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Electronic Supplementary Information (ESI) To:

Intimate Relationship between C–I Reductive Elimination, Aryl Scrambling and Isomerization Processes in Au(III) Complexes

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1. General information

All reactions were carried out under nitrogen atmosphere using Schlenk–tube techniques. Dichloromethane (DCM) and hexane were obtained oxygen– and water–free from an SPS PS–MD-5 solvent purification apparatus. Toluene, chloroform and acetone were dried by the usual procedures and distilled under argon prior to used.¹ TCE- d_2 was directly purchased from Acros.

The starting materials (NBu₄)[AuRf₂] (Rf = $C_6F_3Cl_2-3,5$),² [AuRf₃(OH₂)]·2Et₂O,³ and (NBu₄)*trans*-[AuPf₂I₂] (Pf = C_6F_5),⁴ were prepared according to the published methods. The syntheses of (NBu₄)*trans*-[AuRf₂Cl₂] (**1-Cl**),³ (NBu₄)*cis*-[AuRf₂Cl₂] (**2-Cl**),³ and Rf–I,⁵ were also reported previously. (NBu₄)I was purchased from Sigma Aldrich and used as received.

The technical measurements were carried out with equipment of the LTI services or the IU CINQUIMA (both of the University of Valladolid) unless otherwise stated.

¹⁹F NMR spectra were recorded on a Varian 500/54 Premium Shielded instrument. Chemical shifts (in δ units, parts per million) were referenced to the residual solvent peaks (¹H),⁶ or CFCl₃ (¹⁹F). Coupling constants (*J*) are given in hertz (Hz). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad).

The elemental analyzes were performed by the Elemental Analysis Unit of the University of Vigo on a Carlo Erba 1108 CHN analyzer.

2. Synthesis and characterisation of the compounds

(NBu₄)trans-[AuRf₂I₂] (1)

I₂ (155 mg, 0.6 mmol) was added slowly to a solution of (NBu₄)[AuRf₂] (0.50 g, 0.60 mmol) in dry CH₂Cl₂ (20 mL). The reaction was stirred for 1 hour at room temperature and the solvent was evaporated to dryness. Then, the residue was recrystallized from dichloromethane-hexane, washed with hexane and vacuum dried. **1** was isolated as a microcrystalline orange solid. **Yield:** 512 mg (79 %). Crystals valid for X-Ray diffraction analysis (molecular structure in Figure S6, left) were obtained by slow diffusion of *n*-hexane in a solution of the compound in CH₂Cl₂. *Anal. Calcd*. for C₂₈H₃₆AuCl₄F₆I₂N: C, 30.76; H, 3.32; N, 1.28. Found: C, 30.84; H, 3.41; N, 1.24. ¹⁹F NMR (470.15 MHz, CDCl₃, 298 K): δ –92.94 (s, 4F_{ortho}), –118.00 (s, 2F_{para}).

(NBu₄)trans-[AuRf₂Br₂] (1-Br)

Br₂ (70 μ L, 3.1 g / mL, 1.36 mmol) was added dropwise to a solution of (NBu₄)[AuRf₂] (0.50 g, 0.60 mmol) in dry CH₂Cl₂ (20 mL). The reaction was stirred for 1 hour at 273 K and the solvent was evaporated to dryness. Then, the residue was recrystallized from dichloromethane-hexane, washed with hexane and vacuum dried. **1-Br** was isolated as a microcrystalline yellow solid. **Yield:** 540 mg (90 %). Crystals valid for X-Ray diffraction analysis (molecular structure in Figure S6, right) were obtained by slow diffusion of *n*-hexane in a solution of the compound in CH₂Cl₂. *Anal. Calcd.* for C₂₈H₃₆AuBr₂Cl₄F₆N: C, 33.66; H, 3.63; N, 1.40. Found: C, 33.70; H, 3.60; N, 1.42.

¹⁹F NMR (470.15 MHz, CDCl₃, 298 K): δ –95.98 (s, 4F_o), –117.63 (s, 2F_p).

(NBu₄)cis-[AuRf₂Br₂] (2-Br)

A toluene solution of **1-Br** (150 mg, 0.15 mmol) was refluxed for 12 h. After that time, the solvent was removed under reduced pressure and the residue was recrystallized from dichloromethanehexane, washed with hexane and vacuum dried. **2-Br** was isolated as a microcrystalline yellow solid. **Yield:** 122 mg (81 %).

