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Evidence of hybrid homo-heterogeneous catalysis in a Pt/Au heterobimetallic system

José Miguel Alonso[‡a] and María Paz Muñoz[*‡a]

Abstract: We report here our efforts towards understanding the catalytic species involved in a novel Pt/Au heterobimetallic system capable of efficiently catalyse the tandem cyclisation/C-X coupling reaction of heteroarylallenes with *C-* and *N*-based nucleophiles. Our evidence confirm that homogeneous Au-catalysis is involved at the beginning of the reaction to generate an intermediate that enters the second catalytic cycle where hybrid homogeneous-heterogeneous catalysis by [Pt-Au] clusters could be responsible for the high efficiency. In this part of the cycle [Pt-AuPPh₃] homogeneous clusters (identified by ³¹P NMR) seem to be aided by Pt-Au particles in the heterogeneous phase (supported by Hg poisoning and filtration experiments, and characterization of the possible catalytic species by several techniques, e.g. ³¹P NMR, ICP-MS, SEM, DLS), with full Pt-to-Au transmetallation not being observed in contrast with other reported bimetallic systems. There are a few examples of hybrid homogeneous-heterogeneous catalysis in monometallic systems, but to the best of our knowledge this is the first example of hybrid homo-heterogeneous catalysis in systems involving two different metals.

Introduction

Bimetallic catalysis has appeared in recent year as a powerful strategy to develop new efficient synthetic methods for the synthesis of complex molecules difficult to make under single catalyst conditions.[1] Most of the examples of bimetallic catalysis using two different metals in homogeneous systems involve a transmetallation step that links two tandem catalytic cycles, with the challenge of finding redox compatible pairs still being one of the most common limitations in developing true catalytic systems in both metals. In this area, gold complexes have been explored in dual catalysis in systems involving transmetallation with rhodium,[2] iron,[3] ruthenium[3] and palladium,[4] as well as several examples where two different gold species (eg. Au(I) and Au(III)) are involved.[5]

Although transmetallation from Au(I)-to-Pt(II) complexes is not widely reported, ethynyl-[6] and bis(ortho-amine)aryl-gold(I) complexes[7] have been described to undergo exchange with Pt(II) complexes. More recently, Chen *et al.* reported the Pt(II)-to-Au(I) transmetallation of methyl groups to occur through bimetallic complexes where Pt-Au bond formation was the first step in the transfer of the organic group.[8] However, to the best of our knowledge, there are no examples of truly catalytic homogenous

reactions involving Au and Pt complexes in transmetallation processes.

In contrast, bimetallic catalysis in heterogeneous systems is more common, with many examples reporting the increase of the activity and selectivity of group VIII metal nanoparticles, in particular platinum, in the presence of gold.[9]

Understanding the true nature of the catalytic species involved in new reactions is crucial for the development of more efficient processes and the rational design of more potent and efficient catalysts. Gold catalysis using discrete complexes stabilised with ancillary ligands is well documented to occur in homogeneous phase.[10] However, recently studies have shown that small gold clusters in very low concentration, formed from conventional gold complexes in solution, are able to catalyse organic reactions very efficiently even at room temperature,[11] opening the question of are these reactions truly homogeneous or do they have a heterogeneous component?[12] This question has been raised already for reactions using platinum(II) complexes and several groups have already tried to answer it, leading to the conclusion that not a single experiment will give the answer, but a combined approach using physical organic chemistry techniques is needed to address this question in each case study.[13]

We have recently discovered a new Pt-Au bimetallic system that is able to catalyse very efficiently the tandem cyclisation/C-X coupling reaction of heteroarylallenes (such as **1a**, Scheme 1) with *C-* and *N*-based nucleophiles **2** to give a family of multi heteroaromatic structures (**4** and **5**, Scheme 1) with potential use in pharmaceutical industry.[14] Our previous studies have shown that the reactions proceed through cyclic intermediates (such us **3a** and **3a'**, Scheme 1), the first of which (**3a**) is formed in a very fast process catalysed mainly by gold(I), and suggested that Pt-Au interaction was needed for the nucleophilic attack and the efficient evolution of these intermediates into the final products *via* an heterobimetallic carbene as the key intermediate in a second catalytic cycle (Scheme 1).

