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Unexplored Complexity of Simple Au(III) Reactions: Striking Ligand-Disproportionative Cl/aryl Scrambling Promoted by OEt$_2$. Driving Forces and Mechanisms

Sara Fernández-Moyano,[a] Marconi N. Peñas-Defrutos,[a] Camino Bartolomé,[a,]* and Pablo Espinet [a,]*

Aryl rearrangements triggered by Cl extraction from starting from *trans*-[Au^{III}(Rf)$_2$Cl$_2$]$^-$ (Rf = C$_6$F$_3$Cl$_2$-3,5), led fastly to a mixture of [Au(Rf)$_3$(solv)], [Au(Rf)$_2$Cl(solv)], and [Au(Rf)Cl$_2$(solv)] (solv = OEt$_2$, OH$_2$). ^{19}F NMR and X-ray diffraction studies led us to identify the species present in solution and the role of the solvent in their formation, while DFT calculations confirm the thermodynamic basis of their evolution.

Organometallic complexes bearing pentafluorophenyl (Pf) or other fluorinated aryls have been used in chemistry since decades because of the extra stability of the M–(fluoroaryl) bonds. Their use in gold chemistry in the 1970 decade was decisive for an explosive development of different families of gold complexes,[1] which later have made accessible the study of properties linked to gold complexes such as aurophilicity and luminescent properties.[2]

A few years ago Toste *et al.* reported an extremely fast aryl–aryl coupling based in the Au^{III}/Au^I redox couple, occurring at very low temperatures and not needing the use of ligands specially designed for such purpose.[3] This finding boomed the interest in the topic. Very recent reviews on this field are available.[4,5] The eventual Ar–Ar coupling requires, obviously, the formation of intermediates with *cis*-Au^{III}Ar$_2$ arrangement.

The work presented here started because of a casual discovery when we wanted to prepare stable gold (III) complexes containing the *cis*-Au^{III}(Rf)$_2$ fragment (Rf = C$_6$F$_3$Cl$_2$-3,5). The syntheses of *trans*-[Au^{III}(Pf)$_2$X$_2$]$^-$,[6] *cis*-[Au^{III}(Pf)$_2$X$_2$]$^-$,[6] and (μ-Cl)$_2$[Au(Pf)$_2$]$_2$,[7,8] complexes had been reported forty years ago, but we prefer to use Rf derivatives because they greatly simplify the ^{19}F NMR spectra (there is no intra-ring ^{19}F-^{19}F coupling in C$_6$F$_3$Cl$_2$-3,5).[9] This NMR simplification is useful to

separate signals that with C$_6$F$_5$ can overlap in mixtures due to their multiplicity. For this reason, we choose to synthesize the *cis*- and *trans*-Au^{III}(Rf)$_2$ complexes mentioned above.

In our large experience, Rf and Pf behave identically as far as chemical reactivity of their complexes is concerned. For this reason we were surprised when, applying with Rf the same synthetic procedures reported for Pf-complexes,[6,7] we observed the formation of tris-Rf and mono-Rf complexes. This complication was not mentioned for Pf complexes in the original papers or, more likely, it went unnoticed in the syntheses. Its formation reveals the occurrence of some unexpected and unreported aryl scrambling processes. These complications deserve attention because they can be a serious problem in the context of cross-coupling catalysis. In Pd, they are a frequent source of loss of selectivity, giving rise to homocoupling products and opening the door to other undesired reaction pathways. The scrambling mechanisms operating in gold (III) are poorly known and understood. In fact, to the best of our knowledge, only three aryl rearrangement reactions involving Au^{III}, by the way, Pf derivatives, have been reported in modern times,[10,11,12] but they occur in very different conditions. In all of them, either strong oxidants (nitrosyl, selectfluor, or PhI(OAc)$_2$), or mixtures of gold compounds with different oxidation states are involved. In the study that follows we take advantage of the highly informative observation of Rf complexes to uncover the origin and mechanistic details of scrambling processes in gold chemistry.

