

# Supplementary Information

## Reactivity of gold hydrides: O<sub>2</sub> insertion into the Au-H bond

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### Synthetic and spectroscopic details

#### Kinetics in the presence and absence of radical scavengers

#### X-ray crystallography

### 1. Synthesis

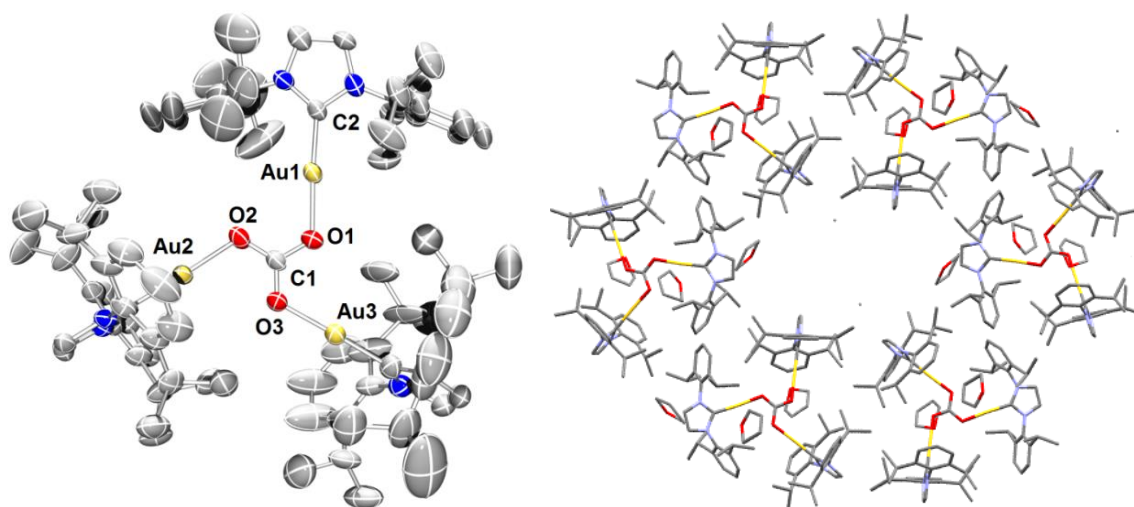
**General Considerations.** Unless otherwise stated, all experiments were performed in air using bench solvents. Exceptionally, manipulations were performed using standard Schlenk techniques under dry nitrogen or in a glovebox. Nitrogen was purified by passing through columns of supported P<sub>2</sub>O<sub>5</sub>, with moisture indicator, and activated 4 Å molecular sieves. Anhydrous solvents were freshly distilled from appropriate drying agents. (IPr)AuH (**1**) and (IPr)AuD (**1D**) were prepared following literature methods.<sup>7</sup> Galvinoxyl (Aldrich), TEMPO (Aldrich), P(*p*-tol)<sub>3</sub> (Aldrich), O<sub>2</sub> (BOC) were commercially available and used as received. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer. <sup>1</sup>H NMR spectra (300.13 MHz) were referenced to the residual protons of the deuterated solvent used. <sup>13</sup>C{<sup>1</sup>H} NMR spectra (75.47 MHz) were referenced internally to the D-coupled <sup>13</sup>C resonances of the NMR solvent. Elemental analyses were performed by London Metropolitan University.

#### Reaction of (IPr)AuH with O<sub>2</sub>

A solution of (IPr)AuH (**1**) (2.0 mg, 3.4 µmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) was subjected to three freeze-pump-thaw cycles and was backfilled with O<sub>2</sub> (1 atm). The reaction was monitored by <sup>1</sup>H NMR spectroscopy at 25 °C showing the disappearance of the hydride resonance (δ<sub>H</sub> 5.11) and clean conversion to a new compound, **2**. After the first half-life of the conversion of **1**, the OH signal of (IPr)AuOH (**3**) also became evident (δ -0.26), and after 48 h a comparison of the IPr signal intensity

with that of the OH signal of **3** suggested a ratio of **2**:**3** of about 1:3. Storing this solution in C<sub>6</sub>D<sub>6</sub> under O<sub>2</sub> produced a small crop of single crystals of the peroxide (IPr)AuOOAu(IPr) (**4**), while storing the solution in C<sub>6</sub>D<sub>6</sub> under air produced crystals of the carbonate **5**. The crystals of **4** and **5** were identified by X-ray diffraction methods.

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.18-7.16 (t, overlapping with residual C<sub>6</sub>H<sub>6</sub> signal, 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>) 7.04 (d, *J* = 7.3 Hz, 2H, 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 6.21 (s, 1H, im), 2.58 (sept, *J* = 8 Hz, CH), 1.39 (d, *J* = 6.5 Hz, 12H, CH<sub>3</sub>), 1.03 (d, *J* = 6.5 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR spectra could not be obtained due to the fast decomposition of **2** into **3**.



