sigma(F_o^2)$). wR_2 and GOF based on F_o^2, R_1 based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. [b] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data, p = number of parameters varied; $w = [\sigma^2F_o^2 + (0.0638P)^2]^{-1}$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table S2.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+[Au^ICl_2]^-$ (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au(1)	4651(1)	8491(1)	3659(1)	13(1)
Au(2)	2998(1)	5043(1)	2724(1)	28(1)
Rh(1)	3773(1)	7514(1)	2988(1)	12(1)
Cl(1)	5336(1)	9503(1)	4109(1)	20(1)
Cl(2)	5688(1)	7637(1)	4599(1)	21(1)
Cl(3)	2948(1)	6687(1)	2340(1)	20(1)
Cl(4)	1592(1)	5044(1)	2629(1)	43(1)
Cl(5)	4406(1)	5025(1)	2799(1)	44(1)
P(1)	5549(1)	8469(1)	2663(1)	15(1)
P(2)	3686(1)	8587(1)	4587(1)	14(1)
P(3)	4892(1)	7168(1)	2302(1)	14(1)
P(4)	2587(1)	7792(1)	3597(1)	14(1)
N(1)	5614(2)	7755(1)	2194(2)	16(1)
N(2)	2753(2)	8248(2)	4402(2)	17(1)
N(3)	3984(2)	6548(1)	4403(2)	18(1)
N(4)	3318(2)	8317(2)	1482(2)	19(1)
C(1)	6250(2)	7666(2)	1601(2)	23(1)
C(2)	2159(2)	8267(2)	5039(2)	32(1)
C(3)	3979(2)	6906(2)	3887(2)	16(1)
C(4)	4027(2)	6126(2)	5106(2)	21(1)
C(5)	3720(4)	6546(2)	5760(3)	41(1)
C(6)	3477(3)	5521(2)	4934(3)	31(1)
C(7)	4938(2)	5937(2)	5247(2)	29(1)
C(8)	3492(2)	8082(2)	2069(2)	16(1)
C(9)	3062(2)	8535(2)	694(2)	23(1)
C(10)	3219(3)	7951(2)	156(2)	37(1)
C(11)	3561(4)	9139(3)	499(3)	49(1)
C(12)	2131(3)	8693(2)	699(3)	35(1)
C(13)	6984(2)	8487(2)	3552(2)	28(1)
C(14)	7861(3)	8523(2)	3334(3)	33(1)
C(15)	5507(2)	9682(2)	2066(2)	22(1)

C(16)	6032(2)	9884(2)	1412(2)	23(1)
C(17)	4591(2)	8510(2)	5912(2)	22(1)
C(18)	4207(3)	8601(2)	6685(2)	26(1)
C(19)	3366(2)	9883(2)	4392(2)	22(1)
C(20)	2506(3)	10129(2)	4544(3)	33(1)
C(21)	5745(2)	6316(2)	3248(2)	21(1)
C(22)	6633(3)	6143(2)	3128(2)	30(1)
C(23)	4339(2)	6397(2)	1120(2)	20(1)
C(24)	4911(2)	6160(2)	517(2)	25(1)
C(25)	1142(2)	8420(2)	3188(2)	29(1)
C(26)	521(2)	8184(2)	2569(3)	39(1)
C(27)	1648(2)	6659(2)	3669(2)	21(1)
C(28)	1001(3)	6497(2)	4232(3)	31(1)
F(1)	8024(2)	8115(2)	2756(2)	67(1)
F(2)	8075(2)	9123(2)	3097(2)	58(1)
F(3)	8370(2)	8374(2)	3941(2)	51(1)
F(4)	6747(1)	9553(1)	1402(2)	38(1)
F(5)	6215(2)	10536(1)	1478(1)	34(1)
F(6)	5639(2)	9795(1)	718(1)	32(1)
F(7)	4791(2)	8812(1)	7211(1)	37(1)
F(8)	3592(2)	9054(1)	6658(1)	38(1)
F(9)	3884(2)	8037(1)	6945(1)	36(1)
F(10)	2381(2)	10708(2)	4186(2)	60(1)
F(11)	2395(2)	10219(1)	5296(2)	41(1)
F(12)	1912(2)	9710(2)	4281(2)	50(1)
F(13)	6722(2)	5695(2)	2575(2)	56(1)
F(14)	7083(2)	6675(2)	2942(2)	53(1)
F(15)	6984(2)	5892(1)	3785(2)	42(1)
F(16)	5671(1)	6009(1)	810(2)	34(1)
F(17)	5012(2)	6614(1)	–43(1)	32(1)
F(18)	4590(2)	5620(1)	168(2)	43(1)
F(19)	721(2)	8350(2)	1866(2)	48(1)
F(20)	445(2)	7523(2)	2571(3)	92(2)
F(21)	–219(2)	8443(2)	2685(2)	66(1)
F(22)	474(2)	7007(2)	4335(2)	51(1)
F(23)	1335(2)	6351(2)	4934(2)	49(1)

F(24)	540(2)	5980(1)	3989(2)	52(1)
O(1)	6479(2)	8682(1)	2875(1)	18(1)
O(2)	5343(2)	8978(1)	1985(1)	19(1)
O(3)	3941(2)	8247(1)	5387(1)	18(1)
O(4)	3525(1)	9318(1)	4883(1)	17(1)
O(5)	5376(2)	6502(1)	2503(2)	19(1)
O(6)	4660(1)	7022(1)	1415(1)	18(1)
O(7)	1941(1)	8153(1)	3018(1)	18(1)
O(8)	2094(2)	7214(1)	4005(1)	19(1)

Table S2.3. Bond lengths (Å) for $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+[Au^ICl_2]^-$ (**2**).

Au(1)–P(2)	2.2969(10)	C(14)–F(2)	1.327(5)
Au(1)–P(1)	2.3035(10)	C(14)–F(1)	1.329(5)
Au(1)–Cl(1)	2.4267(8)	C(14)–F(3)	1.335(5)
Au(1)–Rh(1)	2.6549(4)	C(15)–O(2)	1.448(4)
Au(1)–Cl(2)	2.8492(9)	C(15)–C(16)	1.501(5)
Au(2)–Cl(4)	2.2643(13)	C(16)–F(4)	1.331(4)
Au(2)–Cl(5)	2.2664(13)	C(16)–F(6)	1.343(5)
Rh(1)–C(8)	1.991(3)	C(16)–F(5)	1.348(4)
Rh(1)–C(3)	1.994(3)	C(17)–O(3)	1.453(4)
Rh(1)–P(4)	2.2958(9)	C(17)–C(18)	1.512(6)
Rh(1)–P(3)	2.3136(9)	C(18)–F(9)	1.336(4)
Rh(1)–Cl(3)	2.3764(9)	C(18)–F(7)	1.343(4)
P(1)–O(2)	1.580(3)	C(18)–F(8)	1.345(5)
P(1)–O(1)	1.583(2)	C(19)–O(4)	1.434(4)
P(1)–N(1)	1.656(3)	C(19)–C(20)	1.505(6)
P(2)–O(3)	1.580(3)	C(20)–F(10)	1.330(5)
P(2)–O(4)	1.585(2)	C(20)–F(11)	1.334(5)
P(2)–N(2)	1.667(3)	C(20)–F(12)	1.338(5)
P(3)–O(5)	1.582(2)	C(21)–O(5)	1.441(4)
P(3)–O(6)	1.588(3)	C(21)–C(22)	1.497(5)
P(3)–N(1)	1.674(3)	C(22)–F(13)	1.327(5)
P(4)–O(7)	1.586(2)	C(22)–F(14)	1.339(5)
P(4)–O(8)	1.593(3)	C(22)–F(15)	1.344(5)
P(4)–N(2)	1.678(3)	C(23)–O(6)	1.443(4)
N(1)–C(1)	1.497(5)	C(23)–C(24)	1.502(5)
N(2)–C(2)	1.496(5)	C(24)–F(18)	1.335(4)
N(3)–C(3)	1.147(4)	C(24)–F(16)	1.338(4)
N(3)–C(4)	1.482(4)	C(24)–F(17)	1.347(5)
N(4)–C(8)	1.143(4)	C(25)–O(7)	1.438(4)
N(4)–C(9)	1.471(5)	C(25)–C(26)	1.506(6)
C(4)–C(5)	1.514(6)	C(26)–F(19)	1.316(6)
C(4)–C(7)	1.525(5)	C(26)–F(21)	1.326(5)
C(4)–C(6)	1.527(5)	C(26)–F(20)	1.336(5)
C(9)–C(11)	1.504(6)	C(27)–O(8)	1.435(4)

C(9)–C(10)	1.528(6)	C(27)–C(28)	1.496(6)
C(9)–C(12)	1.533(6)	C(28)–F(24)	1.334(4)
C(13)–O(1)	1.447(4)	C(28)–F(23)	1.337(5)
C(13)–C(14)	1.483(6)	C(28)–F(22)	1.349(5)

Table S2.4. Bond angles (°) for $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+[Au^ICl_2]^-$ (**2**).

