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## Heterobimetallic rhodium-gold halide and hydride complexes †‡

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Heterobimetallic  $Rh^{I}Au^{I}$  halide complexes react with LiHBEt<sub>3</sub> to afford the corresponding hydride, and they are oxidised by halogen to afford thermally stable  $Rh^{II}Au^{II}$  complexes. The hydride complex reacts with acid and halogen sources to produce  $H_{2}$  and HCl, respectively. The  $Rh^{II}Au^{II}$  complexes exhibit optical and photochemical properties that are derived from the bimetallic core.

Photocatalytic hydrogen production from hydrohalic acids can be mediated by phosphazane-bridged dirhodium complexes, though ultimately the efficiency is limited by the poor quantum yield of halogen ( $X_2$ ) photoelimination.<sup>1–3</sup> We have demonstrated the first systems that are able to photoreductively eliminate  $X_2$ .<sup>4–7</sup> Our interest in heterobimetallic complexes, specifically those featuring rhodium, is rooted in the potential to couple  $H_2$  generation<sup>1,2,8</sup> with  $X_2$  elimination. An initial foray into Rh<sup>II</sup>Au<sup>II</sup> heterobimetallic complexes, bridged by the phosphazane [P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>NMe (tfepma), yielded products whose thermal instability precluded reliable examination of their thermal and photochemical reactivity.<sup>9</sup> Motivated by our recent success with analogous iridium-gold complexes,<sup>7</sup> we report here a suite of thermally stable halide and hydride-bound rhodium-gold complexes bridged by bis(dicyclohexylphosphino)methane (dcpm).

Rh<sup>I</sup>Au<sup>I</sup> halide complexes are prepared in the stepwise procedure outlined in Scheme 1, generating heterobimetallic complexes 1–4, which are isolated as either PF<sub>6</sub><sup>-</sup> (1–3) or OTf<sup>-</sup> (4) salts in isolated yields of 74–83%. The Rh<sup>I</sup>Au<sup>I</sup> complexes are readily identified by their <sup>31</sup>P{<sup>1</sup>H} NMR spectra, which show two AA'XX' multiplets largely reminiscent of the splitting observed for isostructural Ir<sup>I</sup>Au<sup>I</sup> complexes,<sup>7</sup> with observed <sup>1</sup>J<sub>Rh-P</sub> values of 113–120 Hz. The Rh<sup>I</sup>Au<sup>I</sup> halide



Department of Chemistry, Massachusetts Institute of Technology, 6-335, 77 Massachusetts Ave., Cambridge, MA 02139-4307, USA. E-mail: nocera@mit.edu; Fax: +1 617 253 7670; Tel: +1 617 253 5537 complexes also show a single, strong absorption feature in the visible region (Fig. S1–S4, ESI‡), attributed to a  $d\sigma^* \rightarrow p\sigma$  transition characteristic of  $d^8 \cdots d^{10}$  complexes.<sup>10</sup> Full characterization of all complexes is provided in ESI.‡

Halogen oxidation of 1–4 affords  $Rh^{II}Au^{II}$  complexes 5–8 quantitatively, as shown in Scheme 1. A substantial upfield shift of the <sup>31</sup>P resonances of the Rh<sup>I</sup>Au<sup>I</sup> precursor occurs upon its treatment with PhICl<sub>2</sub> or Br<sub>2</sub>. An apparent triplet splitting pattern is observed, and <sup>1</sup>J<sub>Rh-P</sub> values are slightly smaller at 74–79 Hz. Whereas dppm-bridged 7 and 8 decompose above –20 °C to an intractable mixture of products, dcpm-bridged 5 and 6 are stable in solution at room temperature for at least 8 h with no observable change in the <sup>31</sup>P spectrum.

Crystallographic characterisation of complexes 5-(PF<sub>6</sub>)§ and 6-(PF<sub>6</sub>)¶ reveals the presence of a metal–metal bond. The thermal ellipsoid plots for complexes 1 and 5 are depicted in Fig. 1. X-Ray structures of 2–4 and 6 are shown in Fig. S6–S9, ESI.‡ The intermetallic distances of 2.9250(4) Å in 1|| and 2.9187(2) Å in 2\*\* contract to 2.6812(4) Å in 5 and 2.6960(3) Å in 6, consistent with formation of a metal–metal bond. The typical octahedral coordination environment of metal–metal bonded d<sup>7</sup> Rh<sup>II</sup> and the square planar environment of d<sup>9</sup> Au<sup>II</sup> centres are readily apparent in the crystal structures.