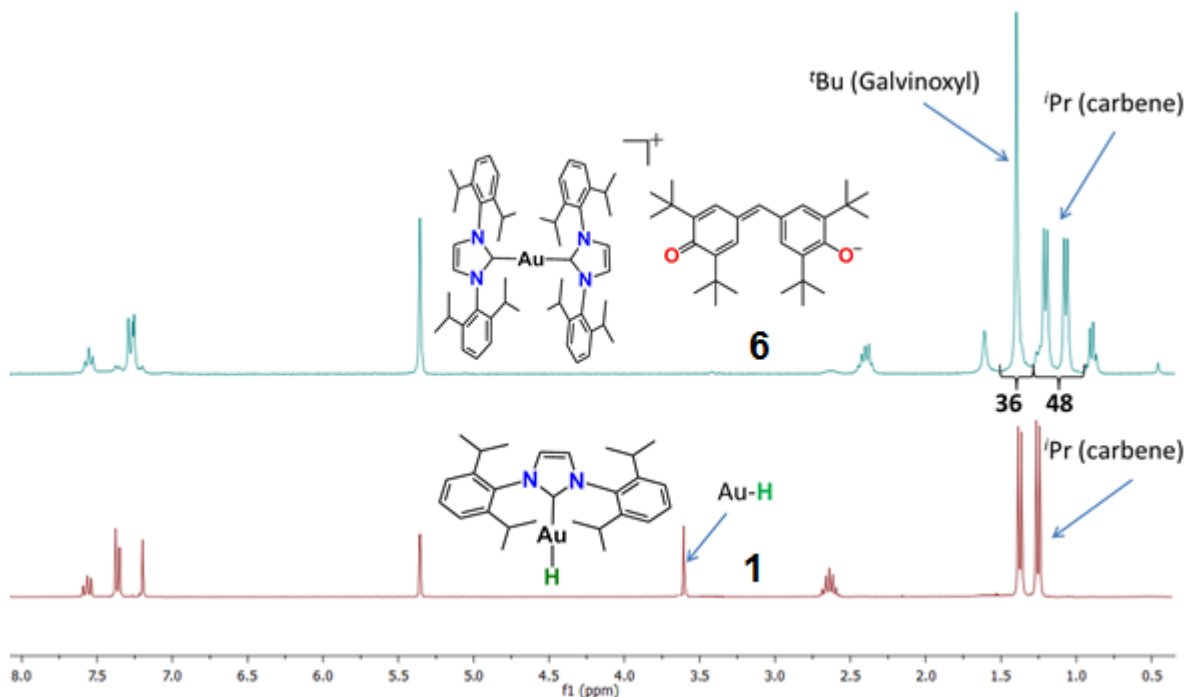
**Figure S1.** Left: Molecular structure of **5**·3THF. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms are omitted. The anion fragment could not be located in the final difference density map. Selected bond distances (Å) and angles (°): Au1-C(2) 1.942(3), Au1-O(1) 2.045(3), O(1)-C(1) 1.272(5), C(2)-Au(1)-O(1) 176.76(32), O(1)-C(1)-O(2) 118.93(43), Au-O(1)-C(1) 115.54(31). Right: View along the *a* axis highlighting solvent accessible voids.

### Synthesis of [Au(IPr)<sub>2</sub>]<sup>+</sup>[galvinoxide]<sup>-</sup> (**6**)

To a solution of **1** (100 mg, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was added galvinoxyl (72 mg, 0.17 mmol). The purple solution obtained was stirred for 30 min at room temperature. Evaporation of the solvent followed by trituration of the residue with light petroleum (3 × 5 ml) afforded **6** as a purple solid (73 mg, 61%). Crystals suitable for X-ray diffraction were obtained by storing benzene solutions of **6** at room temperature.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.51 (t, *J* = 8 Hz, 4H, 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.40 (s, 4H, phenyl H in galvinoxide), 7.25 (s, 4H, im), 7.22 (d, *J* = 4.0 Hz, 4H, 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>) 7.03 (s, 1H, galvinoxide HC=C bridge), 2.36 (sept, *J* = 7 Hz, 8H, CH), 1.36 (s, 36H, *t*-butyl of galvinoxide), 1.16 (d, *J* = 6.9 Hz, 24H, CH<sub>3</sub>), 1.03 (d, *J* = 6.9 Hz, 24H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -25 °C) δ 186.5 (s, C-Au), 180.7 (s,

C=O), 149.2 (s, C<sub>Ar</sub>), 145.7 (s, C<sub>Ar</sub>), 145.4 (s, CH<sub>Ar</sub>), 141.3 (s, CH<sub>Ar</sub>), 133.1 (s, CH<sub>Ar</sub>), 131.4 (s, CH<sub>imid</sub>), 130.9 (s, CH<sub>Ar</sub>), 124.3 (CH<sub>Ar</sub>), 123.4 (C<sub>Ar</sub>), 117.5 (s, galvinoxide HC=C), 34.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.5(s, (CH<sub>3</sub>)<sub>3</sub>C), 28.6(s, CH(CH<sub>3</sub>)<sub>2</sub>), 24.5(s, (CH<sub>3</sub>)<sub>2</sub>CH), 23.5 (s, (CH<sub>3</sub>)<sub>2</sub>CH). Anal. Calcd for C<sub>83</sub>H<sub>115</sub>N<sub>4</sub>AuO<sub>2</sub> (1397.82): C, 71.32; H, 8.29; N, 4.11. Found: C, 71.21 H, 8.46 N, 3.85.