Following the procedures reported in the literature for the Pf complexes, the oxidative addition of (NBu$_4$)[Au(Rf)$_2$],[13] using a CCl$_4$ solution of Cl$_2$, led to the expected gold(III) complex (NBu$_4$)(*trans*-[Au(Rf)$_2$Cl$_2$]) (**1**), which was isolated and fully characterized. Also as expected, the cis isomer (NBu$_4$)(*cis*-[Au(Rf)$_2$Cl$_2$]) (**2**) was obtained upon heating a solution of **1** in toluene, and was fully characterized (Scheme 1). The X-ray structures of **1** and **2** are shown in Figures ESI1 and ESI2 respectively. The cis isomer is thermodynamically preferred, obeying the antisymbiotic effect that avoids strongly donor

a. IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071-Valladolid, Spain. E-mail: espinet@qi.uva.es

ligands in mutually *trans* positions,[14] but the *trans* isomer does not isomerize unless it is submitted to heating.
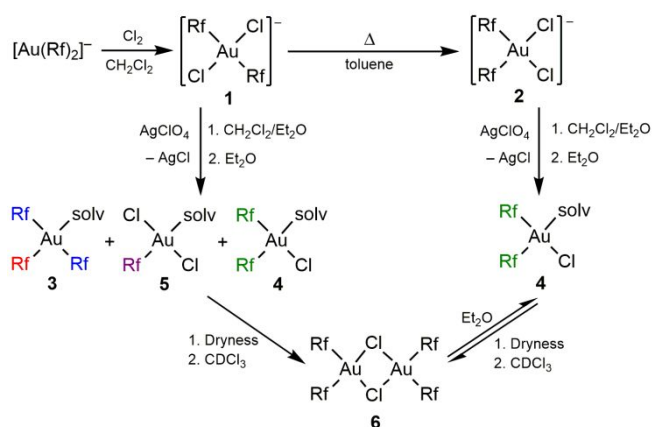
Scheme 1. Synthesis of Rf dichlorodiaryl gold (III) anionic complexes, following the literature procedure for Pf analogue, and evolution with $AgClO_4$ (1:1). The cation is $(NBu_4)^+$.

In the literature, both **1** and **2** are indistinctly precursors for the synthesis of $(\mu\text{-Cl})_2[Au(Rf)_2]_2$ (**6**) by reaction with 1 equivalent of $AgClO_4$.[7] However, the reaction of **1** carried out in CH_2Cl_2/Et_2O, leads fastly to a mixture of compounds **3**-**5**, which requires aryl rearrangement (Scheme 1). Fig. 1 shows the ^{19}F NMR spectrum recorded from an aliquot of this reaction after solvent evaporation and subsequent extraction with Et_2O in order to remove NBu_4ClO_4 (see experimental details in ESI). The F_{para} region (upper right corner) shows five signals corresponding to the five non-equivalent Rf groups of the three species in Scheme 1. The multiplicity of the F_{ortho} signals, due to through-space F_{ortho}-F_{ortho} coupling, has been perfectly studied for square planar complexes with this particular aryl,[9] and allows for unambiguous assignment of a tris-aryl fragment (1:2 quintuplet:triplet, labelled in red and blue respectively), and a *cis*-diaryl fragment with two non-equivalent Rf groups (two 1:1 pseudotriplets labelled in green). The solv ligand (Et_2O or adventitious water, both O-donor ligands) takes the coordination vacancies, leading to $[Au(Rf)_3(solv)]$ (**3**), *cis*-$[Au(Rf)_2Cl(solv)]$ (**4**), and *trans*-$[Au(Rf)Cl_2(solv)]$ (**5**). This ligand-disproportionative scrambling of aryl and chloro ligands replaces in these conditions the expected formation of $(\mu\text{-Cl})_2[Au(Rf)_2]_2$ (**6**).
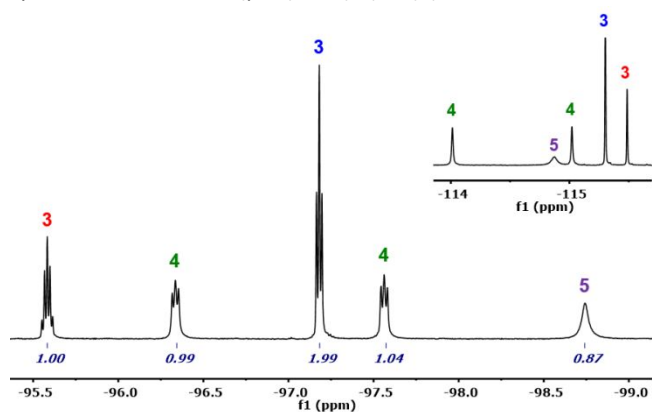

Fig. 1. ^{19}F NMR spectrum of an aliquot (in Et_2O, ref. acetone-d_6) from the reaction of **1** with $AgClO_4$. Expansion of the F_{ortho} region with integrated signals. F_{para} region in upper right corner.