The optical spectra of 5-(PF<sub>6</sub>) and 6-(PF<sub>6</sub>), depicted in Fig. 2, are similar to those of the isostructural iridium–gold complexes but red-shifted.<sup>7</sup> Substitution of the chlorides in 5 with bromides in 6 causes a noticeable bathochromic shift in the absorption features, indicative of LMCT character in the excited states.

The LMCT character of **5** and **6** suggests that a halogen elimination photochemistry may be accessible. Indeed, irradiation of acetonitrile solutions of complexes **5**-(PF<sub>6</sub>) or **6**-(PF<sub>6</sub>) with the UV light in the presence of 2,3-dimethyl-1,3butadiene (DMBD) as a halogen trap results in smooth



Fig. 1 X-Ray crystal structures for complexes 1 (left) and 5 (right), depicted at the 50% probability level with hydrogen atoms, counterions, and solvents of crystallization omitted.

<sup>†</sup> This article is part of a ChemComm 'Hydrogen' web-based themed issue.

<sup>‡</sup> Electronic supplementary information (ESI) available: Experimental details, additional spectra and crystallographic tables. CCDC 789594–789600. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc03261a



Fig. 2 Room temperature UV-vis absorption spectra of 5-(PF<sub>6</sub>) (-) and 6-(PF<sub>6</sub>) (--) recorded in CH<sub>2</sub>Cl<sub>2</sub> solution.



**Fig. 3** Spectral evolution for the photolysis of **5** with monochromatic 320 nm light in acetonitrile with 2.2 M DMBD at 283 K. Traces shown from 0 to 39 min in 3 min intervals.

conversion to the corresponding Rh<sup>I</sup>Au<sup>I</sup> complexes 1-(PF<sub>6</sub>) and 2-(PF<sub>6</sub>). Fig. 3 shows the evolution of the UV-vis spectra during the photoconversion of a 40  $\mu$ M solution of chloride complex 5 to 1 when irradiated at 320 nm in the presence of 2.2 M DMBD. Well-anchored isosbestic points are maintained at 400 and 440 nm, and the final spectrum matches an authentic spectrum of 1. The product-forming quantum yield ( $\Phi_p$ ) for this transformation was found to be 9.4(8)% in 2.2 M DMBD. The quantum efficiency is minimally responsive to the DMBD concentration in the range of 0.55 to 4.4 M (Table S3, ESI<sup>‡</sup>).

Photoconversion of bromide-substituted **6** to its Rh<sup>1</sup>Au<sup>1</sup> precursor **2** is likewise facile with 320 nm excitation, as gleaned from the UV-vis traces in Fig. 4. Isosbestic points are maintained at 416 and 429 nm, and again quantitative photo-reduction is apparent. For this conversion, the quantum yield,  $\Phi_{\rm p}$ , increases significantly as the [DMBD] is increased, as shown in the inset of Fig. 4 and the data listed in Table S3, ESI.<sup>‡</sup> The  $\Phi_{\rm p}$  at 0.055 M DMBD is 3.1(2)%, and a value of 18.2(5)% is attained when the DMBD concentration is 4.4 M.

Having established the halogen elimination photochemistry of rhodium–gold complexes, we next sought to prepare hydride-bound analogues that would be likely intermediates in a HX-splitting scheme. As depicted in Scheme 2, treatment of chloride-bound  $Rh^{I}Au^{I}$  complex 1-(PF<sub>6</sub>) with a stoichiometric amount of LiHBEt<sub>3</sub> (Super-Hydride<sup>®</sup>) yields the hydride complex [ $Rh^{I}Au^{I}(dcpm)_{2}(CO)H$ ](PF<sub>6</sub>) (9), which was isolated in 86% yield. An analogous strategy has been



**Fig. 4** Spectral evolution for the photolysis of **6** with monochromatic 320 nm light in acetonitrile with 2.2 M DMBD at 283 K. Spectra shown from 0 to 8 min; 2 min interval for the first spectrum and 1 min intervals afterward.



used to prepare a gold(I) hydride,<sup>11</sup> though in our case the hydride is bound to rhodium owing to the strong tendency of gold(I) to remain in a linear, two-coordinate geometry. The most definitive evidence for the presence of a hydride ligand comes from the <sup>1</sup>H NMR spectrum (Fig. S10, ESI<sup>‡</sup>), which shows a symmetric nine-line multiplet centered at -4.41 ppm for the hydride bound to rhodium. <sup>1</sup>H{<sup>31</sup>P} NMR spectra provided additional insight into the splitting pattern. A fully decoupled  ${}^{1}H{}^{31}P{}$  spectrum shows a doublet splitting pattern, with  ${}^{1}J_{\text{H-Rh}} = 12 \text{ Hz}$  (Fig. S11, ESI<sup>‡</sup>). With a lower decoupling power, only short-range <sup>31</sup>P coupling is observed, resulting in an apparent quartet splitting pattern indicative of a  ${}^{2}J_{H-P}$ coupling constant that is also 12 Hz (Fig. S12, ESI<sup>‡</sup>). The remainder of the nine-line splitting pattern is generated by considering long-range  ${}^{3}J_{H-P}$  coupling with a value of 6 Hz. This collection of coupling constants predicts а 1:2:4:6:6:4:2:1 nonet, which is precisely what is observed. The optical spectrum of 9 (Fig. S5, ESI<sup>‡</sup>) is consistent with the formulation of a  $d^8 \cdots d^{10}$  electronic structure.