C-NuH = indoles, pyrrol, furane, 1,3,5-trimethoxybenzene. Yields 55-95%.
N-NuH = pyrazole, triazole, indazole, benzotriazole. Yields 70-80%.
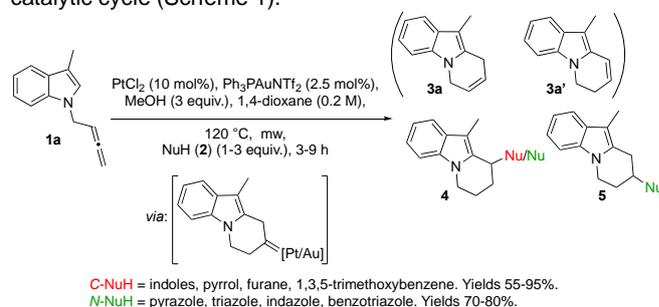
Scheme 1. Pt-Au catalysed tandem cyclisation/C-X coupling reaction of heteroarylallenes with *C-* and *N*-based nucleophiles.[14]

We hypothesised that heterobimetallic [Pt-Au] complexes formed in solution with or without a Au-to-Pt or Pt-to-Au

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transmetallation event to connect the cycles, could be responsible for the observed enhanced reactivity in our system when gold was present in the reaction. Alternatively, heterogeneous Pt-Au particles could be responsible for the enhanced catalytic activity.[9] Indeed, a black solid was observed during and after the reaction, suggesting that metallic particles were present.

Here we report our efforts towards the understanding of the true nature of the catalysis species involved in the reaction, the possibility of a transmetallation event and the involvement of both homo-and heterogeneous catalysis. Our evidence further support the suspected gold(I)-homogeneous catalysis in the first cycle followed by hybrid homo-heterogeneous catalysis, not reported to date in heterobimetallic systems, operating cooperatively in the second catalytic cycle in this reaction.[15]

Results and Discussion

Our previous results[14] showed that gold(I) alone was not able to promote the isomerization of **3a** to **3a'**, *via* a gold carbene, or the nucleophilic attacks to form **4** or **5**. Therefore, we initially hypothesised that once **3a** is formed (by whatever means), it would only interact with the platinum complex to enter the second catalytic cycle. However, to explain the increase reactivity of the systems when gold is present, involvement of the gold complex is needed at some stage in the second cycle.

A Pt-to-Au transmetallation could be proposed in a similar process as described by Chen *et al.*,[8] where a R-(L)Pt-AuPPh₃ could be formed in the first instance in any of the intermediates of the second cycle (e.g. at the carbene stage, shown in Scheme 2), followed by dissociation to form [(L)PtPPh₃] and R-Au (*path a*, Scheme 2) or (L)Pt and R-AuPPh₃ (*path b*, Scheme 2) that could now complete the second catalytic cycle more efficiently to form **4** and promote the *N*-nucleophilic attack to a gold carbene to form **5** (Scheme 3, *vide infra*).[16],[17],[18]
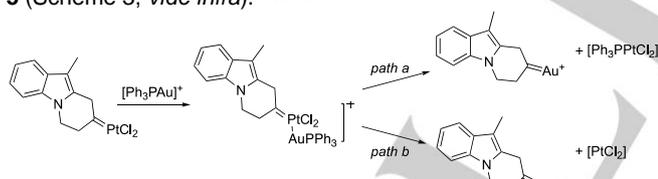
Scheme 2. Possible pathways for Pt-to-Au transmetallation in the second catalytic cycle showed at the carbene stage.

³¹P NMR experiments were carried out using *N*-indolylallene **1a** as model substrate with indole **2a** and pyrazole **2b** as model nucleophiles under the optimised reaction conditions as described previously.[14] It was observed that in both reactions the gold-phosphorus bond remained intact during the first stage until formation of compound **3a** is complete. Once this compound starts to isomerise to compound **3a'** and final products **4** and **5** (only formed with pyrazole) start to appear, the ³¹P NMR signal changes dramatically from 33 ppm to 6 ppm in the case of the reaction with indole (Figure 1), and two signals at 2 and -1.6 ppm in the case of pyrazole (see SI for details). This suggests that the