**Figure S2.** <sup>1</sup>H NMR spectra of (IPr)Au<sup>I</sup>H **1** (red) and **6** (blue) at room temperature (CD<sub>2</sub>Cl<sub>2</sub>).

## 2. Kinetic Data

### Typical reaction procedure:

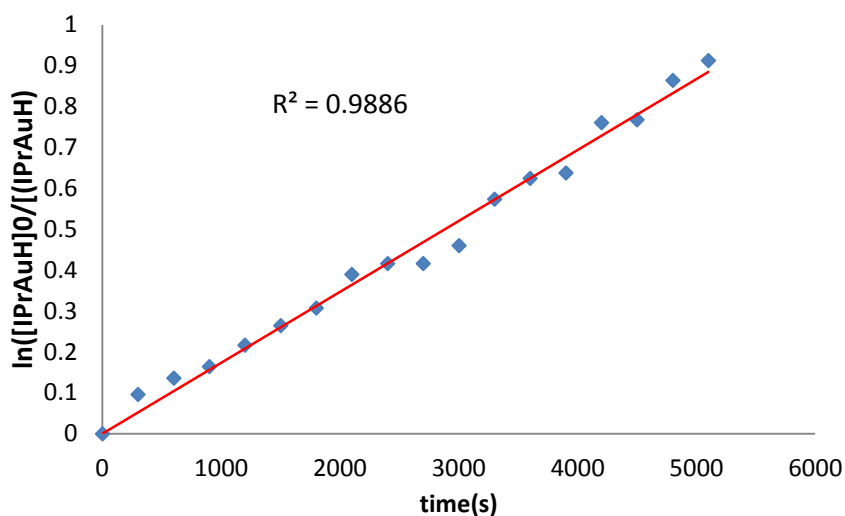
Stock solutions of **1** (9.25 mM), TEMPO (185 mM) and pentamethylbenzene (internal standard, 26 mM) in benzene-*d*<sub>6</sub> were prepared.

In a heavy-walled NMR tube, to a solution of **1** (0.2 mL, 9.25 mM, 1.85 μmol) in C<sub>6</sub>D<sub>6</sub> was added a solution of pentamethylbenzene (10 μL, 26 mM, 0.26 μmol). The mixture was then subjected to three freeze-pump-thaw cycles and placed on a methanol bath (-20°C). Under the exclusion of light, the tube was pressurised with an appropriate amount of O<sub>2</sub> (typically between 4 – 9 bar). The NMR tube was briefly shaken before being inserted into the NMR probe, which was pre-heated to the appropriate temperature. The reaction was monitored by <sup>1</sup>H NMR spectroscopy. Data points were collected at regular intervals (typically 300 s, with D1 = 1 s, AQ= 5.3 s and NS = 8 scans). Observed rates were determined under pseudo-first order conditions by monitoring the disappearance of the hydride resonance for (IPr)AuH, (δ = 5.11) *versus* the resonance of the internal standard C<sub>6</sub>Me<sub>5</sub>H (δ<sub>H</sub> = 2.15). Spectra were integrated

automatically using the multi\_integ3 command in TopSpin and the baseline correction was made manually.

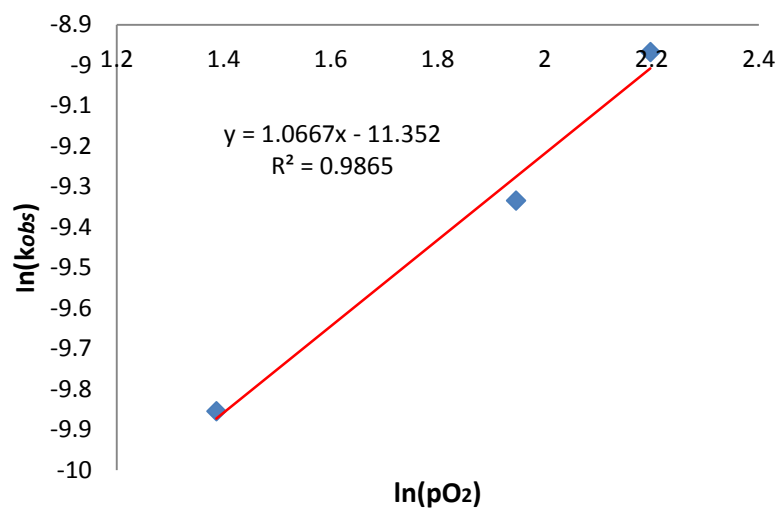
### ***Determination of reaction orders***