Anal. Calcd. for C₂₈H₃₆AuBr₂Cl₄F₆N: C, 33.66; H, 3.63; N, 1.40. Found: C, 33.60; H, 3.62; N, 1.38.

¹⁹F NMR (470.15 MHz, CDCl₃, 298 K): δ –95.04 (s, 4F_{ortho}), -115.59 (s, 2F_{para}).

* Note that upon heating of solutions of **2-Br** in tetrachloroethane (TCE) at 393 K, no traces of Rf/Br scrambling or organic Rf–Br were detected. In fact, slow formation of Rf–Rf was observed. Therefore, the evolution is similar to the one found for the **1-Cl/2-Cl** analogues.

$(NBu_4)[AuRf_3I](3)$

Equimolar quantities of (NBu₄)I (19 mg, 0.052 mmol) and $[AuRf_3(OH_2)] \cdot 2Et_2O$ (50 mg, 0.052 mmol) were dissolved CH₂Cl₂. After stirring for one hour, the solvent was evaporated to dryness. Then, the residue was recrystallized from dichloromethane-hexane, washed with hexane and vacuum dried. **3** was isolated as a white solid. **Yield:** 53 mg (87 %). Crystals valid for X-ray diffraction analysis (molecular structure shown in Figure S7) were grown by slow evaporation of a concentrated solution of the compound in toluene.

Anal. Calcd. for C₃₄H₃₆AuCl₆F₉IN: C, 35.02; H, 3.11; N, 1.20. Found: C, 35.24; H, 3.12; N, 1.24. ¹⁹F NMR (470.15 MHz, CDCl₃, 298 K): δ –93.35 (m, 4F_{ortho}), –96.05 (m, 2F_{ortho}), –116.35 (s, 2F_{para}), –117.71 (s, 1F_{para}).

¹⁹F NMR (470.15 MHz, TCE-*d*₂, 298 K): δ –91.93 (m, 4F_{ortho}), –94.54 (m, 2F_{ortho}), –114.80 (s, 2F_{para}), –116.17 (s, 1F_{para}).

Identification of (NBu₄)cis-[AuRf₂I₂] (2):

Large excess of KI (104 mg, 0.63 mmol) was added to a solution of **2-Cl** (57 mg, 0.063 mmol) in acetone. The reaction was vigorously stirred for 3 hours at room temperature and the solvent was evaporated to dryness. Then, residue was recrystallized in acetone-heptane, washed with hexane and vacuum dried.

The solid obtained was a mixture of $(NBu_4)cis$ - $[AuRf_2I_2]$ (2) as the major product, and $(NBu_4)trans$ - $[AuRf_2I_2]$ (1) (see Figure S15).

¹⁹F NMR (470.15 MHz, CDCl₃, 298 K): δ –94.52 (s, 4F_{ortho}), -116.20 (s, 2F_{para}).

¹⁹F NMR (470.15 MHz, TCE-*d*₂, 298 K): δ –92.86 (s, 4F_{ortho}), –114.58 (s, 2F_{para}).

3. Aryl Scrambling ¹⁹F NMR Spectra

Behaviour of (NBu₄)trans-[AuPf₂I₂] in CH₂Cl₂ solution

Selective isomerization to $(NBu_4)cis$ -[AuPf₂I₂] after reflux in CH₂Cl₂ solutions was reported long ago,⁴ in the absence of ¹⁹F NMR data. In those conditions, we confirmed that Pf/I also occurs, similarly to the Rf case (see Figure S1, analogue to the spectrum shown in Figure 1).



Figure S1. F_{ortho} region of the ¹⁹F NMR spectrum recorded after refluxing a solution of (NBu₄)*trans*-[AuPf₂I₂] in CH₂Cl₂ (ref. acetone-*d*₆) for 5 days.

Behaviour of (NBu₄)trans-[AuRf₂I₂] (1) in CDCl₃ solution (Fig S2)



Figure S2. F_{ortho} region of the ¹⁹F NMR spectrum recorded from solutions of **1** in CDCl₃ after heating at 323 K for 1 day. Assignment of the signals is also included.

Behaviour of (NBu₄)trans-[AuRf₂I₂] (1) in TCE-d₂ solution (Fig S3-5)



Figure S3. Full ¹⁹F NMR spectrum recorded from solutions of **1** in TCE- d_2 after heating at 323 K for 1 day (see Figure 1 for zoom into the F_{ortho} region). Assignment of the signals and corresponding integrals.