first catalytic cycle to form **3a** is homogenous in nature and only gold is involved in it with both nucleophiles (cycle 1, Scheme 3).
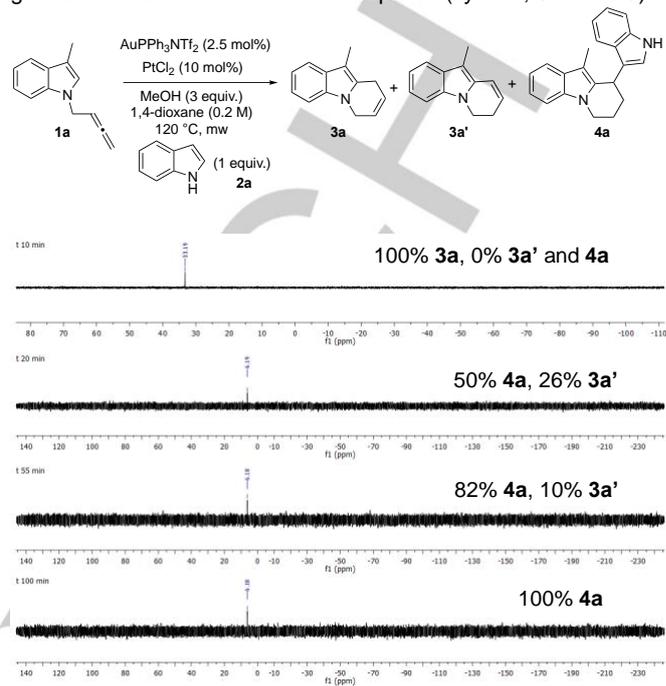
Figure 1. ³¹P NMR spectra (202 MHz, CDCl₃) of the reaction if **1a** with indole **2a** at different times indicating the NMR yield of different components of the reaction mixture at those times.

The dramatic change in the ³¹P NMR signal could suggest transmetallation with formation of R-Au (*path a*, Scheme 2) intermediates as proposed by Chen. However, the chemical shifts of the new signals do not correspond to platinum-phosphine complexes (15 ppm for Ph₃PPtCl₂ and 19 ppm for (Ph₃P)₂PtCl₂), so it is unlikely that full transmetallation occurs in that manner. Besides, formation of R-AuPPh₃ (*path b*, Scheme 2) could also be ruled out, as the signal for the gold-phosphine bond is not expected to change so dramatically.[19] Alternatively, the chemical shift of the Ph₃P in a [Pt]-AuPPh₃ complexes has been reported to appear at ~ 4 ppm,[20,21] supporting a (L)ClₙPt-AuPPh₃ cluster complex as the homogeneous active catalytic species for the isomerisation and second nucleophilic attack with both nucleophiles (cycles 2 and 3, Scheme 3).[22]

Nevertheless, it seems that the active species are slightly different with the carbon or nitrogen-based nucleophiles, which could be explained by the further interaction of the nucleophiles with the metals as ligands and the formation of [M(pyrazole)] complexes that can occur *in situ*.[14a]

The heterobimetallic [(L)ClₙPt-AuPPh₃] cluster could also explain the different reactivity of carbon- versus nitrogen-based nucleophiles. Nucleophilic attack to form products **4** occurs to a benzylic carbocation intermediate (**G**, cycle 2, Scheme 3), formed by 1,2-H shift form the key carbine intermediate (**E**, cycle 2 Scheme 3) or by reinsertion of the bimetallic system into the alkene of compound **3a'** (**I**, cycle 3, scheme 3), a true intermediate on the formation of compound **4**. This carbocation **G** would be

stable and very accessible and whichever nucleophile available could react with it to form **4**. However, to form products **5**, nucleophilic attack has to happen directly at the electrophilic carbene carbon, which depends on its accessibility and the metal involved. The increased activity of a Pt-Au carbene (**E**, cycle 2, Scheme 3) in comparison with only Pt or Au catalysis could be explained by the relativistic effect in gold atoms, as the closed 5d shell would attenuate the interaction of the bimetallic system with the carbene-carbon so instead of the positive charge being localised in the gold metal centre (e.g. metal carbenoid character, **E**, cycle 2 Scheme 3), it would have more metal-stabilised carbocationic character, with a build-up of the delocalised positive charge on the carbon (e.g. α-metallocarbenium, **F**, Scheme 3) making it more accessible for the nucleophilic attack.[19],[23] Besides, the *N*-nucleophiles used in this work are much better nucleophiles than the indoles, as they react through very acidic N-H groups, in contrast to the stronger C-H bond in position 3 of the indoles.[24] Therefore they will be able to react more readily with an activated bimetallic-stabilised carbocation such as **E ⇔ F**, explaining the selectivity observed in our system.