For the determination of the reaction order of **1** and O<sub>2</sub>, data were collected at 309 K using an excess of O<sub>2</sub> ([IPrAuH]<sub>0</sub> : [O<sub>2</sub>]<sub>0</sub>, 1 : 8.75).<sup>S1</sup> Plotting  $\ln([IPrAuH]_0/[IPrAuH]_t)$  vs time gives a linear regression fit with  $R^2 = 0.9886$ , suggesting a partial reaction order of 1 for [IPrAuH]. (Figure S3)

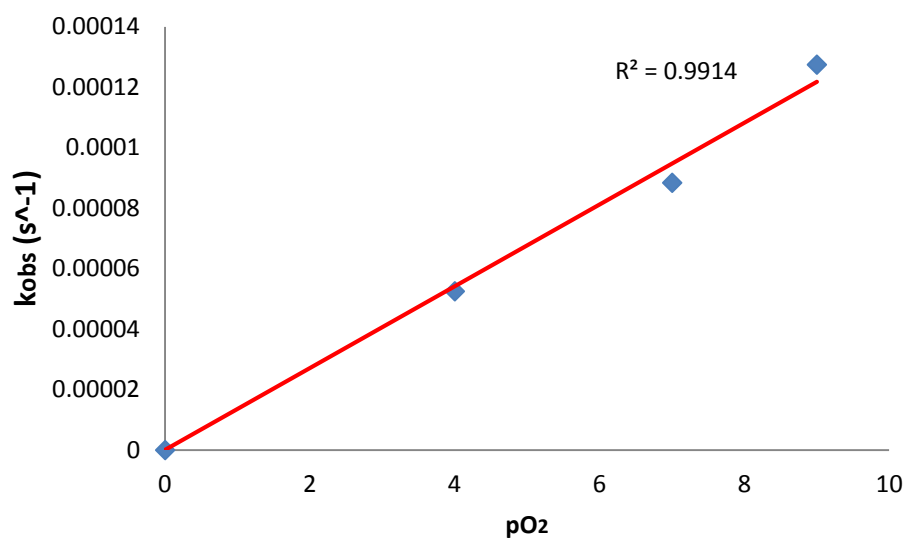


**Figure S3.** Plot of  $\ln([1]_0/[1])$  versus time at 309 K under 9 bar of O<sub>2</sub>.

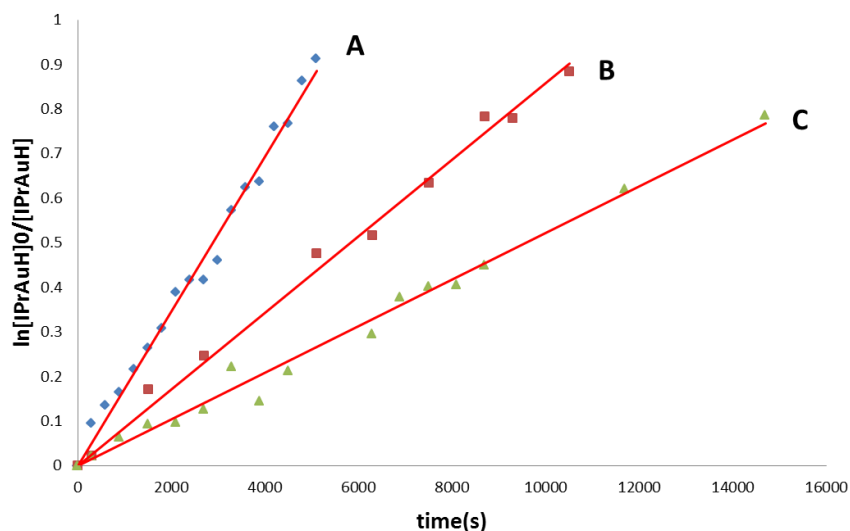
In order to determine the partial order of reaction of the O<sub>2</sub>, several measurements were conducted at 309 K, varying the partial pressure of O<sub>2</sub> at fixed **1**. The plot  $\ln(k_{\text{obs}})$  vs  $\ln [pO_2]$  is linear and the gradient of the best-fit line is 1.07 (Figure S4).



**Figure S4.** Plot of  $\ln(k_{\text{obs}})$  versus  $\ln [p\text{O}_2]$  at various partial pressures of  $\text{O}_2$  at 309 K .