P(2)–Au(1)–P(1)	174.64(3)	C(11)–C(9)–C(10)	112.2(4)
P(2)–Au(1)–Cl(1)	91.04(3)	N(4)–C(9)–C(12)	106.6(3)
P(1)–Au(1)–Cl(1)	87.88(3)	C(11)–C(9)–C(12)	111.6(4)
P(2)–Au(1)–Rh(1)	90.18(2)	C(10)–C(9)–C(12)	110.7(3)
P(1)–Au(1)–Rh(1)	90.00(2)	O(1)–C(13)–C(14)	106.6(3)
Cl(1)–Au(1)–Rh(1)	170.28(2)	F(2)–C(14)–F(1)	105.4(4)
P(2)–Au(1)–Cl(2)	92.84(3)	F(2)–C(14)–F(3)	106.7(3)
P(1)–Au(1)–Cl(2)	92.48(3)	F(1)–C(14)–F(3)	108.5(4)
Cl(1)–Au(1)–Cl(2)	94.50(3)	F(2)–C(14)–C(13)	112.9(4)
Rh(1)–Au(1)–Cl(2)	95.07(2)	F(1)–C(14)–C(13)	112.9(4)
Cl(4)–Au(2)–Cl(5)	178.80(5)	F(3)–C(14)–C(13)	110.2(4)
C(8)–Rh(1)–C(3)	175.73(13)	O(2)–C(15)–C(16)	107.3(3)
C(8)–Rh(1)–P(4)	93.76(10)	F(4)–C(16)–F(6)	107.0(3)
C(3)–Rh(1)–P(4)	84.37(10)	F(4)–C(16)–F(5)	107.6(3)
C(8)–Rh(1)–P(3)	85.14(10)	F(6)–C(16)–F(5)	107.2(3)
C(3)–Rh(1)–P(3)	96.37(10)	F(4)–C(16)–C(15)	113.3(3)
P(4)–Rh(1)–P(3)	174.62(3)	F(6)–C(16)–C(15)	112.3(3)
C(8)–Rh(1)–Cl(3)	85.73(9)	F(5)–C(16)–C(15)	109.2(3)
C(3)–Rh(1)–Cl(3)	90.31(9)	O(3)–C(17)–C(18)	106.5(3)
P(4)–Rh(1)–Cl(3)	85.89(3)	F(9)–C(18)–F(7)	108.1(3)
P(3)–Rh(1)–Cl(3)	88.77(3)	F(9)–C(18)–F(8)	106.7(3)
C(8)–Rh(1)–Au(1)	91.14(9)	F(7)–C(18)–F(8)	107.5(3)
C(3)–Rh(1)–Au(1)	92.80(9)	F(9)–C(18)–C(17)	112.2(3)
P(4)–Rh(1)–Au(1)	93.25(2)	F(7)–C(18)–C(17)	109.5(3)
P(3)–Rh(1)–Au(1)	92.04(2)	F(8)–C(18)–C(17)	112.6(3)
Cl(3)–Rh(1)–Au(1)	176.68(2)	O(4)–C(19)–C(20)	107.2(3)
O(2)–P(1)–O(1)	99.18(14)	F(10)–C(20)–F(11)	108.0(4)
O(2)–P(1)–N(1)	102.35(14)	F(10)–C(20)–F(12)	107.7(3)
O(1)–P(1)–N(1)	105.47(14)	F(11)–C(20)–F(12)	106.8(4)
O(2)–P(1)–Au(1)	115.21(10)	F(10)–C(20)–C(19)	109.1(4)
O(1)–P(1)–Au(1)	116.35(10)	F(11)–C(20)–C(19)	112.5(3)
N(1)–P(1)–Au(1)	116.04(11)	F(12)–C(20)–C(19)	112.5(3)
O(3)–P(2)–O(4)	99.08(13)	O(5)–C(21)–C(22)	106.9(3)
O(3)–P(2)–N(2)	100.63(14)	F(13)–C(22)–F(14)	107.0(4)

O(4)–P(2)–N(2)	106.37(14)	F(13)–C(22)–F(15)	107.4(3)
O(3)–P(2)–Au(1)	114.84(10)	F(14)–C(22)–F(15)	107.1(3)
O(4)–P(2)–Au(1)	115.54(10)	F(13)–C(22)–C(21)	113.2(3)
N(2)–P(2)–Au(1)	117.82(11)	F(14)–C(22)–C(21)	112.3(3)
O(5)–P(3)–O(6)	98.43(13)	F(15)–C(22)–C(21)	109.6(3)
O(5)–P(3)–N(1)	106.49(14)	O(6)–C(23)–C(24)	107.6(3)
O(6)–P(3)–N(1)	98.95(14)	F(18)–C(24)–F(16)	108.3(3)
O(5)–P(3)–Rh(1)	122.07(11)	F(18)–C(24)–F(17)	106.6(3)
O(6)–P(3)–Rh(1)	113.51(10)	F(16)–C(24)–F(17)	106.5(3)
N(1)–P(3)–Rh(1)	114.02(11)	F(18)–C(24)–C(23)	109.6(3)
O(7)–P(4)–O(8)	106.74(13)	F(16)–C(24)–C(23)	112.9(3)
O(7)–P(4)–N(2)	110.29(14)	F(17)–C(24)–C(23)	112.6(3)
O(8)–P(4)–N(2)	95.43(14)	O(7)–C(25)–C(26)	107.9(3)
O(7)–P(4)–Rh(1)	110.89(10)	F(19)–C(26)–F(21)	107.6(4)
O(8)–P(4)–Rh(1)	118.04(10)	F(19)–C(26)–F(20)	106.4(5)
N(2)–P(4)–Rh(1)	114.33(11)	F(21)–C(26)–F(20)	107.9(4)
C(1)–N(1)–P(1)	120.0(2)	F(19)–C(26)–C(25)	113.1(4)
C(1)–N(1)–P(3)	119.7(2)	F(21)–C(26)–C(25)	109.9(4)
P(1)–N(1)–P(3)	119.84(17)	F(20)–C(26)–C(25)	111.7(4)
C(2)–N(2)–P(2)	116.9(2)	O(8)–C(27)–C(28)	104.9(3)
C(2)–N(2)–P(4)	122.9(2)	F(24)–C(28)–F(23)	108.0(4)
P(2)–N(2)–P(4)	119.21(18)	F(24)–C(28)–F(22)	106.8(4)
C(3)–N(3)–C(4)	175.4(3)	F(23)–C(28)–F(22)	106.0(4)
C(8)–N(4)–C(9)	172.9(4)	F(24)–C(28)–C(27)	111.1(3)
N(3)–C(3)–Rh(1)	170.8(3)	F(23)–C(28)–C(27)	112.2(4)
N(3)–C(4)–C(5)	106.9(3)	F(22)–C(28)–C(27)	112.6(3)
N(3)–C(4)–C(7)	106.3(3)	C(13)–O(1)–P(1)	127.0(2)
C(5)–C(4)–C(7)	111.6(4)	C(15)–O(2)–P(1)	122.1(2)
N(3)–C(4)–C(6)	107.0(3)	C(17)–O(3)–P(2)	122.6(2)
C(5)–C(4)–C(6)	112.5(4)	C(19)–O(4)–P(2)	124.8(2)
C(7)–C(4)–C(6)	112.1(3)	C(21)–O(5)–P(3)	126.5(2)
N(4)–C(8)–Rh(1)	169.4(3)	C(23)–O(6)–P(3)	124.5(2)
N(4)–C(9)–C(11)	108.6(3)	C(25)–O(7)–P(4)	127.5(2)
N(4)–C(9)–C(10)	106.7(3)	C(27)–O(8)–P(4)	129.8(2)