Figure S4. F_{ortho} region of the ¹⁹F NMR spectra in TCE- d_2 , recorded from the different species independently synthetized (B-E), overlapped with the mixture shown in Figure 1 of the manuscript. Assignment of the signals is also included.



Figure S5. ¹⁹F NMR spectrum recorded from solutions of **1** in TCE- d_2 after heating at 383 K for 1 day. Assignment of the signals and corresponding integrals.

5. X-ray diffraction details

Refinement of the X-Ray structures gives the residuals shown in Tables S1 and S2.

A crystal was attached to a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector. Data collection was performed with Mo-K α radiation ($\lambda =$ 0.71073 Å) or Cu-K α ($\lambda =$ 1.54184 Å). Data integration, scaling and empirical absorption correction was carried out using the CrysAlisPro program package.⁷ The crystal was kept at 294 K or 210 K during data collection. Using Olex2,⁸ the structure was solved with the ShelxT,⁹ and refined with ShelxL program.¹⁰ The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. CCDC 2221886-2221889 contains the supporting crystallographic data for this paper. These data can be obtained free of charge at <u>www.ccdc.cam.ac.uk/conts/retrieving.html</u> [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: <u>deposit@ccdc.cam.ac.uk</u>]. Figure S6 gathers the molecular structures of **1** and **1-Br** anions, and Figure S7 those of **3** and **5**.

* Note that other structures of $(NBu_4)[AuI_2]$ (5) were already reported with different cell-unit parameters,¹¹ but the detection of 5, after scrambling completeness in TCE-*d*₂ (Scheme 2), was only possible in our case by X-Ray diffraction.



Figure S6. Molecular structures of **1** (left) and **1-Br** (right). NBu₄ cations are omitted for clarity. Selected bond lengths (Å) for **1**: Au(1)–C(1) = 2.073(6); Au(1)–C(11) = 2.057(6); Au(1)–I(1) = 2.5938(5); Au(1)–I(2) = 2.6036(5). For **1-Br**: Au(1)–C(1) = 2.060(5); Au(1)–C(11) = 2.071(5); Au(1)–Br(1) = 2.4090(7); Au(1)–Br(2) = 2.4187(7).



Figure S7. Molecular structures of **3** (left) and **5** (right). NBu₄ cations are omitted for clarity. Selected bond lengths (Å) for **3**: Au(1)–C(1) = 2.082(7); Au(1)–I(1) = 2.6214(6); Au(1)–C(11) = 2.065(6) ; Au(1)–C(21) = 2.054(6). For **5**: Au(1)–I(1) = 2.5386(10); Au(1)–I(2) = 2.5347(11). Only one of the two slightly different anions of **5** that constitute the asymmetric unit is shown.

Table S1. Crystal data and structure refinements for (NBu ₄) <i>trans</i> -[AuRf ₂ I ₂] (1), (NBu ₄) <i>trans</i> -[AuRf ₂ Br ₂]
(1-Br).

	1	1-Br
Empirical formula	$C_{28}H_{36}AuCl_4F_6I_2N$	$C_{28}H_{36}NF_6Cl_4Br_2Au$
Formula weight	1093.14	999.16
Temperature/K	294	294
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.8115(7)	12.6800(6)
b/Å	13.1017(7)	13.0574(8)
c/Å	13.5212(9)	13.4650(9)
α/°	61.966(6)	61.032(7)
β/°	67.199(6)	67.105(5)
γ/°	77.309(4)	78.673(5)
Volume/Å ³	1844.8(2)	1796.7(2)
Z	2	2
$\rho_{calc}g/cm^3$	1.968	1.847
µ/mm ⁻¹	6	6.666
F(000)	1036	964
Crystal size/mm ³	$0.628 \times 0.177 \times 0.073$	$0.637 \times 0.213 \times 0.115$
Radiation	MoKa ($\lambda = 0.71073$)	MoKa ($\lambda = 0.71073$)
2θ range for data collection/°	7.054 to 59.13	6.68 to 59.032
Index ranges	$-16 \le h \le 14, -12 \le k \le 16, -18 \le l \le 18$	$-17 \le h \le 15, -16 \le k \le 16, -18 \le l \le 17$
Reflections collected	12899	12463
Independent reflections	$\begin{array}{l} 8482 \; [R_{int}=0.0278, \\ R_{sigma}=0.0622] \end{array}$	$\begin{array}{l} 8264 \; [R_{int} = 0.0257, \\ R_{sigma} = 0.0614] \end{array}$
Data/restraints/parameters	8482/0/393	8264/0/383
Goodness-of-fit on F ²	1.024	1.027
Final R indexes $[I \ge 2\sigma(I)]$	$\begin{array}{c} R_1 = 0.03 \overline{89}, \ wR_2 = \\ 0.0642 \end{array}$	$\begin{array}{c} R_1 = 0.04\overline{45}, wR_2 = \\ 0.0830 \end{array}$
Final R indexes [all data]	$R_1 = 0.0743, wR_2 = 0.0811$	$\begin{array}{c} R_1 = 0.0769, \ wR_2 = \\ 0.0997 \end{array}$
Largest diff. peak/hole / eÅ ⁻³	0.68/-1.22	0.77/-1.19