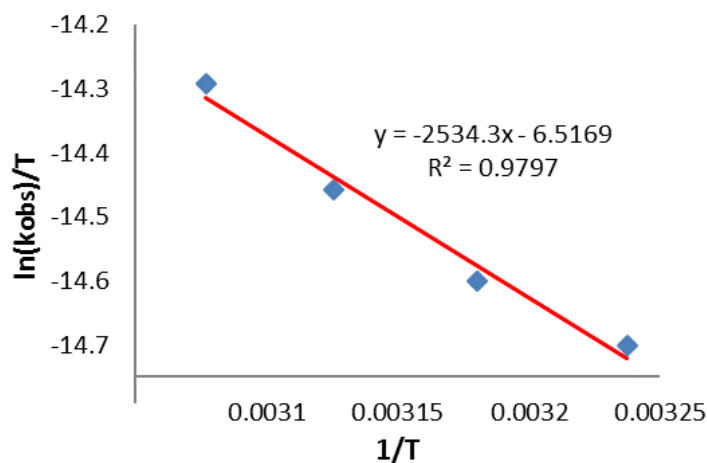
**Figure S5.** Plot of  $k_{\text{obs}}$  versus  $[p\text{O}_2]_0$  at various oxygen partial pressures (4 – 9 bar) at 309 K.



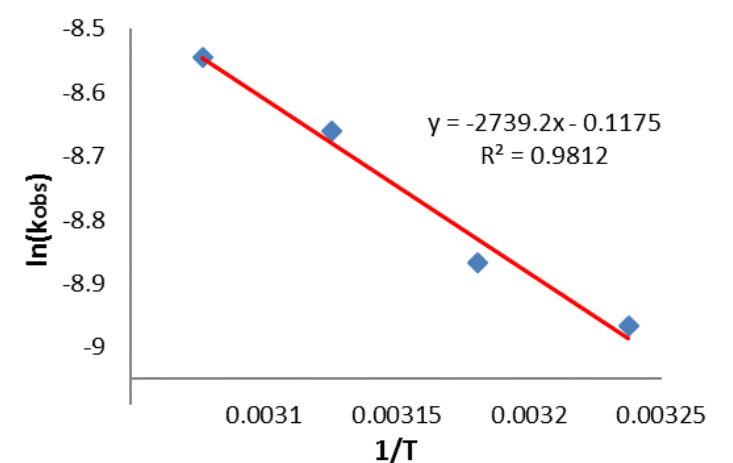
**Figure S6.** Semilogarithmic plot of conversion of (IPr)AuOH *vs* reaction time at various oxygen partial pressures at 309 K ( $[(\text{IPr})\text{AuH}]_0 = 9.25 \text{ mM}$ ) **A**,  $p_{\text{O}_2} 9 \text{ atm}$ ,  $k_{\text{obs}} = 1.27(1) \times 10^{-4} \text{ s}^{-1}$ ; **B**,  $p_{\text{O}_2} 7 \text{ atm}$ ,  $k_{\text{obs}} = 0.88(2) \times 10^{-4} \text{ s}^{-1}$ ; **C**,  $p_{\text{O}_2} 4 \text{ atm}$ ,  $k_{\text{obs}} = 0.54(1) \times 10^{-4} \text{ s}^{-1}$ .

#### ***Determination of activation parameters***

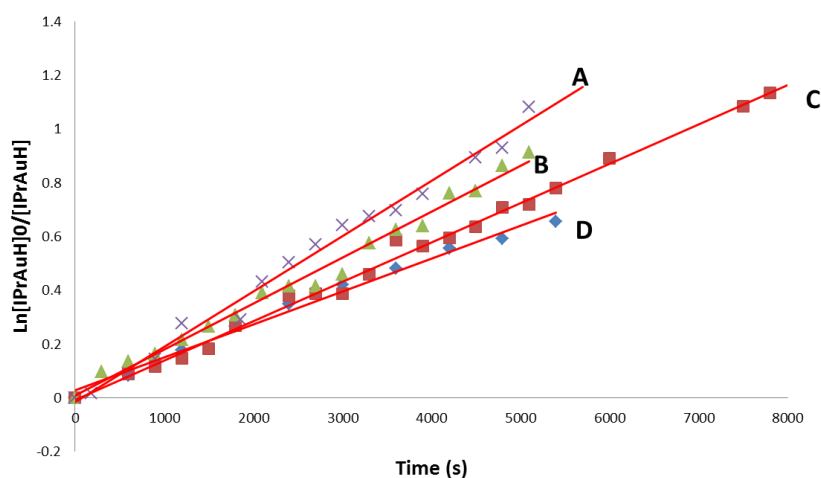
Measurements were conducted at fixed concentrations ( $[(\text{IPr})\text{AuH}]_0 = 9.25 \text{ mM}$ ,  $p_{\text{O}_2} 9 \text{ atm}$ ) in the temperature range of 309 to 325 K. In each case, the reaction was first order in **[1]**. The observed rate constants were computed from the semilogarithmic plot of (IPr)AuOH conversion *versus* reaction time. The activation parameters  $\Delta H^\ddagger = 21.10(14) \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -251.5(2) \text{ J mol}^{-1} \text{ K}^{-1}$  were calculated from the plot of  $\ln(k_{\text{obs}}/T)$  *versus*  $1/T$  (Figure S7) using the Eyring equation. The activation energy  $E_a = 22.76(11) \text{ kJ mol}^{-1}$  was calculated from the plot of  $\ln(k_{\text{obs}})$  *versus*  $1/T$  (Figure S8) using the Arrhenius equation.