Table S2.5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+[Au^ICl_2]^-$ (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	12(1)	13(1)	13(1)	–2(1)	1(1)	–1(1)
Au(2)	35(1)	24(1)	24(1)	1(1)	–1(1)	–7(1)
Rh(1)	12(1)	11(1)	12(1)	0(1)	1(1)	–1(1)
Cl(1)	19(1)	17(1)	23(1)	–6(1)	2(1)	–4(1)
Cl(2)	20(1)	21(1)	21(1)	1(1)	–2(1)	2(1)
Cl(3)	19(1)	20(1)	20(1)	–6(1)	3(1)	–6(1)
Cl(4)	35(1)	60(1)	35(1)	–7(1)	9(1)	–8(1)
Cl(5)	36(1)	32(1)	61(1)	9(1)	–10(1)	–8(1)
P(1)	15(1)	14(1)	16(1)	–2(1)	2(1)	–3(1)
P(2)	14(1)	14(1)	14(1)	–2(1)	1(1)	0(1)
P(3)	14(1)	12(1)	15(1)	–1(1)	2(1)	–1(1)
P(4)	12(1)	15(1)	14(1)	–1(1)	1(1)	–1(1)
N(1)	16(1)	16(1)	18(2)	–2(1)	6(1)	–4(1)
N(2)	15(1)	21(1)	16(2)	–5(1)	6(1)	–2(1)
N(3)	17(1)	16(1)	21(2)	2(1)	0(1)	0(1)
N(4)	19(1)	22(1)	17(2)	3(1)	3(1)	–1(1)
C(1)	21(2)	23(2)	26(2)	–7(2)	10(2)	–6(2)
C(2)	22(2)	50(3)	26(2)	–13(2)	13(2)	–11(2)
C(3)	13(2)	14(2)	19(2)	–4(1)	0(1)	0(1)
C(4)	29(2)	15(2)	19(2)	7(1)	–1(2)	1(1)
C(5)	71(3)	31(2)	20(2)	5(2)	6(2)	11(2)
C(6)	32(2)	25(2)	35(2)	8(2)	–7(2)	–9(2)
C(7)	29(2)	26(2)	31(2)	10(2)	–6(2)	2(2)
C(8)	13(2)	17(2)	17(2)	–4(1)	4(1)	–2(1)
C(9)	29(2)	25(2)	15(2)	5(1)	–3(2)	–3(2)
C(10)	46(3)	46(3)	19(2)	–3(2)	0(2)	11(2)
C(11)	64(3)	55(3)	28(2)	16(2)	0(2)	–24(3)
C(12)	38(2)	40(2)	25(2)	1(2)	–8(2)	10(2)
C(13)	18(2)	38(2)	27(2)	3(2)	–3(2)	–6(2)
C(14)	21(2)	38(2)	40(3)	–3(2)	–2(2)	–1(2)
C(15)	28(2)	12(2)	26(2)	0(1)	7(2)	–2(1)

C(16)	28(2)	16(2)	27(2)	1(1)	7(2)	–2(2)
C(17)	20(2)	24(2)	20(2)	–3(1)	–2(2)	–1(1)
C(18)	32(2)	22(2)	22(2)	–1(2)	–1(2)	2(2)
C(19)	26(2)	20(2)	21(2)	2(1)	–2(2)	6(2)
C(20)	32(2)	34(2)	31(2)	–3(2)	–5(2)	15(2)
C(21)	23(2)	18(2)	20(2)	1(1)	–1(2)	5(1)
C(22)	27(2)	39(2)	25(2)	–1(2)	–3(2)	8(2)
C(23)	18(2)	20(2)	22(2)	–9(1)	3(1)	–5(1)
C(24)	22(2)	24(2)	31(2)	–10(2)	7(2)	–5(2)
C(25)	20(2)	41(2)	26(2)	3(2)	2(2)	11(2)
C(26)	18(2)	32(2)	68(4)	15(2)	–8(2)	–1(2)
C(27)	22(2)	20(2)	21(2)	–3(1)	4(2)	–7(1)
C(28)	33(2)	32(2)	29(2)	–8(2)	10(2)	–16(2)
F(1)	29(2)	95(3)	78(2)	–42(2)	2(2)	18(2)
F(2)	32(1)	65(2)	76(2)	25(2)	–6(1)	–24(1)
F(3)	22(1)	75(2)	55(2)	11(2)	–12(1)	–1(1)
F(4)	25(1)	36(1)	54(2)	6(1)	17(1)	3(1)
F(5)	46(1)	21(1)	35(1)	0(1)	10(1)	–12(1)
F(6)	49(2)	28(1)	20(1)	1(1)	5(1)	–7(1)
F(7)	52(2)	39(1)	20(1)	–9(1)	–10(1)	–1(1)
F(8)	43(1)	40(1)	31(1)	–8(1)	7(1)	17(1)
F(9)	51(2)	34(1)	23(1)	7(1)	6(1)	–7(1)
F(10)	68(2)	52(2)	59(2)	11(2)	0(2)	44(2)
F(11)	42(2)	47(2)	33(2)	–12(1)	6(1)	18(1)
F(12)	22(1)	70(2)	54(2)	–18(2)	–14(1)	10(1)
F(13)	54(2)	74(2)	39(2)	–21(2)	–6(1)	42(2)
F(14)	23(1)	73(2)	62(2)	18(2)	1(1)	–8(1)
F(15)	36(1)	57(2)	32(1)	3(1)	–9(1)	19(1)
F(16)	24(1)	37(1)	44(2)	–4(1)	10(1)	7(1)
F(17)	34(1)	42(1)	20(1)	–2(1)	9(1)	–2(1)
F(18)	46(2)	35(1)	48(2)	–29(1)	16(1)	–11(1)
F(19)	42(2)	65(2)	36(2)	–7(1)	–18(1)	14(1)
F(20)	62(2)	41(2)	165(4)	34(2)	–65(2)	–26(2)
F(21)	15(1)	111(3)	71(2)	32(2)	2(1)	11(2)
F(22)	30(1)	51(2)	74(2)	–12(2)	27(1)	–4(1)
F(23)	69(2)	52(2)	26(1)	11(1)	12(1)	–25(2)

F(24)	55(2)	53(2)	51(2)	–20(1)	24(1)	–41(2)
O(1)	15(1)	22(1)	19(1)	–2(1)	3(1)	–5(1)
O(2)	24(1)	14(1)	19(1)	2(1)	2(1)	–4(1)
O(3)	20(1)	17(1)	16(1)	0(1)	1(1)	–1(1)
O(4)	17(1)	13(1)	20(1)	–2(1)	1(1)	2(1)
O(5)	21(1)	15(1)	19(1)	–1(1)	2(1)	4(1)
O(6)	19(1)	17(1)	18(1)	–3(1)	1(1)	–2(1)
O(7)	14(1)	22(1)	18(1)	2(1)	0(1)	2(1)
O(8)	20(1)	18(1)	18(1)	–1(1)	1(1)	–7(1)

Table S2.6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+[Au^ICl_2]^-$ (**2**).