In contrast, the only platinum-carbene analogue would have a strong bonding with the carbon making it less susceptible to nucleophilic attack (more metal carbenoid character, platinum only analogue of **E** in Scheme 3). Indeed, intermolecular nucleophilic attack to platinum carbenes is rare. On the other hand, our previous results showed that an only gold-carbene analogue is not possible to access under this reaction conditions. This would explain why neither of the metals display this reactivity on its own and will further support the bimetallic catalysis and the formation of [(L)Cl$_n$Pt-AuPPh$_3$] clusters in these systems.[22]
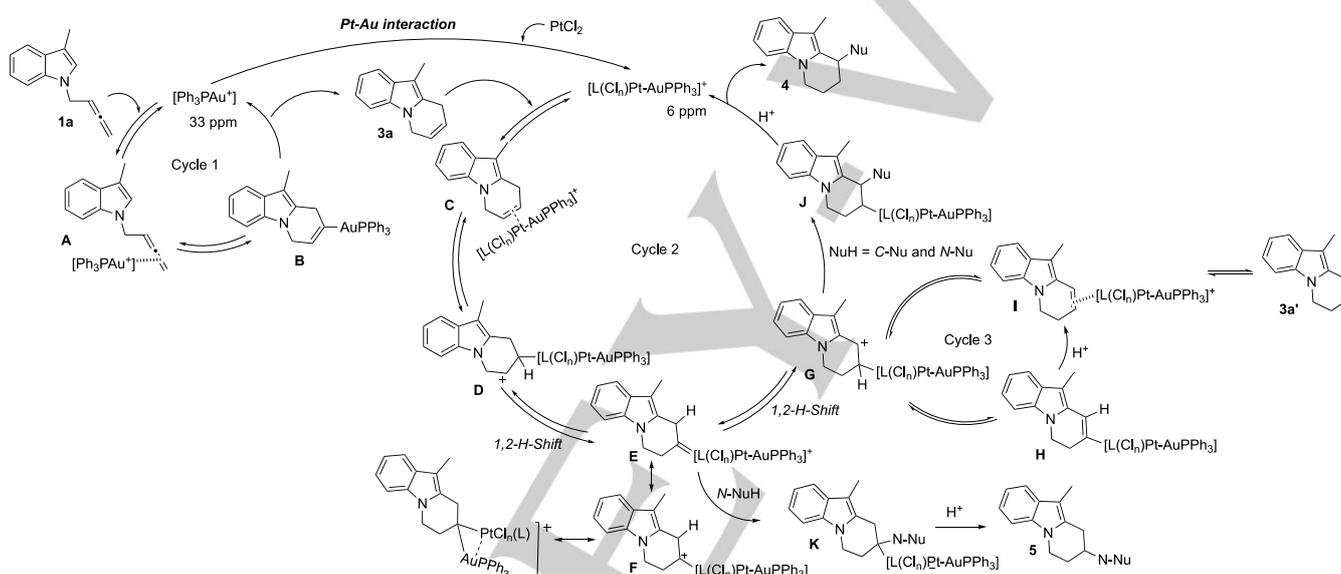
Scheme 3. Full proposed mechanism highlighting the formation of [Pt-Au] complexes as the key active species in the second catalytic cycle.

In all experiments, a black solid precipitate was observed during and after the reaction. This black solid did not promote cyclisation of **1a** under the optimised reaction conditions in the presence of indole. However, it was catalytically active in the reaction of **3a** with indole as nucleophile, giving a mixture of recovered **3a**, **3a'** and **4a** after 3 h (Scheme 3), suggesting that heterogeneous Pt-Au particles might also be involved in the catalysis but only in the second catalytic cycle once intermediate **3a** has been formed. The lower conversion obtained with the black solid would indicate that the solution state Pt-Au cluster complex is still needed for high efficiency either as a reservoir of solution state bimetallic catalysis or as true heterogeneous catalysts, either way supporting a hybrid homo-heterogeneous catalysis operating in this reaction.
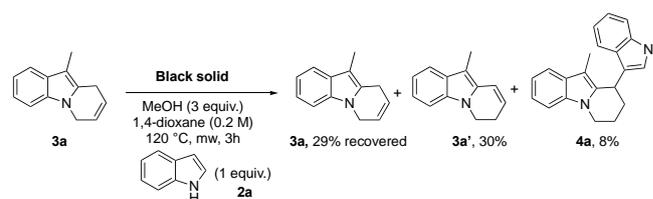
Scheme 3. Reaction using the black solid as catalysts.

In order to gather more evidence of the homogeneous or heterogeneous nature of the Pt-Au clusters we carried out several experiments in the presence of different amounts of Hg that is known to poison metallic species in 0 oxidation state and therefore is used as a test for the heterogeneity of the reactions.[25] Results are shown in Table 1. The reaction with indole as nucleophile in the presence of 30% mol of Hg (entry 2, table 1) shows that first cyclisation occurs, supporting again the

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involvement of homogeneous gold catalysis in this step. Isomerisation is also complete but the second nucleophilic attack is partially inhibited. The effect is more pronounced when 1 equiv. of Hg is used, that seems to inhibit also the isomerization (entry 3, Table 1).