Crystallographic characterisation verifies the identity of 9,†† as shown in the thermal ellipsoid plot in Fig. 5. The



Fig. 5 Thermal ellipsoid plot for complex 9, depicted at the 50% probability level with carbon-bound hydrogen atoms, counterions, and solvents of crystallization omitted.



intermetallic distance of 2.8556(5) Å in **9** is only slightly shorter than the one found in **1** and is consistent with a weak metal–metal interaction, as observed in other  $d^{8} \cdots d^{10}$ complexes.<sup>4,7,9,12</sup> The coordination geometries around the metal centres are also reminiscent of these previous examples. Additionally, the *trans* influence of the hydride ligand, which was located in the difference map, is evident when comparing the structure of hydride complex **9** to those of halide complexes **1** and **2**. The Rh–C internuclear distance, which is 1.828(4) Å in **1** and 1.807(3) Å in **2**, lengthens to 1.885(4) Å in **9**.

Mixed hydrido-halide complexes have been shown to be intermediates in HX-splitting mediated by dirhodium complexes.<sup>2</sup> With the goal of accessing a mixed hydrido-halide Rh<sup>II</sup>Au<sup>II</sup> complex, 9 was treated with one equivalent of PhICl<sub>2</sub>. <sup>31</sup>P NMR of the reaction mixture showed a *ca*. 1 : 1 mixture of Rh<sup>I</sup>Au<sup>I</sup> chloride complex 1 and the Rh<sup>II</sup>Au<sup>II</sup> complex 5, suggesting that hydride 9 is completely consumed with a sub-stoichiometric amount of PhICl<sub>2</sub>. Indeed, treatment of hydride-bound 9 with 0.5 equivalents of PhICl<sub>2</sub> furnishes 1 cleanly. The same reaction, carried out in benzene in the presence of 2.6-lutidine, leads to precipitation of 2,6-lutidinium hydrochloride (LutH<sup>+</sup>Cl<sup>-</sup>) and incomplete consumption of 9, demonstrating that HCl is produced during the reaction. Hydride complex 9 reacts rapidly with LutH<sup>+</sup>Cl<sup>-</sup> in solvents such as acetonitrile, where both are substantially soluble. The overall reactivity of complex 9 is summarised in Scheme 3. Such reactivity is well-documented for late-transition metal hydride complexes,<sup>13</sup> and precludes the isolation of mixed hydrido-halide Rh<sup>II</sup>Au<sup>II</sup> complexes.

Further support of the reaction pathways depicted in Scheme 3 is provided by GC analysis of the headspace gases evolved from each of the reactions. For both reactions, GC measurements demonstrated that  $H_2$  was the exclusive gaseous product. Reaction of **9** with one equivalent of LutH<sup>+</sup>Cl<sup>-</sup> yielded 0.84  $\pm$  0.08 equivalents of H<sub>2</sub>, in good agreement with the expected stoichiometry. The reaction of **9** with 0.5 equivalents of PhICl<sub>2</sub> produced 0.38  $\pm$  0.03 equivalents of H<sub>2</sub> (relative to **9**), again reasonably close to the expected 0.5 equivalents.

Several heterobimetallic RhAu complexes have been synthesized and they exhibit active thermal oxidative-addition and photochemical reductive chemistries. In contrast to a previous Rh<sup>II</sup>Au<sup>II</sup> complex,<sup>9</sup> [Rh<sup>II</sup>Au<sup>II</sup>(dcpm)<sub>2</sub>(CO)X<sub>3</sub>](PF<sub>6</sub>) (X = Cl, Br) are thermally robust, allowing for the photochemical characterisation of RhAu heterobimetallic complexes for the first time. Irradiation of the Rh<sup>II</sup>Au<sup>II</sup> complexes with UV light in the presence of a halogen trap results in clean photoreduction to the corresponding Rh<sup>I</sup>Au<sup>I</sup> complex. These complexes are consistent with the emerging trend that d<sup>7</sup>–d<sup>9</sup> complexes can efficiently eliminate halogen when irradiated. In addition, a hydride-bound  $Rh^{I}Au^{I}$  complex is accessed by treating chloride complex 1 with LiHBEt<sub>3</sub>. <sup>1</sup>H NMR and X-ray crystallography clearly reveal the presence of a rhodium-bound hydride, unprecedented in rhodium–gold heterobimetallic chemistry. The rhodium-hydride moiety is quite reactive, producing HCl upon treatment with PhICl<sub>2</sub> and H<sub>2</sub> upon treatment with acid. Our interest in new platforms for HX-splitting is ongoing, and will likely lead us to pursue other mixed-metal hydrido-halide complexes.