If the reaction mixture in Fig. 1 is evaporated to dryness and then dissolved in non-coordinating dry $CDCl_3$, only one species is observed in solution. Its ^{19}F NMR spectrum (Fig. 2, above) displays two singlets (2:1), assigned respectively to F_{ortho} and F_{para} of the desired dimer $(\mu\text{-Cl})_2[Au(Rf)_2]_2$ (**6**). Additionally, signals of the coupling product Rf–Rf start to be observed. If, once more, the $CDCl_3$ is removed completely and Et_2O is added, the coordinating solvent (or adventitious water in it) splits the weak Cl bridges and only *cis*-$[Au(Rf)_2Cl(solv)]$ (**4**) is found in the ^{19}F NMR spectrum (Fig. 2, below, see details in ESI). This unexpected sequence of quickly reversible or partially reversible scrambling processes explains why they could go unnoticed in the reported synthesis of the Pf analogue of **6**,[6,7] depending on the use of solvents, often varied in synthesis, on the use or not of frequent NMR monitoring, and on the more difficult observation of independent signals with C_6F_5. There is no reason to expect different chemical behavior for Pf and Rf, and we have confirmed that the same unreported aryl scrambling occurs with the Pf analogue under identical conditions.

On the other hand, one halide abstraction from $(NBu_4)($*cis*-$[Au(Rf)_2Cl_2])$ (**2**) produces selectively *cis*-$[Au(Rf)_2Cl(solv)]$ (**4**) in coordinating solvents, or **6** in non-coordinating ones. The products **3** and **5** are not observed in this case.
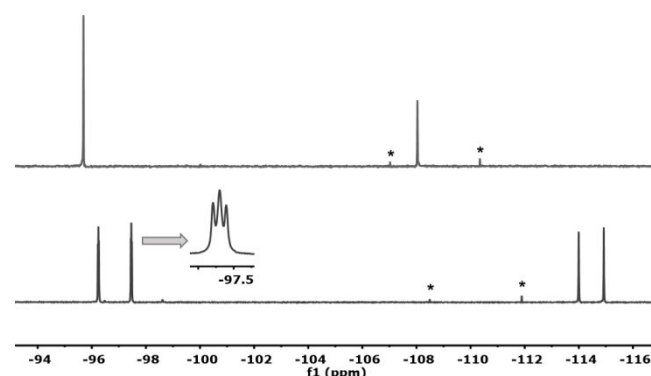

Fig. 2. ^{19}F NMR spectra of **6** formed in $CDCl_3$ (above), and **4** formed in Et_2O (below), ref. acetone-d_6 capillary. Asterisks denote signals of the coupling product Rf–Rf formed from **6**.

Slow evaporation of the mixture of products in Fig. 1 led to isolation of colorless crystals of $[Au(Rf)_3(OH_2)]\cdot 2Et_2O$ (**3·OH₂**) in up to 20% yield, further confirming the aryl scrambling process (Fig. 3). This is one of the few gold(III) aquo-complexes ever reported.[15,16] The fourth coordination position in the crystal is, as expected, occupied by a water molecule, in this case H-bonded to two diethyl ether molecules. In solution, fast ligand exchange between Et_2O and water is expected. The Au–C distance of the aryl group *trans* to OH_2 is 1.987(12) Å, significantly shorter than those found for the other two mutually trans Rf groups, with longer Au–C distances of 2.056(7) Å. This is expected from the high *trans influence* of Rf and the low *trans influence* of OH_2. The dimer $(\mu\text{-Cl})_2[Au(Rf)_2]_2$ (**6**) could also be crystallized and characterized by X-ray diffraction (Fig. 4).[17]
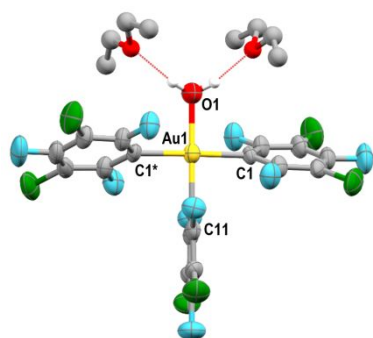
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Fig. 3. X-ray structure of **3·OH₂**. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–O(1) = 2.077(10); Au(1)–C(11) = 1.989(12); Au(1)–C(1) = 2.058(7); C(11)–Au(1)–O(1) = 180.0; C(11)–Au(1)–C(1) = 89.4(2); C(1)–Au(1)–O(1) = 90.6(2); C(1)–Au(1)–C(1*) = 178.8(5).
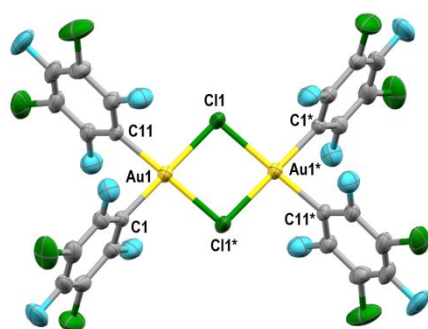