	3	5
Empirical formula	C34H36NF9Cl6IAu	$C_{16}H_{36}AuI_2N$
Formula weight	1166.2	693.22
Temperature/K	210.15	294
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.3231(6)	9.4636(6)
b/Å	13.6119(5)	15.8178(9)
c/Å	13.8716(5)	15.9489(11)
α/°	88.973(3)	94.940(5)
β/°	76.149(3)	96.324(6)
γ/°	82.152(3)	105.988(5)
Volume/Å ³	2237.75(16)	2264.1(3)
Z	2	4
$\rho_{calc}g/cm^3$	1.731	2.034
μ/mm ⁻¹	4.397	9.22
F(000)	1124	1296
Crystal size/mm ³	$0.423 \times 0.174 \times 0.053$	$0.247 \times 0.07 \times 0.043$
Radiation	MoK α ($\lambda = 0.71073$)	MoKa ($\lambda = 0.71073$)
2θ range for data collection/°	6.718 to 59.176	6.816 to 59.466
Index ranges	$\begin{array}{c} -15 \leq h \leq 16, -17 \leq k \leq \\ 16, -17 \leq l \leq 12 \end{array}$	$-12 \le h \le 9, -20 \le k \le 16, -19 \le 1 \le 20$
Reflections collected	15662	15897
Independent reflections	$\begin{array}{l} 10205 \; [R_{int} = 0.0400, \\ R_{sigma} = 0.0826] \end{array}$	$\frac{10382 \ [R_{int} = 0.0379,}{R_{sigma} = 0.0939]}$
Data/restraints/parameters	10205/0/483	10382/0/369
Goodness-of-fit on F ²	1.029	0.986
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0494, wR_2 = 0.0900$	$R_1 = 0.0572, wR_2 = 0.0860$
Final R indexes [all data]	$R_1 = 0.0778, wR_2 = 0.1060$	$R_1 = 0.1528, wR_2 = 0.1193$
Largest diff. peak/hole / $eÅ^{-3}$	1.50/-1.10	1.70/-0.83

Table S2. Crystal data and structure refinements for $(NBu_4)[AuRf_3I]$ (3) and $(NBu_4)[AuI_2]$ (5). Half molecule of toluene (with a disordered methyl group) is also present in the asymmetric unit of 3, but we decided to use solvent mask to remove it.

6. Computational section

Density functional theory (DFT) calculations reported in this work were carried out using the dispersion corrected hybrid functional ω B97X-D developed by Head-Gordon and Chai,¹² and the Gaussian16 software.¹³ The choice of this level of theory is based on the satisfactory results obtained in previous theoretical studies on previous mechanistic studies with Au derivatives.^{3,14} C atoms were described using the double- ζ basis set 6-31G(d,p), whereas the same basis set plus diffuse functions was employed to describe the more electronegative Cl and F atoms. Au and I were described using the effective core potential LANL2DZ¹⁵ including f-polarization functions for Au (exponent: 1.050)¹⁶ and d-polarization functions for I (exponent: 0.289).¹⁷

Geometry optimizations in vacuum were performed without imposing any constraint and the nature of all the stationary points was further verified through vibrational frequency analysis. As expected, all the energy minima display only real vibrational frequencies, whereas transition states (TS) were found to exhibit one single imaginary frequency. For the latter, geometry relaxations along the reaction coordinate were also carried out to confirm they connect the corresponding reaction energy minima.

The effect of the solvent (chloroform: $\varepsilon = 4.711$) was introduced through single-point calculations at the optimized geometries in vacuum using the SMD solvation model.¹⁸ Note that TCE cannot be found in the solvent list of Gaussian and the behaviour in CHCl₃ is similar (see Figure S2).