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## Notes and references

§ Crystallographic data for **5**-(PF<sub>6</sub>)·CH<sub>2</sub>Cl<sub>2</sub>: C<sub>52</sub>H<sub>94</sub>AuCl<sub>5</sub>F<sub>6</sub>OP<sub>5</sub>Rh, M = 1481.25, monoclinic,  $P2_1/c$ , a = 14.6050(13), b = 20.5013(17), c = 20.6567(18),  $\beta = 95.374(2)^\circ$ , V = 6157.9(9), Z = 4,  $\mu = 3.048$  mm<sup>-1</sup>, T = 100(2) K,  $R_1 = 0.0552$ ,  $wR_2 = 0.0899$  (based on all reflections), GooF = 1.060, reflections measured = 122466, unique reflections = 16655,  $R_{int} = 0.0685$ .

¶ Crystallographic data for **6**-(PF<sub>6</sub>)·CH<sub>2</sub>Cl<sub>2</sub>: C<sub>52</sub>H<sub>94</sub>AuBr<sub>3</sub>Cl<sub>2</sub>F<sub>6</sub>OP<sub>5</sub>Rh, M = 1614.63, monoclinic,  $P2_1/c$ , a = 14.6332(13), b = 20.6673(18), c = 20.6771(18),  $\beta = 95.422(2)^\circ$ , V = 6225.4(9), Z = 4,  $\mu = 4.812$  mm<sup>-1</sup>, T = 100(2) K,  $R_1 = 0.0461$ ,  $wR_2 = 0.0829$  (based on all reflections), GooF = 1.041, reflections measured = 143038, unique reflections = 18943,  $R_{int} = 0.0525$ .

|| Crystallographic data for 1-(PF<sub>6</sub>)·CH<sub>2</sub>Cl<sub>2</sub>: C<sub>52</sub>H<sub>94</sub>AuCl<sub>3</sub>F<sub>6</sub>OP<sub>5</sub>Rh, M = 1410.35, monoclinic,  $P2_1/n$ , a = 15.031(2), b = 21.469(3), c = 20.325(3),  $\beta = 102.251(2)^\circ$ , V = 6409.6(16), Z = 4,  $\mu = 2.844$  mm<sup>-1</sup>, T = 100(2) K,  $R_1 = 0.0401$ ,  $wR_2 = 0.0978$  (based on all reflections), GooF = 1.071, reflections measured = 145.895, unique reflections = 18.727,  $R_{int} = 0.0514$ .

\*\* Crystallographic data for **2**-(PF<sub>6</sub>)·Et<sub>2</sub>O: C<sub>55</sub>H<sub>102</sub>AuBrF<sub>6</sub>O<sub>2</sub>P<sub>5</sub>Rh, M = 1444.00, monoclinic,  $P_{21/n}$ , a = 15.0137(12), b = 21.2486(17), c = 20.3833(16),  $\beta = 102.5770(10)^{\circ}$ , V = 6346.6(9), Z = 4,  $\mu = 3.379$  mm<sup>-1</sup>, T = 100(2) K,  $R_1 = 0.0390$ ,  $wR_2 = 0.0640$  (based on all reflections), GooF = 1.034, reflections measured = 147939, unique reflections = 19764,  $R_{int} = 0.0492$ .

†† Crystallographic data for  $9.2.5(C_6H_6)$ :  $C_{66}H_{108}AuF_6OP_5Rh$ , M = 1486.25, triclinic,  $P\bar{1}$ , a = 13.5672(15), b = 14.0811(15), c = 19.974(2),  $\alpha = 76.123(2)^\circ$ ,  $\beta = 82.666(2)^\circ$ ,  $\gamma = 66.756(2)$ , V = 3401.4(6), Z = 2,  $\mu = 2.570$  mm<sup>-1</sup>, T = 100(2) K,  $R_1 = 0.0394$ ,  $wR_2 = 0.0723$  (based on all reflections), GooF = 1.117, reflections measured = 78 297, unique reflections = 19 683,  $R_{int} = 0.0395$ .

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