Fig. 4. X-ray structure of **6**. Selected bond lengths (Å) and angles (°): Au(1)–Cl(1) = 2.3902(12); Au(1)–Cl(1*) = 2.3904(14); Au(1)–C(11) = 2.010(5); Au(1)–C(1) = 2.000(4); Cl(1*)–Au(1)–Cl(1) = 86.54(5); C(11)–Au(1)–C(1) = 93.25(13); C(1)–Au(1)–Cl(1*) = 93.02(14); C(1)–Au(1)–C(11) = 87.18(18).

Although solutions of **6** in Et₂O (forming **4**) are stable for days at room temperature, homocoupling to Rf–Rf occurs fast in CDCl₃ solution. Complex **2** requires heating in toluene above 373 K to observe reductive elimination (RE). The RE rates observed, **6** > **4** >> **2**, suggest coupling *via* dissociation to a tricoordinate intermediate. The coordinating ability of CDCl₃, bridging Cl, OEt₂/OH₂, or Cl⁻ as the fourth ligand determines this rate sequence. This behavior is in line with the extremely fast Ar–CF₃ coupling from [Au(Ar)(CF₃)I(PR₃)] coupling in CH₂Cl₂ by treatment with AgSbF₆,[18] and the high-energy barrier for Ar–Ar' coupling in four-coordinated [Au(Ar)(Ar')Cl(PR₃)].[19]

The results allow for some mechanistic analysis of the processes sketched there. First of all, a concerted mechanism for the oxidative addition of Cl₂ to [Au^{I}Rf₂]⁻ can be excluded: it should produce *cis*-[Au^{III}Rf₂Cl₂]⁻ (**2**), which is the most stable isomer, and **1** would never be observed. Consequently, an electrophilic attack to gold by Cl–Cl, followed by Cl⁻ release and coordination must operate (Scheme 2).
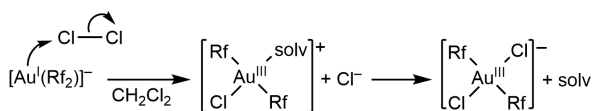
Scheme 2. Most plausible mechanism for the oxidative addition of Cl₂ to the nucleophilic anionic gold(I) complex.

The thermodynamically driven **1** to **2** isomerization must follow the mechanism very early proposed by Kochi and Hoffmann from studies combining experiment and calculations.[20] Isomerization consist of ligand dissociation (Cl⁻

dissociation in this case), followed by topomerization from *trans*-R₂ to the thermodynamically favorable *cis*-R₂ coordination, and ligand (Cl⁻) recoordination (Scheme 3). If the first easy leaving chloride is precipitated with a silver salt of a non-coordinating anion, AgClO₄, the remaining chloride coordinates additionally to the empty coordination position created, to form a bridged dimer **6** in non-coordinating chloroform. These chloro bridges are not very strong. In fact, they are easily split by coordinating molecules such as Et₂O or OH₂, forming *cis*-[Au(Rf)₂Cl(solv)] (**4**) (Scheme 1).
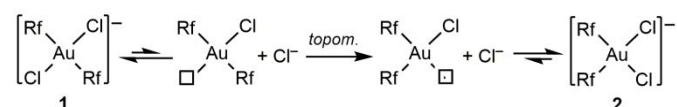
Scheme 3. Isomerization via ligand dissociation plus topomerization.