	x	y	z	U(eq)
H(1A)	6009	7792	1090	35
H(1B)	6426	7200	1591	35
H(1C)	6731	7950	1732	35
H(2A)	2293	7908	5408	48
H(2B)	1590	8208	4822	48
H(2C)	2204	8696	5306	48
H(5A)	4099	6921	5857	61
H(5B)	3699	6275	6229	61
H(5C)	3162	6714	5617	61
H(6A)	2897	5663	4859	47
H(6B)	3529	5210	5369	47
H(6C)	3653	5301	4463	47
H(7A)	5106	5642	4832	44
H(7B)	5012	5707	5745	44
H(7C)	5281	6339	5254	44
H(10A)	3808	7827	203	56
H(10B)	3073	8080	–380	56
H(10C)	2878	7571	299	56
H(11A)	3491	9482	892	74
H(11B)	3368	9309	–9	74
H(11C)	4150	9018	488	74
H(12A)	1822	8285	802	52
H(12B)	1942	8873	194	52
H(12C)	2034	9021	1103	52
H(13A)	6843	8030	3711	33
H(13B)	6889	8792	3989	33
H(15A)	5804	9774	2569	26
H(15B)	4979	9935	2043	26
H(17A)	4795	8940	5719	26
H(17B)	5064	8196	5960	26
H(19A)	3399	9754	3842	27
H(19B)	3781	10236	4510	27

H(21A)	5450	5929	3458	25
H(21B)	5712	6689	3618	25
H(23A)	3770	6457	889	24
H(23B)	4319	6067	1544	24
H(25A)	1163	8912	3193	35
H(25B)	980	8265	3702	35
H(27A)	2024	6276	3603	25
H(27B)	1386	6779	3158	25

Table S2.7. Selected torsion angles (°) for $[Rh^{II}Au^{II}(tfepma)_2(CN^tBu)_2Cl_3]^+[Au^ICl_2]^-$ (**2**).

P(1)–Au(1)–Rh(1)–P(3)	22.55(3)
P(2)–Au(1)–Rh(1)–P(4)	18.18(3)

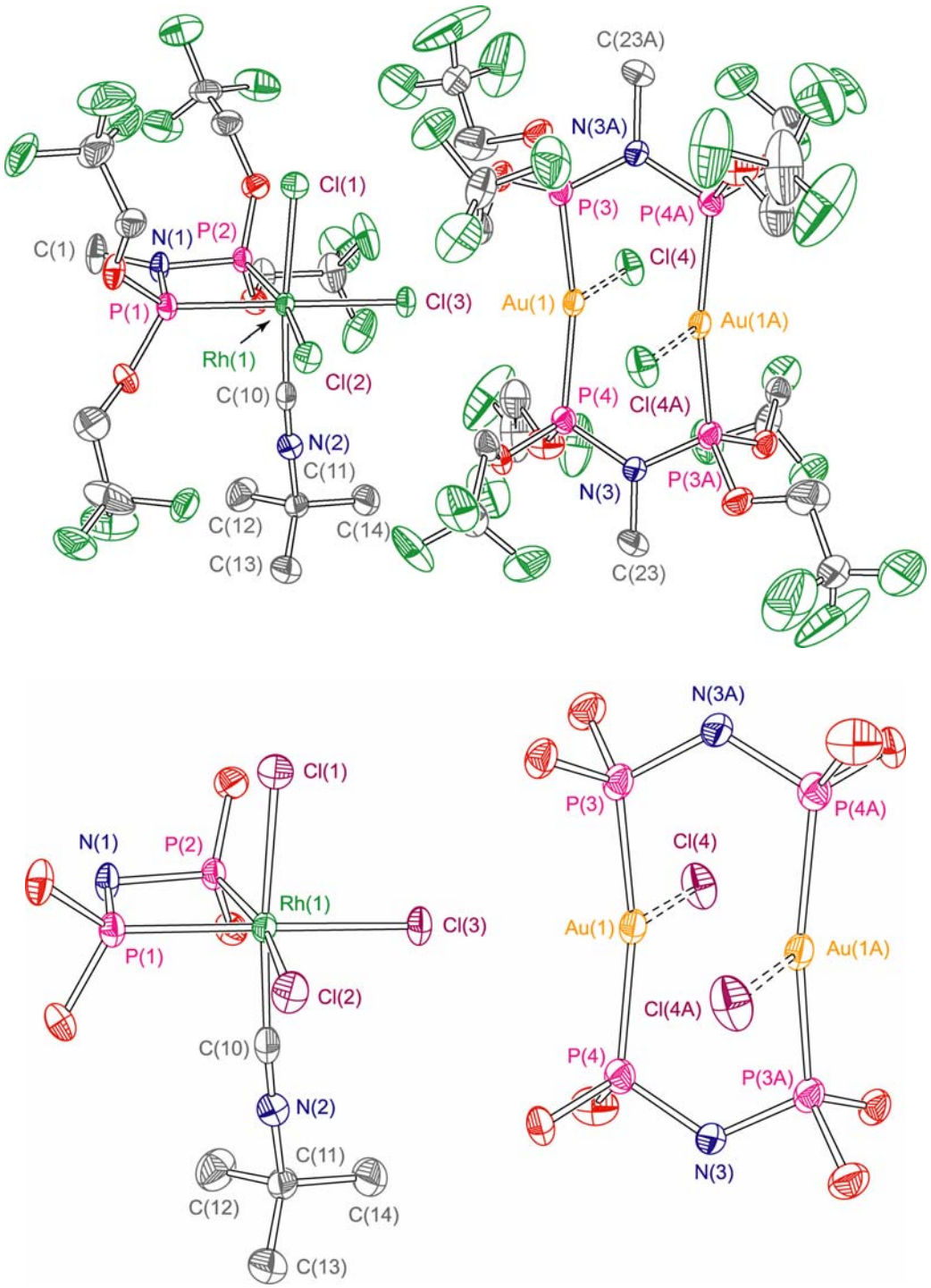

Figure S3. Thermal ellipsoid plot of cocrystallized *fac*–Rh^{III}(tfepma)(CN^tBu)Cl_3 (**3**) and $Au_2^{I,I}$(tfepma)$_2Cl_2$ (**4**). Complex **4** sits on a special position in the asymmetric unit of the crystal lattice and thus half of the molecule is generated by symmetry. These images are rendered directly from the structural solution after using the 'GROW' command to complete complex **4**. Thermal ellipsoids are drawn at the 50% probability level with –OCH_2CF_3 and –N–Me groups (bottom) hydrogens (top and bottom) omitted for clarity.

Table S3.1. Crystal data and structure refinement for *fac*–Rh^{III}(tfepma)(CN^tBu)Cl_3 (**3**) and $Au_2^{I,I}$(tfepma)$_2Cl_2$ (**4**).

Identification code	C06040_p21n	
Empirical formula	$C_{23}H_{31}N_3O_8F_{24}P_4Cl_4RhAu$	
Formula weight	1499.06	
Temperature	–173(2)°C	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*2(1)/*n*	
Unit cell dimensions	a = 12.9108(14) Å	α = 90°
	b = 24.1573(3) Å	β = 103.708(4)°
	c = 16.0473(17) Å	γ = 90°
Volume	4862.4(9) $Å^3$	
Z	4	
Density (calculated)	2.048 Mg/m^3	
Absorption coefficient	3.840 mm^{-1}	
F(000)	2888	
Crystal size	0.20 × 0.10 × 0.05 mm^3	
Θ range for data collection	1.55 to 26.44°	
Index ranges	$-16 \leq h \leq 13$, $-30 \leq k \leq 26$, $-19 \leq \ell \leq 20$	
Reflections collected	29054	
Independent reflections	9971 [R_{int} = 0.0546]	
Completeness to Θ = 28.29°	99.5 %	
Absorption correction	Empirical SADABS	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	9971 / 0 / 628	
Goodness–of–fit on F^2	1.094	
Final R indices [I>2σ(I)]	R_1 = 0.0434, wR_2 = 0.01090	
R indices (all data)	R_1 = 0.0607, wR_2 = 0.1274	
Largest diff. peak and hole	1.727 and –1.203 e/$Å^3$	