Surprisingly, the reaction with the CN-indole derivative is not affected when 1 equiv. of Hg is present (entry 7, Table 1). It is worth noting that $PtCl_2$ alone is not able promote the reaction with this nucleophile, highlighting the need of the gold for an efficient process in this step when poor nucleophiles are present. This result may suggest that the [Pt-AuPh₃P] cluster that is active in the isomerisation/second nucleophilic attack is acting mainly in solution in homogeneous fashion at least with less active nucleophiles. The results in the reaction with the indole might imply that the reaction is catalysed by both, the $PtCl_2$ (in excess to gold at the beginning of the reaction) and the [Pt-AuPh₃P] cluster. $PtCl_2$ is not fully soluble in dioxane and under the reaction conditions (heating in the presence of methanol), can form colloidal platinum that could be poisoned by Hg, explaining the observed partial inhibition.[26,13] Alternatively, the insoluble platinum colloids could act as a reservoir of catalytically active species that get involved in the reaction when needed.

Table 1. Experiments in the presence of Hg.

Entry	NuH	Hg (%mol)	3a (%)	3a' (%)	4 (%)	5 (%)
1	2a	-	-	-	4a, 95	-
2	2a	30	-	37	4a, 52	-
3	2a	100	32	17	4a, 24	-
4[a]	2a	-	-	-	4a, 50	-
5[a]	2a	100	24	5	4a, 2	-
6	2b	-	-	32	4b, 55	-
7	2b	100	-	28	4b, 53	-
8	2c	-	13	11	4c, 5	5c, 43
9	2c	10	39	17	4c, 3	5c, 7
10	2c	30	50	10	4c, < 1	5c, 7
11	2c	60	61	9	-	-

[a] Experiments using $PtCl_2(MeCN)_2$ (10 mol%) as catalyst.

Indeed, dynamic light scattering (DLS) experiments confirmed the presence of insoluble micro particles even before the reaction was heated (A, Figure 2). DLS analysis of the reaction at different times showed that particles of different sizes (~ 700 – 10000 nm) seem to be in equilibrium, aggregating and disaggregating during the reaction (B: 10 min, 120 °C, mw, **3a** (100%); C: +50 min, 120 °C, mw, **3a** (28%), **3a'** (49%) and **4b** (9%), Figure 2). Comparing the samples from the reaction with a sample only containing $PtCl_2$ treated under same conditions (D, Figure 2), showed different particle sizes and distribution, which could imply that Pt-Au cluster particles are also present in the heterogeneous phase.
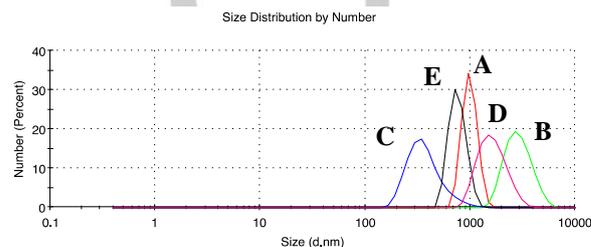
Figure 2. Dynamic Light Scattering experiments showing particles distribution at different times of the reaction with Pt/Au system. **A**: before heating; **B**: after 10 min at 120 °C; **C**: after 60 min at 120 °C. **D**: sample containing only $PtCl_2$. **E**: sample using **Complex 1F** as catalysts (*vide infra*).

Interestingly, when the experiments were carried out with indole and the soluble complex $PtCl_2(MeCN)_2$ as the platinum source (entries 4 and 5, Table 1), inhibition of the isomerisation and nucleophilic attack were also observed in the presence of Hg. It is worth noting that although this complex is thought to be involved in purely homogeneous catalysis and it is fully soluble at the beginning of the reaction, a black precipitated was observed at the end of the reaction, suggesting that the similar species are formed under the reaction conditions in the presence of gold.

In the reaction with pyrazole, isomerization happens even with high loading of Hg (entries 9-11, Table 1). The second nucleophilic attack to form compound **4** is only affected at high Hg loading. However, the nucleophilic attack to form compound **5** is inhibited even at low Hg loading, implying that this process is mainly heterogeneous.