Figure S8 gathers the optimized structures of the TSs for C–I coupling from **4** (left) and that for C–C coupling from **2** (right) with selected distances and angles (entries 4 and 5 of Table 1). All the DFT data underlying this work, including the Cartesian coordinates of the modelled

structures and energies, are available at the following ioChem-BD,¹⁹ online data set:

https://www.iochem-bd.org/handle/10/309236



Figure S8. Optimized geometries of the TSs for C–I coupling from **4** (left) and that for C–C coupling from **2** (right) with selected distances (Å) and angles (°). Note that the sum of angles proves square-planar geometries in both cases.

6. Kinetic monitoring and microkinetic modelling details

For the kinetic experiment shown in Figure 2, 5.46 mg of **1** (0.005 mmol) were completely dissolved in 0.50 mL of TCE- d_2 at room temperature. Then, the tube was placed into a thermostated probe in a Varian 500 apparatus and the reaction was monitored at 338 K by ¹⁹F NMR. A scaling factor of 1.05 was used for the organic RfI to compensate its integral loss. Two additional corrections were applied: *i*) the concentration of scrambling species ([RfI] + [**4**] = [**3**]) was normalized; *ii*) the sum of concentrations of the observed species was normalized to 0.01 M.

The measured concentration *vs*. time experimental data were fitted (see continuous lines in Figure 2) by nonlinear least-squares (NLLS) regression, using the kinetic model depicted in Scheme S1 and the COPASI software.²⁰ Table S3 summarizes the adjusted kinetic constants. The units of the rate constants are (s⁻¹), (mol⁻¹ × L × s⁻¹) or (mol⁻² × L² × s⁻¹) for first, second and third order kinetic reactions respectively. Figures S9-12 gather different time-course simulations and Figure S13 shows the weighed errors of the fitting.

Scheme S1. Kinetic model proposed, summarizing the plausible reaction pathways, to explain the evolution of the reaction.



Table S3. Fitted rate constants. Starting conditions: $[1]_0 = 1.00 \times 10^{-2} \text{ mol} \times \text{L}^{-1}$. Best value of the fitting = 4.26×10^{-7} .

k_A	1.500×10^{-3}
k-A	$5.486 imes 10^{-6}$
k_B	3.129×10^{-2}
k-B	2.384×10^{-4}
kc	$9.249 imes 10^5$
k -c	$5.020 imes 10^{0}$
k_D	$1.550 imes 10^5$
k-D	$1.079 imes 10^{0}$
k_E	$9.427 imes 10^5$
k_{-E}	5.776×10^{-1}
k _F	1.344×10^{-4}



Figure S9. Time-course simulation corresponding to the kinetic monitorization shown in Figure 2, using the kinetic parameters gathered in Table S3.



Figure S10. Time-course simulation at longer reaction times highlighting the behaviour of **2** (pink trace) as intermediate in favour of the formation of RfI (orange trace, complex **3** omitted for clarity). Note that the concentration of $[AuI_2]^-(5)$ is exactly the same as RfI (equimolar decomposition from **4**).



Figure S11. Time-course simulation at longer reaction times highlighting the behaviour of **2** (pink trace) as intermediate in favour of the formation of **3** (black trace, RfI omitted for clarity).



Figure S12. Time-course simulation at even longer reaction times showing the complete disappearance of 2 leading to 3 + 5 + RfI (see Scheme 2 in the manuscript and Figure S5).



Figure S13. Weighed errors between experimental data and fitted values. Color code: [1], [2], [3], [4] and [Rf–I]. *y*-axis denotes concentration in mol L⁻¹ (M) while the *x*-axis corresponds to reaction time. *Note that the errors are random and in any case are higher than $\pm 8 \times 10^{-5}$ M. Considering that the initial concentration is 0.01 M, the error is in the worst case lower than 0.8%.

7. NMR spectra



Figure S14. ¹⁹F NMR (470 MHz, CDCl₃, 298 K) of (NBu₄)*trans*-[AuRf₂l₂] (1).



Figure S16. ¹⁹F NMR (470 MHz, CDCl₃, 298 K) of (NBu₄)*trans*-[AuRf₂Br₂] (1-Br).





Figure S18. $^{19}\mathrm{F}$ NMR (470 MHz, CDCl_3, 298 K) of (NBu_4)[AuRf_3I] (3).

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