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. Refinement on F_o^2 for all reflections (having $F_o^2 \geq -3\sigma(F_o^2)$). wR_2 and GOF based on F_o^2, R_1 based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. [b] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data, p = number of parameters varied; $w = [\sigma^2 F_o^2 + (0.0638P)^2]^{-1}$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table S3.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *fac*-Rh^{III}(tfepma)(CN^tBu)Cl_3 (**3**) and $Au_2^{I,I}$(tfepma)$_2Cl_2$ (**4**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au(1)	9572(1)	505(1)	9615(1)	24(1)
Rh(1)	6473(1)	1073(1)	6723(1)	18(1)
P(1)	5255(1)	1302(1)	5554(1)	21(1)
P(2)	6082(1)	1959(1)	6790(1)	21(1)
P(3)	8072(1)	370(1)	10125(1)	26(1)
P(4)	10709(1)	452(1)	8720(1)	27(1)
Cl(1)	5214(1)	890(1)	7550(1)	29(1)
Cl(2)	6578(1)	106(1)	6376(1)	28(1)
Cl(3)	7900(1)	1035(1)	7994(1)	26(1)
Cl(4)	10558(2)	1207(1)	10797(1)	38(1)
N(1)	5151(4)	1951(2)	5864(3)	24(1)
N(2)	8313(4)	1372(2)	5880(3)	29(1)
N(3)	11758(4)	29(2)	9009(3)	34(1)
C(1)	4518(6)	2408(3)	5375(4)	36(2)
C(2)	3596(5)	638(3)	5622(4)	31(2)
C(3)	2643(6)	916(4)	5801(5)	51(2)
C(4)	5402(6)	988(3)	3995(5)	46(2)
C(5)	6316(8)	904(4)	3660(6)	62(3)
C(6)	4556(5)	2208(3)	7630(5)	34(2)
C(7)	4281(6)	2806(3)	7784(5)	39(2)
C(8)	7173(6)	2919(3)	7136(4)	33(2)
C(9)	8017(6)	2867(3)	7929(5)	45(2)
C(10)	7601(5)	1243(2)	6160(4)	25(1)
C(11)	9227(5)	1576(3)	5576(4)	31(2)
C(12)	8855(6)	2134(3)	5159(6)	46(2)
C(13)	9468(6)	1171(3)	4947(5)	39(2)
C(14)	10134(6)	1641(3)	6364(5)	45(2)
C(15)	10859(7)	1531(3)	8710(6)	50(2)
C(16)	11660(9)	1948(4)	8631(7)	80(4)
C(17)	9442(5)	–133(3)	7546(4)	28(1)
C(18)	9704(7)	–457(3)	6829(5)	43(2)

C(19)	7001(5)	–209(3)	8795(4)	29(1)
C(20)	6255(6)	–668(3)	8867(5)	41(2)
C(21)	7280(8)	1366(3)	9938(6)	58(2)
C(22)	6590(7)	1725(4)	10289(5)	49(2)
C(23)	12612(6)	56(4)	8519(5)	48(2)
F(1)	2889(4)	1346(2)	6334(3)	60(1)
F(2)	2089(5)	564(3)	6159(4)	81(2)
F(3)	1986(4)	1107(3)	5096(3)	79(2)
F(4)	6865(5)	1315(2)	3521(4)	78(2)
F(6)	6136(4)	550(2)	3011(3)	59(1)
F(7)	3317(4)	2824(2)	7942(3)	62(1)
F(8)	4967(4)	3013(2)	8471(3)	59(1)
F(9)	4298(5)	3129(2)	7131(3)	66(2)
F(10)	8193(5)	3350(2)	8328(3)	72(2)
F(11)	7781(4)	2506(2)	8476(3)	62(1)
F(12)	8954(4)	2702(2)	7779(4)	71(2)
F(13)	12597(5)	1870(2)	9212(4)	97(2)
F(14)	11320(5)	2430(2)	8723(6)	123(3)
F(15)	11970(5)	1920(3)	7874(4)	98(2)
F(16)	9610(5)	–160(2)	6124(3)	65(2)
F(17)	9021(4)	–885(2)	6636(3)	56(1)
F(18)	10675(4)	–663(2)	7037(3)	60(1)
F(19)	5268(3)	–489(2)	8819(3)	54(1)
F(20)	6555(4)	–952(2)	9590(3)	64(1)
F(21)	6208(4)	–1025(2)	8216(3)	55(1)
F(22)	5819(6)	1516(3)	10480(8)	161(5)
F(23)	7150(7)	1953(3)	11014(5)	141(4)
F(24)	6280(6)	2160(2)	9810(4)	95(2)
F(5A)	7076(4)	631(2)	4309(4)	40(2)
F(5B)	5624(18)	1466(7)	2991(11)	74(7)
O(1)	4128(3)	1036(2)	5217(3)	30(1)
O(2)	5582(4)	1386(2)	4675(3)	28(1)
O(3)	5619(3)	2238(2)	7511(3)	29(1)
O(4)	6984(3)	2378(2)	6725(3)	27(1)
O(5)	11290(4)	1011(2)	8563(3)	43(1)
O(6)	10194(4)	313(2)	7741(3)	27(1)

O(7)	7009(3)	170(2)	9482(3)	29(1)
O(8)	7590(4)	907(2)	10486(3)	37(1)

Table S3.3. Bond lengths (Å) for *fac*-Rh^{III}(tfepma)(CN^tBu)Cl_3 (**3**) and $Au_2^{I,I}$(tfepma)$_2Cl_2$ (**4**).

Au(1)–P(4)	2.2878(17)	C(5)–F(5A)	1.413(12)
Au(1)–P(3)	2.2973(18)	C(5)–F(5B)	1.83(2)
Au(1)–Cl(4)	2.6364(16)	C(6)–O(3)	1.431(8)
Au(1)–Au(1)[a]	2.8390(5)	C(6)–C(7)	1.520(10)
Rh(1)–C(10)	1.931(7)	C(7)–F(9)	1.312(8)
Rh(1)–P(2)	2.2083(16)	C(7)–F(7)	1.328(8)
Rh(1)–P(1)	2.2144(16)	C(7)–F(8)	1.337(9)
Rh(1)–Cl(1)	2.3707(15)	C(8)–O(4)	1.458(7)
Rh(1)–Cl(3)	2.4047(15)	C(8)–C(9)	1.471(10)
Rh(1)–Cl(2)	2.4128(16)	C(9)–F(11)	1.322(9)
P(1)–O(1)	1.565(4)	C(9)–F(10)	1.325(8)
P(1)–O(2)	1.578(4)	C(9)–F(12)	1.348(10)
P(1)–N(1)	1.659(5)	C(11)–C(13)	1.491(9)
P(2)–O(4)	1.566(4)	C(11)–C(14)	1.513(10)
P(2)–O(3)	1.575(4)	C(11)–C(12)	1.531(9)
P(2)–N(1)	1.676(5)	C(15)–O(5)	1.416(9)
P(3)–O(7)	1.584(4)	C(15)–C(16)	1.469(13)
P(3)–O(8)	1.606(5)	C(16)–F(14)	1.265(12)
P(3)–N(3)[a]	1.663(6)	C(16)–F(13)	1.354(11)
P(4)–O(6)	1.589(4)	C(16)–F(15)	1.369(14)
P(4)–O(5)	1.593(5)	C(17)–O(6)	1.435(7)
P(4)–N(3)	1.673(5)	C(17)–C(18)	1.494(9)
N(1)–C(1)	1.481(8)	C(18)–F(18)	1.317(10)
N(2)–C(10)	1.157(8)	C(18)–F(16)	1.321(8)
N(2)–C(11)	1.466(8)	C(18)–F(17)	1.346(9)
N(3)–C(23)	1.500(8)	C(19)–O(7)	1.432(7)
N(3)–P(3)[a]	1.663(6)	C(19)–C(20)	1.492(10)
C(2)–O(1)	1.424(8)	C(20)–F(20)	1.324(9)
C(2)–C(3)	1.489(10)	C(20)–F(19)	1.331(8)
C(3)–F(3)	1.326(10)	C(20)–F(21)	1.345(9)
C(3)–F(2)	1.327(10)	C(21)–O(8)	1.411(9)
C(3)–F(1)	1.334(9)	C(21)–C(22)	1.450(11)
C(4)–C(5)	1.422(11)	C(22)–F(22)	1.219(10)
C(4)–O(2)	1.432(8)	C(22)–F(24)	1.306(10)

C(5)–F(4)	1.271(10)	C(22)–F(23)	1.335(11)
C(5)–F(6)	1.324(9)	F(4)–F(5B)	1.67(2)

Symmetry transformations used to generate equivalent atoms: [a] –x + 2, –y, –z + 2

Table S3.4. Bond angles (°) for *fac*-Rh^{III}(tfepma)(CN^tBu)Cl_3 (**3**) and $Au_2^{I,I}$(tfepma)$_2Cl_2$ (**4**).