Although these experiments show some inhibition when Hg is present after the first cycle has been formed, and may suggest that the reaction is partially heterogeneous, catalysed by Pt-Au metallic particles, they alone cannot be used as full proof that of the heterogeneous nature of the reaction. Therefore, experiments with indole and with pyrazole were carried out filtrating the reaction mixtures after 20 min of reaction. Comparing the evolution towards the products after the filtration (experiment B, Table 2) with the reaction without filtering (experiment A, Table 2) clearly showed that in both cases, with indole and pyrazole, when the solid material is filtered the catalytic activity decreases significantly, although the reaction progresses slowly toward the isomerisation and the nucleophilic addition products (Figure 3, Table 2 for reaction with indole. See SI for the reaction with pyrazole).

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The lower rate of reaction towards the products after filtration could be explained by the heterobimetallic particle clusters being a reservoir of solution state and the unbalance of the equilibrium between the two systems after filtration. However, the fact that the black solid formed in situ during the reaction and isolated by filtration was moderately catalytically active in the isomerisation of **3** to **3'** and formation of **4**, as well as the Hg poison experiments, would indicate that the metallic particles are indeed active and crucial part of the catalysis, supporting the hybrid homo-heterogeneous nature of the system.

Table 2. Experiments on filtrated reaction mixtures using indole as nucleophile.
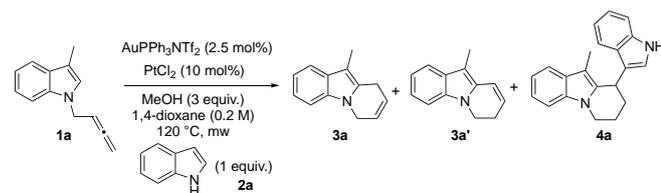
Exp A	3a	3a'	4a	Exp B	3a	3a'	4a
20 min	34%	27%	39%	**20 min**	34%	23%	43%
+ 35 min	0%	15%	85%	**+ 35 min after filtration**	22%	21%	57%
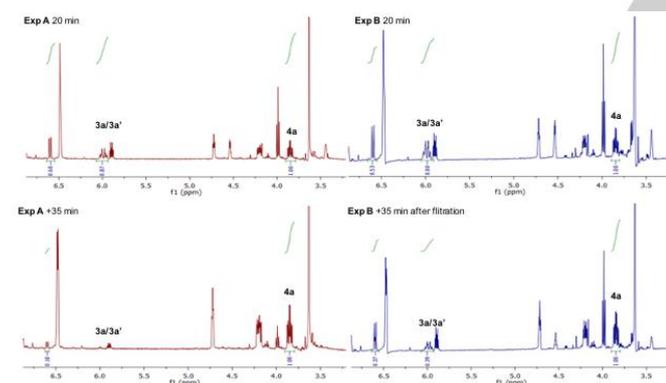
Figure 3. ^{1}H NMR spectra (500 MHz, CDCl$_3$) of experiments A and B with indole.

To gather more information about the components in the homogeneous solution we carried out the reaction under normal conditions at 120 °C for 1h under microwave irradiation. ICP-AES analysis of the reaction mixture after filtration through a 0.45 μ m, 0.2 μ m and 0.1 μ m porous size filter consecutively, was carried out to determine the amount of both metals present in solution after the reaction (see SI for details). Analysis showed that from 1250 mg/L of Pt, 343 mg/L of Au, and 106 mg/L of P used in the reaction, 692 mg/L of Pt, 4 mg/L of Au and 89 mg/L of P are detected in solution after the reaction has finished. No particles were observed after the digestion of the samples, indicating that in solution, the gold concentration has dropped dramatically. It is worth noting that the ratio Au:P is not 1:1, supporting some displacement of the phosphine from the gold sphere during the

reaction to form gold particles. These results indicate that although both metals are still present in solution at the end of the reaction, the majority of them are in the form of particles, reinforcing the hypothesis of hybrid homogeneous–heterogeneous catalysis.

In order to study the particles responsible for the catalytic activity in the heterogeneous phase, we carried out further experiments mixing all the reaction components in the absence of allene **1** or compound **3** starting materials. The mixture was stirred for 1h at 120 °C under mw irradiation. After that time, the brown dispersion turned into a black heterogeneous mixture (**Complex 1**), which was used without any further treatment in the catalytic reactions (*vide infra*).

To check the catalytic activity of both the precipitate and the soluble parts, after repeating the experiment using identical conditions, the reaction mixture was filtrated under vacuum using filter paper, yielding a black precipitate (**Complex 1F**) and a brown reddish solution (**Complex 1S**).

Complex 1 was analysed by ^{31}P NMR and HRMS. The black particles in **Complex 1F** were analysed by HRMS, SEM and ICP-AES (see SI for full details).