**Figure S7.** Eyring plot for the determination of activation parameters



**Figure S8.** Arrhenius plot for the determination of the activation energy



**Figure S9.** Semilogarithmic plot of conversion of IPrAuH vs reaction time at various temperatures ( $p(\text{O}_2) = 9 \text{ atm}$ ) **A**, 325 K,  $k_{\text{obs}} = 1.94(2) \times 10^{-4} \text{ s}^{-1}$ ; **B**, 319.94 K,  $k_{\text{obs}} = 1.73(1) \times 10^{-4} \text{ s}^{-1}$ ; **C**, 314 K,  $k_{\text{obs}} = 1.41(1) \times 10^{-4} \text{ s}^{-1}$ ; **D**, 308 K,  $k_{\text{obs}} = 1.27(1) \times 10^{-4} \text{ s}^{-1}$ .

#### *Presence vs absence of radical inhibitors*

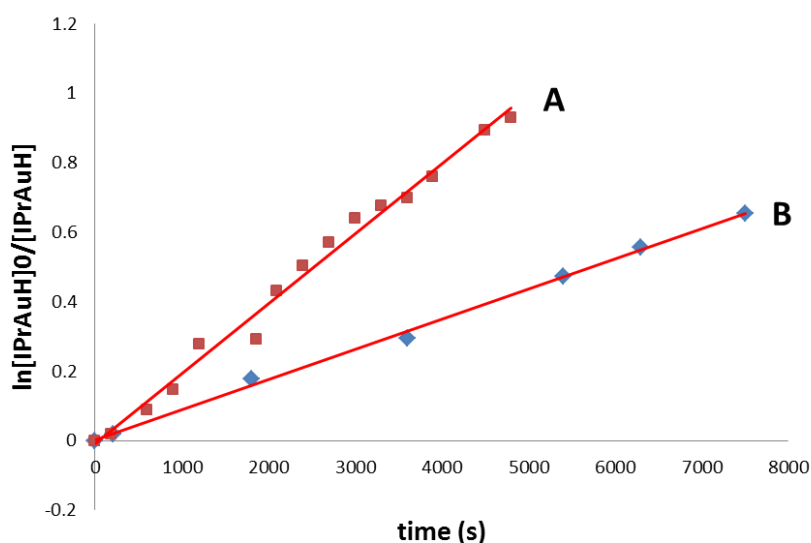
**Presence of TEMPO.** To a solution of **1** (0.2 mL, 9.25 mM, 1.85  $\mu\text{mol}$ ) in  $\text{C}_6\text{D}_6$ , was added a solution of internal standard pentamethylbenzene (10  $\mu\text{L}$ , 26 mM, 0.26  $\mu\text{mol}$ ) and a stock solution of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, 10  $\mu\text{L}$ , 0.185 M, 1.85  $\mu\text{mol}$ ) in  $\text{C}_6\text{D}_6$ . The mixture was subjected to three freeze-pump-thaw cycles and was pressurized with

O<sub>2</sub> (9 bar). The NMR tube was shaken briefly before being introduced into the NMR probe which was pre-warmed at 325 K. The observed rate constant was extracted from the plot of  $\ln([1]_0/[1]_t)$  vs reaction time,  $k_{\text{obs}} = 2.00(2) \times 10^{-4} \text{ s}^{-1}$ .

**Absence of TEMPO.** Following the protocol described above but without the addition of TEMPO, at 325 K,  $k_{\text{obs}} = 1.94(2) \times 10^{-4} \text{ s}^{-1}$ .

**Control reactions.** Following the protocol described above, **1** was treated with TEMPO under N<sub>2</sub>. No reaction was observed by <sup>1</sup>H NMR spectroscopy over the course of 24 h. **1** was found to react with galvinoxyl (see above).

### Kinetic isotope effect



**Figure S10.** Conversion of (IPr)AuH(D) vs reaction time at 325 K under 9 bar of O<sub>2</sub> **A** (IPr)AuH,  $k_{\text{obs}} = 1.94(2) \times 10^{-4} \text{ s}^{-1}$ ; **B**, (IPr)AuD,  $k_{\text{obs}} = 0.82(1) \times 10^{-4} \text{ s}^{-1}$ .