P(4)–Au(1)–P(3)	159.40(6)	F(5A)–C(5)–C(4)	106.4(7)
P(4)–Au(1)–Cl(4)	102.46(6)	F(4)–C(5)–F(5B)	62.0(8)
P(3)–Au(1)–Cl(4)	98.00(6)	F(6)–C(5)–F(5B)	92.7(8)
P(4)–Au(1)–Au(1)[a]	89.08(4)	F(5A)–C(5)–F(5B)	159.5(9)
P(3)–Au(1)–Au(1)[a]	89.81(4)	C(4)–C(5)–F(5B)	77.4(9)
Cl(4)–Au(1)–Au(1)[a]	99.68(4)	O(3)–C(6)–C(7)	104.0(5)
C(10)–Rh(1)–P(2)	91.29(18)	F(9)–C(7)–F(7)	109.0(6)
C(10)–Rh(1)–P(1)	90.79(18)	F(9)–C(7)–F(8)	107.6(6)
P(2)–Rh(1)–P(1)	70.94(6)	F(7)–C(7)–F(8)	107.3(6)
C(10)–Rh(1)–Cl(1)	174.00(18)	F(9)–C(7)–C(6)	112.7(6)
P(2)–Rh(1)–Cl(1)	87.56(6)	F(7)–C(7)–C(6)	109.1(6)
P(1)–Rh(1)–Cl(1)	94.40(6)	F(8)–C(7)–C(6)	110.8(6)
C(10)–Rh(1)–Cl(3)	83.92(18)	O(4)–C(8)–C(9)	108.9(6)
P(2)–Rh(1)–Cl(3)	97.67(6)	F(11)–C(9)–F(10)	107.4(7)
P(1)–Rh(1)–Cl(3)	167.39(6)	F(11)–C(9)–F(12)	106.3(7)
Cl(1)–Rh(1)–Cl(3)	90.39(6)	F(10)–C(9)–F(12)	106.7(6)
C(10)–Rh(1)–Cl(2)	90.53(18)	F(11)–C(9)–C(8)	113.1(6)
P(2)–Rh(1)–Cl(2)	167.40(6)	F(10)–C(9)–C(8)	110.4(7)
P(1)–Rh(1)–Cl(2)	96.57(6)	F(12)–C(9)–C(8)	112.6(7)
Cl(1)–Rh(1)–Cl(2)	91.87(6)	N(2)–C(10)–Rh(1)	174.4(5)
Cl(3)–Rh(1)–Cl(2)	94.91(5)	N(2)–C(11)–C(13)	108.6(6)
O(1)–P(1)–O(2)	99.7(2)	N(2)–C(11)–C(14)	106.3(5)
O(1)–P(1)–N(1)	111.0(3)	C(13)–C(11)–C(14)	112.9(6)
O(2)–P(1)–N(1)	101.8(2)	N(2)–C(11)–C(12)	104.3(5)
O(1)–P(1)–Rh(1)	127.25(18)	C(13)–C(11)–C(12)	112.1(6)
O(2)–P(1)–Rh(1)	120.11(18)	C(14)–C(11)–C(12)	112.0(6)
N(1)–P(1)–Rh(1)	94.28(18)	O(5)–C(15)–C(16)	106.4(8)
O(4)–P(2)–O(3)	100.9(2)	F(14)–C(16)–F(13)	109.0(8)
O(4)–P(2)–N(1)	109.6(3)	F(14)–C(16)–F(15)	109.3(9)
O(3)–P(2)–N(1)	109.8(3)	F(13)–C(16)–F(15)	101.7(10)
O(4)–P(2)–Rh(1)	116.20(18)	F(14)–C(16)–C(15)	110.5(11)
O(3)–P(2)–Rh(1)	125.63(18)	F(13)–C(16)–C(15)	112.2(8)
N(1)–P(2)–Rh(1)	94.04(18)	F(15)–C(16)–C(15)	113.7(8)
O(7)–P(3)–O(8)	97.5(2)	O(6)–C(17)–C(18)	107.3(6)

O(7)–P(3)–N(3)[a]	106.8(3)	F(18)–C(18)–F(16)	108.1(7)
O(8)–P(3)–N(3)[a]	98.8(3)	F(18)–C(18)–F(17)	107.4(6)
O(7)–P(3)–Au(1)	119.01(18)	F(16)–C(18)–F(17)	107.3(7)
O(8)–P(3)–Au(1)	116.5(2)	F(18)–C(18)–C(17)	112.2(7)
N(3)[a]–P(3)–Au(1)	115.1(2)	F(16)–C(18)–C(17)	112.6(6)
O(6)–P(4)–O(5)	97.2(3)	F(17)–C(18)–C(17)	108.9(7)
O(6)–P(4)–N(3)	105.5(3)	O(7)–C(19)–C(20)	107.7(6)
O(5)–P(4)–N(3)	100.4(3)	F(20)–C(20)–F(19)	107.3(7)
O(6)–P(4)–Au(1)	116.88(18)	F(20)–C(20)–F(21)	107.4(6)
O(5)–P(4)–Au(1)	116.61(19)	F(19)–C(20)–F(21)	107.3(6)
N(3)–P(4)–Au(1)	117.2(2)	F(20)–C(20)–C(19)	113.1(6)
C(1)–N(1)–P(1)	128.2(4)	F(19)–C(20)–C(19)	112.3(6)
C(1)–N(1)–P(2)	130.6(4)	F(21)–C(20)–C(19)	109.1(6)
P(1)–N(1)–P(2)	100.6(3)	O(8)–C(21)–C(22)	109.7(7)
C(10)–N(2)–C(11)	175.1(6)	F(22)–C(22)–F(24)	109.0(8)
C(23)–N(3)–P(3)[a]	119.7(5)	F(22)–C(22)–F(23)	104.9(9)
C(23)–N(3)–P(4)	118.4(5)	F(24)–C(22)–F(23)	102.1(8)
P(3)[a]–N(3)–P(4)	121.6(3)	F(22)–C(22)–C(21)	117.6(9)
O(1)–C(2)–C(3)	107.1(6)	F(24)–C(22)–C(21)	112.6(7)
F(3)–C(3)–F(2)	106.9(7)	F(23)–C(22)–C(21)	109.3(8)
F(3)–C(3)–F(1)	106.4(7)	C(5)–F(4)–F(5B)	75.6(9)
F(2)–C(3)–F(1)	107.0(7)	F(4)–F(5B)–C(5)	42.3(6)
F(3)–C(3)–C(2)	112.5(7)	C(2)–O(1)–P(1)	129.0(4)
F(2)–C(3)–C(2)	110.5(7)	C(4)–O(2)–P(1)	124.5(5)
F(1)–C(3)–C(2)	113.1(6)	C(6)–O(3)–P(2)	128.2(4)
C(5)–C(4)–O(2)	112.6(6)	C(8)–O(4)–P(2)	126.7(4)
F(4)–C(5)–F(6)	111.5(7)	C(15)–O(5)–P(4)	120.5(5)
F(4)–C(5)–F(5A)	100.1(8)	C(17)–O(6)–P(4)	118.5(4)
F(6)–C(5)–F(5A)	104.0(8)	C(19)–O(7)–P(3)	122.9(4)
F(4)–C(5)–C(4)	120.2(8)	C(21)–O(8)–P(3)	119.0(4)
F(6)–C(5)–C(4)	112.5(7)		