Analysis of the ^{31}P NMR spectra of the pre-formed **Complex 1** in the absence of starting materials **1** or **3** showed the intact Au-PPh$_3$ complex in a 1:1 ration with a similar signal to the one observed during catalysis at ~ 5 ppm, suggesting that (L)Pt-AuPPh$_3$ clusters could be formed in the absence of the substrates and are partially soluble (Figure 4). However, in the spectra of **Complex 1** we also observed a small signal at 15 ppm that could correspond to platinum phosphine complex, as also suggested by HRMS analysis of the solid filtered **Complex 1F**. It is worth noting that the same signals are not observed at room temperature, or when the gold complex is heated in the absence of platinum.
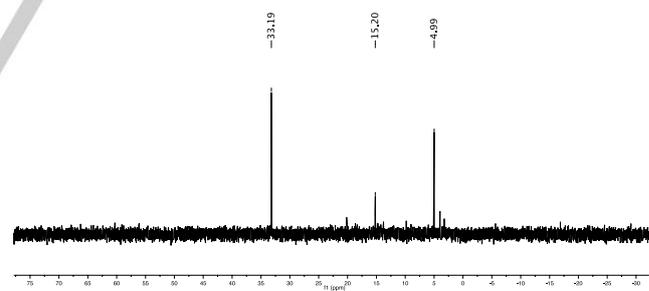
Figure 4. ^{31}P NMR of reaction mixture from AuPPh$_3$NTf$_2$ and PtCl$_2$ in dioxane, 120 °C, 1h under mw irradiation = **Complex 1**.

The only ^{31}P NMR signal observed at the end of the reaction using **Complex 1** as catalyst was at 14.2 ppm, which could correspond to a platinum phosphine complex. It is worth noting that this signal, already present in **Complex 1** before the reaction, was never observed when the reaction was monitored under normal conditions in the presence of the substrates (Figure 1). Besides, platinum phosphine complexes do not catalyse the reaction, which suggests that if some Pt-to-Au transmetallation to form R-Au and (L)PtPPh$_3$ (*vide supra*) is occurring in the formation of

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Complex 1, the platinum-phosphine complexes present in the particles are not the main catalytic species involved in the transformation from **3** to **4**.

ICP-MS of **Complex 1F** showed a ratio 4:1 of Pt:Au. Several images of the particles were taken (Figure 6) and EDS analysis also confirmed a ratio of 4:1 (similar to the initial ratio of metals in the reaction), but the distribution was not homogeneous (see SI for full details).
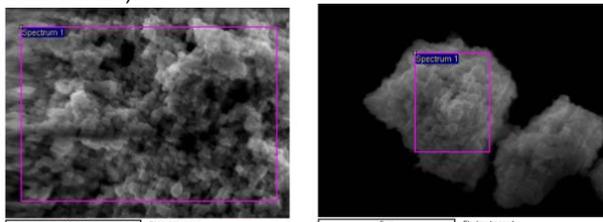
Figure 6. SEM images of particles from **Complex 1F**.

The catalytic activity of **Complex 1F** was tested in the reaction with the indolylallene **1** in the presence and absence of indole (Scheme 4). Interestingly, although some cyclisation, isomerisation and formation of **4** were observed, which suggested heterogeneous catalysis taking place, the conversion and yields are not as good as when the optimised conditions are used (compare with entry 1, Table 1). It is interesting to note that not even the first cyclisation took place with **Complex 1F** when no nucleophile was present in the reaction at room temperature, opposite to what was observed with gold(I) catalysis, which supports the need of the homogeneous catalytic species in the cyclisation step and the hybrid catalysis in the nucleophilic attack.
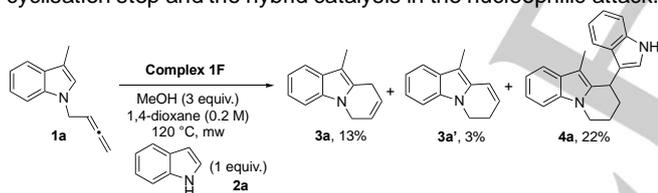
Scheme 4. Reaction of indolylallene **1a** with indole and **Complex 1F** as catalyst.