**Table S1: Observed rates for O<sub>2</sub> insertion reactions**

Temp (K)	[Au] <sub>0</sub> (mM)	pO <sub>2</sub> (bar)	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$	Comments
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309	9.25	9	1.27(1)	
309	9.25	4	0.54(1)	
309	9.25	7	0.88(2)	
314.41	9.25	9	1.41(1)	
320	9.25	9	1.73(1)	
325	9.25	9	1.94(2)	
325	9.25	9	2.00(2)	TEMPO additive
325	9.25	9	0.82(1)	(IPr)AuD used

#### 4. X-ray crystallography

Crystals of each sample were mounted in oil on glass fibres and fixed in the cold nitrogen stream on a diffractometer. Intensities for compound **4**, **5** and **6** were collected at 100(2)K on a Bruker-Nonius Roper CCD diffractometer, equipped with Mo-K $\alpha$  radiation and graphite monochromator at the EPSRC National Crystallographic Service, Southampton, UK.<sup>S2</sup> Data were processed using CrystalClear-SM Expert 3.1 b21 (Rigaku, 2012) programs. The structures of all samples were determined by the direct methods routines in the SHELXS program and refined by full-matrix least-squares methods on F<sup>2</sup> in SHELXL.<sup>S3</sup> Non-hydrogen atoms were generally refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions. No missed symmetry was reported by PLATON.<sup>S4</sup> Computer programs used in this analysis were run through WinGX.<sup>S5</sup> Scattering factors for neutral atoms were taken from reference S6.

**Table S1.** Selected crystal data and structure refinement details for **4**·C<sub>6</sub>H<sub>6</sub>, **5**·3(THF) and **6**·3(C<sub>6</sub>H<sub>6</sub>).

	<b>4</b> ·C <sub>6</sub> H <sub>6</sub>	<b>5</b> ·3(THF)	<b>6</b> ·3(C <sub>6</sub> H <sub>6</sub> )
Empirical formula	C <sub>60</sub> H <sub>78</sub> Au <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>94</sub> H <sub>133</sub> Au <sub>3</sub> N <sub>6</sub> O <sub>7</sub>	C <sub>101</sub> H <sub>133</sub> AuN <sub>4</sub> O <sub>2</sub>
<i>F</i> <sub>w</sub>	1281.20	2049.96	1632.07
T (K)	100(2)	100(2)	100(2)
crystal system, space group	Monoclinic, I 2/a	Monoclinic, P21/n	Monoclinic, P21/n
a(Å)	15.3438(11)	12.4797(9)	15.1887(11)
b(Å)	19.5250(14)	41.783(3)	24.4609(17)
c(Å)	19.6769(14)	21.4315(15)	24.3362(17)
α(deg)	90	90	90
β(deg)	92.122(5)	94.2010(10)	94.2705(11)
γ(deg)	90	90	90
volume (Å <sup>3</sup> )	5890.9(7)	11145.2(14)	9016.5(11)
Z	4	4	4
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.445	1.222	1.202
absorption coefficient (mm <sup>-1</sup> )	5.017	3.984	1.681
F(000)	2560	4128	3448
θ range for data collection (deg)	2.1 to 27.5	3.518 to 25.000	3.642 to 27.494
no of data // restraints // params	5175 // 11 // 297	19432 // 0 // 931	19842 // 0 // 948
goodness-of-fit on F <sup>2</sup> [a]	1.288	1.055	1.095
final R indexes [I>2σ(I)] <sup>[a]</sup>	R1 = 0.0760, wR2 = 0.1764	R1 = 0.0653, wR2 = 0.1778	R1 = 0.1084, wR2 = 0.2919
R indexes (all data) <sup>[a]</sup>	R1 = 0.0775, wR2 = 0.1768	R1 = 0.0932, wR2 = 0.1912	R1 = 0.1570, wR2 = 0.3103
largest diff peak and hole (e.Å <sup>-3</sup> )	4.772 and -3.310	1.919 and -2.662	7.282 and -3.174

<sup>[a]</sup>  $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ ;  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$ ; goodness of fit =  $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\text{obs}} - N_{\text{param}})\}^{1/2}$ ;  $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$ ;  $P = [\max(F_o^2; 0 + 2F_c^2)]/3$ .

### Crystal structure analysis of $\{(\text{IPr})\text{Au}\}_2(\mu\text{-O}_2)\cdot\text{C}_6\text{H}_6$ , compound 4·C<sub>6</sub>H<sub>6</sub>

Crystals are rod-shaped. Data were measured for one, *ca* 0.12 x 0.04 x 0.03 mm. Total no. of reflections recorded, to  $\theta_{\text{max}} = 25^\circ$ , was 22683 of which 5175 were unique ( $R_{\text{int}} = 0.036$ ); 5024 were 'observed' with  $I > 2\sigma_I$ .

The few non-hydrogen atoms with full site occupancy (described below) in the structure were refined with anisotropic thermal parameters; the remainder, at half-occupancy, were refined isotropically. Most of the hydrogen atoms were included in idealized positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms. There were several persistent spurious peaks, mostly lying on twofold symmetry axes, in the difference maps at the conclusion of the refinement; one (at *ca* 6 eÅ<sup>-3</sup>) was included as a gold atom of low site occupancy. Finally,  $wR_2 = 0.177$  and  $R_1 = 0.078$  <sup>S3</sup> for all 5175 reflections weighted  $w = [\sigma^2(F_o^2) + 305.1P]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ ; for the 'observed' data only,  $R_1 = 0.076$ .