Symmetry transformations used to generate equivalent atoms: [a] –x + 2, –y, –z + 2

Table S3.5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for *fac*-Rh^{III}(tfepma)(CN^tBu)-Cl_3 (**3**) and $Au_2^{I,I}$(tfepma)$_2Cl_2$ (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	25(1)	24(1)	21(1)	–2(1)	–1(1)	6(1)
Rh(1)	17(1)	21(1)	17(1)	0(1)	0(1)	2(1)
P(1)	21(1)	21(1)	18(1)	–2(1)	–2(1)	1(1)
P(2)	20(1)	24(1)	17(1)	–1(1)	–1(1)	2(1)
P(3)	24(1)	31(1)	21(1)	–5(1)	–1(1)	6(1)
P(4)	26(1)	30(1)	22(1)	–4(1)	0(1)	1(1)
Cl(1)	26(1)	33(1)	27(1)	3(1)	7(1)	0(1)
Cl(2)	29(1)	23(1)	30(1)	–5(1)	1(1)	2(1)
Cl(3)	25(1)	27(1)	21(1)	1(1)	–5(1)	3(1)
Cl(4)	57(1)	26(1)	26(1)	–6(1)	–2(1)	–4(1)
N(1)	24(3)	22(3)	21(3)	–3(2)	–6(2)	5(2)
N(2)	27(3)	34(3)	25(3)	1(2)	6(2)	1(2)
N(3)	25(3)	56(4)	21(3)	3(3)	4(2)	14(3)
C(1)	41(4)	21(3)	35(4)	1(3)	–14(3)	9(3)
C(2)	23(3)	36(4)	32(4)	–7(3)	5(3)	–6(3)
C(3)	27(4)	73(6)	49(5)	–21(4)	3(4)	–5(4)
C(4)	41(4)	52(5)	42(4)	–26(4)	3(4)	–4(3)
C(5)	78(7)	69(6)	50(5)	–32(5)	35(5)	–32(5)
C(6)	30(4)	41(4)	33(4)	–10(3)	11(3)	–1(3)
C(7)	34(4)	48(4)	40(4)	–2(3)	20(3)	0(3)
C(8)	36(4)	23(3)	34(4)	3(3)	–3(3)	–8(3)
C(9)	43(5)	40(4)	42(4)	–5(3)	–11(4)	–20(3)
C(10)	27(3)	23(3)	20(3)	0(2)	–3(3)	5(2)
C(11)	22(3)	44(4)	27(3)	8(3)	7(3)	2(3)
C(12)	41(5)	43(5)	56(5)	16(4)	14(4)	6(3)
C(13)	35(4)	50(5)	32(4)	1(3)	12(3)	1(3)
C(14)	30(4)	70(6)	33(4)	0(4)	3(3)	–2(4)
C(15)	55(5)	40(5)	51(5)	10(4)	4(4)	1(4)
C(16)	92(8)	41(6)	76(7)	3(5)	–43(6)	–26(5)
C(17)	34(4)	28(3)	19(3)	–4(3)	–1(3)	1(3)
C(18)	59(5)	33(4)	35(4)	–2(3)	7(4)	1(3)

C(19)	29(4)	28(3)	25(3)	–3(3)	–1(3)	–1(3)
C(20)	32(4)	36(4)	48(5)	0(4)	–5(3)	2(3)
C(21)	83(7)	28(4)	73(6)	5(4)	41(5)	15(4)
C(22)	37(5)	70(6)	40(5)	5(4)	9(4)	16(4)
C(23)	40(4)	80(6)	29(4)	10(4)	17(3)	10(4)
F(1)	35(3)	76(3)	65(3)	–31(3)	5(2)	11(2)
F(2)	52(4)	115(5)	90(4)	–22(4)	42(3)	–26(3)
F(3)	27(3)	137(5)	61(3)	–30(3)	–13(2)	20(3)
F(4)	95(5)	62(3)	96(5)	–4(3)	58(4)	–11(3)
F(6)	68(3)	74(3)	39(3)	–28(2)	17(2)	1(2)
F(7)	55(3)	63(3)	76(4)	–8(3)	32(3)	10(2)
F(8)	78(4)	50(3)	57(3)	–29(2)	32(3)	–15(2)
F(9)	84(4)	55(3)	70(3)	20(3)	43(3)	25(3)
F(10)	87(4)	61(3)	59(3)	–24(3)	–2(3)	–39(3)
F(11)	69(3)	68(3)	34(2)	17(2)	–16(2)	–22(3)
F(12)	34(3)	82(4)	83(4)	–3(3)	–10(3)	–5(2)
F(13)	86(5)	58(4)	112(5)	6(3)	–43(4)	–14(3)
F(14)	65(4)	30(3)	257(10)	33(4)	6(5)	–3(3)
F(15)	84(5)	122(6)	81(5)	25(4)	4(4)	–51(4)
F(16)	116(5)	57(3)	21(2)	–4(2)	13(3)	–8(3)
F(17)	80(4)	40(3)	42(3)	–20(2)	3(2)	–6(2)
F(18)	61(3)	49(3)	73(3)	–16(3)	24(3)	12(2)
F(19)	26(2)	58(3)	74(3)	–10(2)	5(2)	–8(2)
F(20)	70(4)	51(3)	68(3)	27(3)	8(3)	–6(2)
F(21)	51(3)	36(2)	71(3)	–23(2)	0(2)	–5(2)
F(22)	96(6)	83(5)	351(14)	81(6)	148(8)	51(4)
F(23)	155(8)	139(7)	103(6)	–64(5)	–21(5)	86(6)
F(24)	139(6)	62(4)	96(5)	16(3)	51(4)	55(4)
F(5A)	26(3)	47(4)	42(4)	–8(3)	–3(3)	8(2)
F(5B)	112(18)	65(12)	47(11)	–1(9)	25(11)	–20(11)
O(1)	22(2)	33(3)	28(2)	2(2)	–8(2)	–4(2)
O(2)	34(3)	31(2)	16(2)	–3(2)	2(2)	–3(2)
O(3)	27(2)	33(2)	27(2)	–9(2)	6(2)	–1(2)
O(4)	30(2)	27(2)	25(2)	–4(2)	5(2)	–4(2)
O(5)	46(3)	38(3)	47(3)	–14(2)	16(3)	–10(2)
O(6)	34(3)	25(2)	19(2)	2(2)	–1(2)	3(2)

O(7)	24(2)	34(3)	25(2)	–6(2)	–2(2)	6(2)
O(8)	31(3)	45(3)	32(3)	–10(2)	5(2)	11(2)

Table S3.6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for Rh^{III}(tfepma)(CN^tBu)Cl_3 (**3**) and $Au_2^{I,I}$(tfepma)$_2Cl_2$ (**4**).

	x	y	z	U(eq)
H(1A)	4656	2427	4801	54
H(1B)	4722	2759	5676	54
H(1C)	3758	2339	5326	54
H(2A)	4075	507	6163	37
H(2B)	3378	315	5240	37
H(4A)	5193	631	4210	55
H(4B)	4803	1115	3527	55
H(6A)	4527	1973	8129	41
H(6B)	4060	2057	7113	41
H(8A)	6510	3057	7272	39
H(8B)	7393	3187	6744	39
H(12A)	8253	2075	4665	70
H(12B)	9442	2310	4967	70
H(12C)	8632	2374	5577	70
H(13A)	9636	810	5226	58
H(13B)	10080	1301	4739	58
H(13C)	8846	1134	4463	58
H(14A)	9901	1873	6785	67
H(14B)	10743	1816	6202	67
H(14C)	10344	1276	6613	67
H(15A)	10719	1543	9290	60
H(15B)	10182	1600	8281	60
H(17A)	8707	14	7371	34
H(17B)	9496	–372	8055	34
H(19A)	7727	–357	8836	35
H(19B)	6760	–19	8236	35
H(21A)	6899	1235	9362	69
H(21B)	7920	1573	9878	69
H(23A)	13294	150	8911	72
H(23B)	12428	340	8072	72
H(23C)	12672	–304	8254	72