At this point it is clear why the presence of a coordinating solvent can be determining for the different fate of **1** when one Cl⁻ is precipitated as AgCl. In dichloromethane, chloroform or toluene the Cl⁻ ligand dissociation required for topomerization makes the isomerization process leading to **2** slow. But in the presence of OEt₂ a non-observed intermediate *trans*-[Au(Rf)₂Cl(solv)] (**I1**) should be formed upon precipitation of AgCl with AgClO₄ which, as the results discussed below prove, topomerises to the cis isomer **4** much more rapidly.

In fact, the final result is more complex because three aryl products **3**, **4** and **5** are formed. Compounds **3** and **5** must have a common pathway that involves disproportionative Cl-for-Rf exchange from the proposed *trans*-[Au(Rf)₂Cl(solv)] (**I1**) intermediate. For this reason, they are in equimolecular proportion in the mixture (Fig. 1). However, it is not possible to find a direct pathway from **I1** to these products. On the other hand, **4** has its own abundance in the mixture and can be formed from **I1** simply by fast topomerization from *trans*-[Au(Rf)₂Cl(solv)] (**I1**). Its presence gives the key for the whole process, assuming that **4** reacts with **I1** to produce a new asymmetric dimeric intermediate **I2** with mixed Rf/Cl bridges (see Figure ESI3). It is worth remarking that the three aryl products **3**, **4** and **5** are not in equilibrium, since the reaction of **6** with Et₂O (solv) only produces **4**. In summary, the ratios of the three complexes obeys to the two rate-competing pathways depicted in Scheme 4. **I1** consumes part of the **4** formed to give equimolar **3** + **5**, and the non-consumed **4** appears also in the mixture.
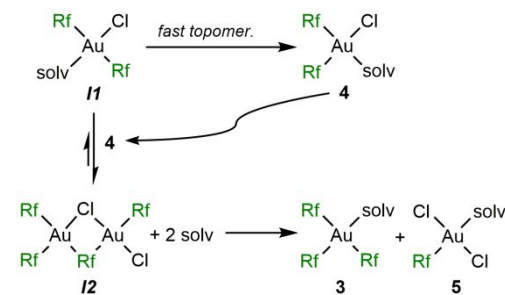
Scheme 4. Ag⁺-fueled mechanism of the ligand-disproportionative Rf/Cl rearrangements from *trans*-[Au(Rf)₂Cl(solv)] in the presence of a coordinating solvent (OEt₂).

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Density Functional Theory (DFT) calculations at wb97x-D level were carried out in order to establish the thermodynamics of the reaction (see computational details in ESI). The results confirm our guess that *trans*-[Au(Rf)$_2$Cl(OEt$_2$)] (*I1*) is the highest energy form.[14] It is however accessible because the formation of insoluble AgCl compensates the thermodynamic balance. Its *cis* isomer **4** is 17.3 kcal mol^{-1} more stable. The rearrangement of *trans*-[Au(Rf)$_2$Cl(OEt$_2$)] (2 equivalents) into [Au(Rf)$_3$(OEt$_2$)] (**3**) + *trans*-[Au(Rf)Cl$_2$(OEt$_2$)] (**5**) (more stable than its *cis* isomer) via *I2* is favorable by 27.5 kcal mol^{-1}, and the splitting of *I2* with 2OEt$_2$ is also favorable by 11.5 kcal mol^{-1}. These values support that isomerization and Rf/Cl rearrangements on OEt$_2$ complexes are irreversible processes with low activation barriers that make the proposed intermediates unobservable. Only the fact that in the end a considerable amount of **4** survives needs to be explained by kinetic reasons: its formation is faster than its consumption rate to produce *I2*, and this rate difference produces neat **4** observed when the process is finished.

In summary, the initially striking variety of complexes produced from a single precursor finds a fully satisfactory explanation. This ligand-disproportionative rearrangement, arising simply depending on the choice of solvent or other often disregarded details, is a warning on possible complexities in catalysis under oxidative conditions where complexes of this kind are formed (e.g. in Ar-Ar coupling via gold(I)/gold(III) cycles), or when using gold(III) complexes for materials.

Conflicts of interest

There are no conflicts to declare.

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