The structure of (IPr)Au-O-O-Au(IPr) shows much disorder, most of which has been resolved, but with the final resolution rather lower than we might wish. The data-set came with the observation that the single-crystal data appeared to overlay some powder-like rings; this had been noted in data from several samples.

The original cell was transformed from a C-centered cell (with  $\beta = 126.622(1)^\circ$ ) to an I-centered cell (with  $\beta = 92.122(5)^\circ$ ). Structure determination in several space groups was attempted and the most promising was I2/a (equivalent to C2/c). Here, one (IPr)Au-O unit was aligned about a two-fold symmetry axis, with the gold atom Au(1) on that axis and its bonded C<sub>3</sub>N<sub>2</sub> ring disordered in two orientations about the axis. The atoms of one C<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr group and its symmetry-related group have full site occupancy; an exception here is that one <sup>i</sup>Pr group can adopt one of two orientations.

The second (IPr)Au-O unit, of Au(2), is disordered about a center of symmetry which is very close to C(41), so that all the atoms of this unit have a site occupancy of 0.5. The overlapping of C<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr groups of the disordered (IPr)Au-O units provided further resolution problems.

There is also one molecule of the solvent C<sub>6</sub>H<sub>6</sub> for each molecule of (IPr)Au-O-O-Au(IPr) in the crystal; this solvent molecule lies over the C=C bond of the first C<sub>3</sub>N<sub>2</sub> ring and is disordered about the twofold symmetry axis; the two C<sub>6</sub> rings are coplanar with the two half-molecules *ca* 1.2 Å apart.

### Crystal structure analysis of $\{(\text{IPr})\text{Au}\}_3(\mu_2\text{-CO}_3)(\text{OH})\cdot 3(\text{THF})$ , compound **5**·3THF

Crystals are rod-shaped. Intensity data were recorded, by thin-slice  $\omega$ - and  $\phi$ -scans, for one, *ca* 0.26 x 0.06 x 0.04 mm. Total no. of reflections recorded, to  $\theta_{\text{max}} = 25^\circ$ , was 110406 of which 19432 were unique ( $R_{\text{int}} = 0.088$ ); 14485 were 'observed' with  $I > 2\sigma_I$ .

There is disorder in the solvent THF molecules and all the non-hydrogen atoms here were refined isotropically. A distinct difference peak was thought to be the oxygen atom of a hydroxyl ion. Hydrogen atoms were included (except in the solvent molecules and hydroxyl ion) in idealized positions and their  $U_{\text{iso}}$  values were set to ride on the  $U_{\text{eq}}$  values of the parent carbon atoms. At the conclusion of the refinement,  $wR_2 = 0.191$  and  $R_1 = 0.093$ <sup>S3</sup> for all 19432 reflections weighted  $w = [\sigma^2(F_o^2) + (0.1125P)^2 + 38.35P]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ ; for the 'observed' data only,  $R_1 = 0.065$ . In the final difference map, the highest peaks (to *ca* 1.9 eÅ<sup>-3</sup>) were close to the gold atoms.

### Crystal structure analysis of $[(\text{IPr})_2\text{Au}][\text{galvinoxide}]\cdot 3(\text{benzene})$ , compound **6**·3(C<sub>6</sub>H<sub>6</sub>)

Crystals are needles. Intensity data were measured for one, *ca* 0.16 x 0.03 x 0.01 mm. Total no. of reflections recorded, to  $\theta_{\text{max}} = 25.24^\circ$ , was 68762 of which 19842 were unique ( $R_{\text{int}} = 0.117$ ); 13069 were 'observed' with  $I > 2\sigma_I$ .

Most of the non-hydrogen atoms were refined with anisotropic thermal parameters; a few behaved poorly and were refined isotropically. Hydrogen atoms were included in idealized positions and their  $U_{\text{iso}}$  values were set to ride on the  $U_{\text{eq}}$  values of the parent carbon atoms. At the conclusion of the refinement,  $wR_2 = 0.310$  and  $R_1 = 0.157$ <sup>S3</sup> for all 19842 reflections weighted  $w = [\sigma^2(F_o^2) + (0.1306P)^2 + 178.6P]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ ; for the 'observed' data only,  $R_1 = 0.108$ . In the final difference map, the highest peaks (to *ca* 7.3 eÅ<sup>-3</sup>) were close to the gold atom.

### References:

- S1 Using an Ostwald coefficient ( $L$ ) of 0.22, the concentration of O<sub>2</sub> in benzene was calculated to be 81 mM under 10 atm partial pressure of O<sub>2</sub> at 25 °C (Battino, R. *Oxygen and Ozone*; Solubility Data Ser.; Pergamon Press: Oxford, 1981; Vol.7).
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