Computational Methods

The Gaussian 98 program suite was employed for computational studies.[6] Geometry optimizations were initiated using atomic coordinates obtained from X-ray diffraction data for complex **2**. Trifluoroethoxy and -N-Me groups on the tfepma ligands and *tert*-butyl groups of the *tert*-butylisonitriles were replaced with protons. DFT calculations were carried out using the three parameter hybrid exchange functional of Becke[7] in conjunction with the correlation functional of Lee, Yang, and Parr, which includes both local and non-local terms (B3LYP).[8,9] Relativistic core potentials were used for rhodium and gold along with the standard Hay-Wadt double zeta basis set (LANL2DZ),[10] and augmented for rhodium by the optimized Rh 5p function of Couty and Hall.[11] The 6-31G(d,p) basis of Pople and co-workers[12,13] was applied to all other atoms. Optimized geometries were confirmed as energy minima by analytical frequency calculations. Time dependent calculations were initiated from the optimized geometry using the B3LYP exchange and correlation functionals. The default "extrafine" grid was used throughout. The calculations reported here are for molecules in the gas phase and no attempt has been made to correct for the effects of solvation. Canonical Kohn-Sham orbitals were imaged using the program Molekel, with the default isodensity values applied.[14,15]

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Table S4. Cartesian Coordinates for the Optimized Geometry of $Rh^{II}Au^{II}(HN[PH_2]_2)_2$ $(CNH)_2Cl_2^{2+}$.

	x	y	z
Au	0.135527	–1.05872	0.794459
Rh	–0.13905	1.084146	–0.8134
Cl	–0.38523	3.011306	–2.25954
Cl	0.388329	–3.02494	2.269437
P	–0.78682	–2.5373	–0.81594
P	–1.08748	–0.14914	–2.59408
P	0.772776	2.60148	0.7543
P	1.083156	0.227162	2.549161
N	1.251191	1.891335	2.234914
N	2.734706	0.656087	–2.05897
N	–1.25976	–1.82276	–2.28641
N	–3.03543	1.687375	0.300215
C	1.687079	0.773789	–1.57321
C	–1.96945	1.427313	–0.07847
H	–1.9044	–3.21495	–0.29908
H	0.110461	–3.57478	–1.12229
H	–0.36983	–0.05603	–3.79972
H	–2.3617	0.299151	–2.98484
H	–0.09232	3.65486	1.099674
H	1.899777	3.299518	0.285369
H	0.336279	0.096236	3.732525
H	2.35057	–0.2632	2.907699
H	1.652626	2.484968	2.960401
H	3.632789	0.598373	–2.51114
H	–1.66089	–2.41914	–3.00981
H	–3.96076	1.955455	0.593891

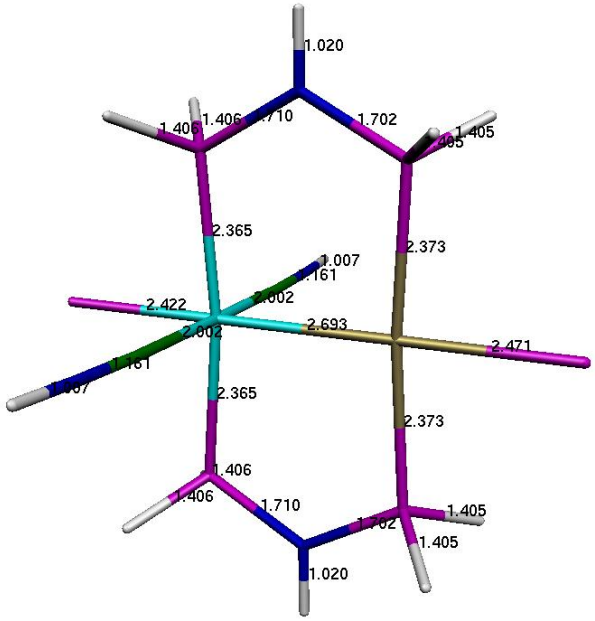

Figure S4. Optimized Geometry for $Rh^{II}Au^{II}(HN[PH_2]_2)_2(CNH)_2Cl_2^{2+}$.

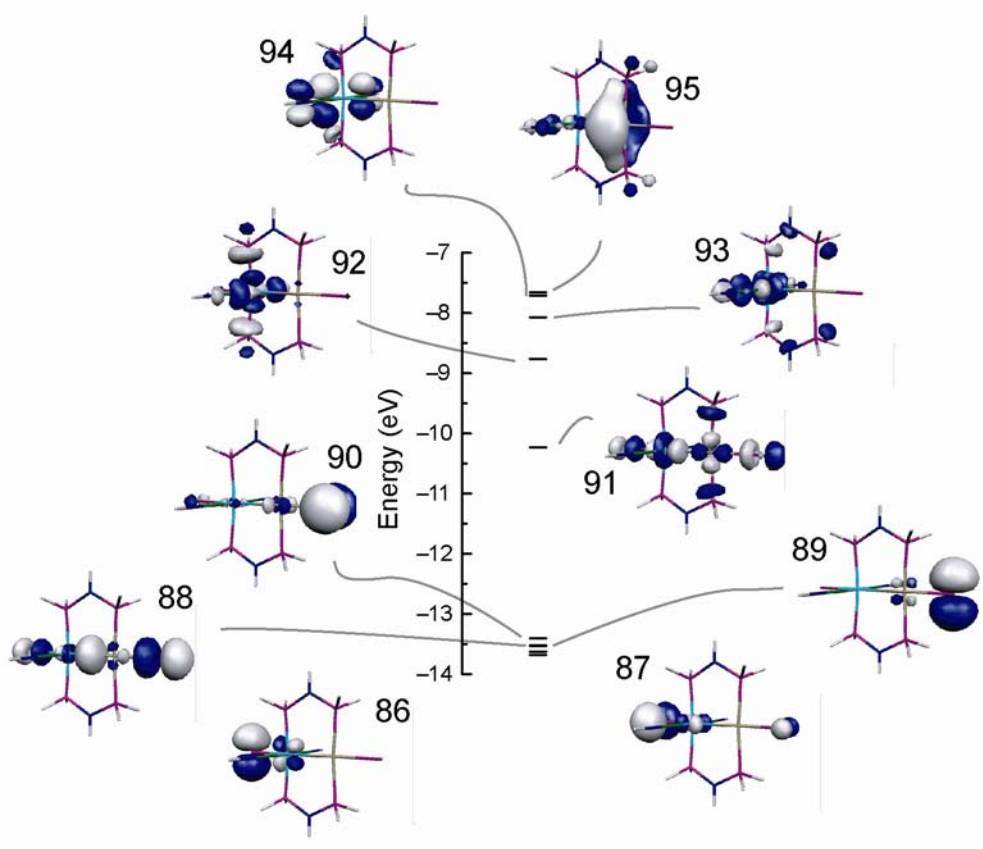

Figure S5. HOMO–4 to LUMO+4 for $Rh^{II}Au^{II}(HN[PH_2]_2)_2(CNH)_2Cl_2^{2+}$.

Table S5. Singlet TDDFT results for $Rh^{II}Au^{II}[CH_2(PH_2)_2]_2(CNH)_2Cl_2^{2+}$ showing only the computed electronic transitions with nonzero oscillator strengths.

Excited State	Singlet Sym	Energy (eV)	λ (nm)	*f*
88→91	0.57697	3.3401	371.20	0.4344
88→92	0.67705	3.9580	313.25	0.0481
78→91	0.20099			
83→91	0.52691	4.0006	309.91	0.0305
86→92	–0.37354			