The activity of **Complex 1**, its soluble (**Complex 1S**) and insoluble (**Complex 1F**) parts in the reaction from compound **3a** with indole (**2a**), 5-CN-indole (**2b**) and pyrazole (**2c**) was diminished in all cases when compared with the reaction performed under optimised conditions (Table 3). Interestingly, in the reaction with the indole (**2a**) the solid catalysts (**complex 1** and **1F**) seem to be more reactive than the soluble part (**complex 1S**), but half as reactive as the reaction under the optimised conditions (Entries 1-4, Table 3). However, in the case of the less reactive 5-CN-indole (**2b**) and the *N*-nucleophile (pyrazole, **2c**) the reactivity of the soluble part (**complex 1S**) seems to be better than the filtrate (**complex 1F**), although still much lower than the reaction under optimised conditions (Entries 5-7 and 8-10, Table 3).

This again supports the need for both parts to achieve the best catalytic performance in the second catalytic cycle, but it also

shows that the catalytic species involved (in both phases) might be different depending on the nucleophile used, as previously suggested by the ^{31}P NMR experiments in the homogeneous phase. Further interaction of the nucleophiles with one or both metals could be taking place forming non-productive intermediates, reducing the concentration of active catalysts present.[27]

The reduce activity of **complexes 1S** and **1F** separately could also be related to a lower overall concentration of the metallic species in the reaction when compare with **complex 1**. This would also be in agreement with the DLS experiments in which the size distribution of the particles when **complex 1F** was used in the reaction was similar to the reaction under optimised conditions before heating when no conversion had occurred (compare traces E and A in Figure 2, *vide supra*).

Table 3. Reactivity of **Complexes 1** from cycle **3a**.
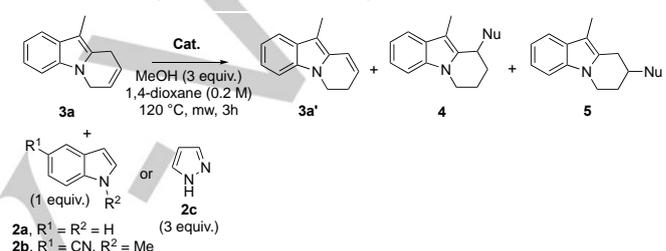
Entry	NuH	Cat.	3a recovered (%)	3a' (%)	4 (%)	5 (%)
1	2a	[Au]/[Pt]	-	-	4a, 95	-
2	2a	Complex 1	-	3	4a, 50	-
3	2a	Complex 1S	27	25	4a, 28	-
4	2a	Complex 1F	-	-	4a, 43	-
5	2b	[Au]/[Pt]	-	-	4b, 61	-
6	2b	Complex 1F	-	32	-	-
7	2b	Complex 1S	25	11	4b, 29	-
8	2c	[Au]/[Pt]	32	28	4c, 9	5c, 27
9	2c	Complex 1F	98	-	-	-
10[a]	2c	Complex 1S	47	32	4c, 1	5c, 6

[a] The experiment was stopped after 10 minutes heating at 120 °C under microwave irradiation because of a heating failure, possible due to a gold mirror-type precipitate covering the walls of the vessel. Although the short reaction time, comparison with experiment using **Complex 1F** (insoluble part) shows a remarkably higher reactivity of the soluble part of the catalytic mixture (**Complex 1S**).

Conclusions

Although the true homo- or heterogeneous nature of complex bimetallic catalytic systems is difficult to establish confidently, we present here a combination of experiments, that support that both

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types of catalysis are operating in the tandem cyclisation/C-X coupling reaction of heteroarylallenes with *C*- and *N*-based nucleophiles, as the first example of hybrid homo-heterogeneous catalysis in heterobimetallic systems.

^{31}P NMR experiments clearly show that the first catalytic cycle to form intermediate **3** occurs predominantly by fast gold(I)-homogeneous catalysis. This intermediate **3** enters a second catalytic cycle initially promoted by Pt, where Pt-Au interaction seems crucial to explain the enhance reactivity with poor *C*-nucleophiles and the novel reactivity with *N*-nucleophiles not observed so far. It is in this second catalytic cycle where the hybrid homo-heterogeneous catalysis seems to take place.

^{31}P NMR experiments and ICP-AES analysis support the formation of [Pt-AuPPh$_3$] complexes as the active components in the homogeneous phase, while Hg poison, filtration and DLS experiments suggest formation of heterogeneous Pt-Au particle clusters of different sizes in equilibrium. Although these clusters are moderately active catalysts in the isomerisation of **3** to **3'** and the nucleophilic attacks by *C*- and *N*-nucleophiles, they do not seem to promote the first cyclisation from **1** to **3**, emphasising the gold(I)-homogeneous catalysis in the first part of the cycle. The lower activity of the heterogeneous clusters in the second part of the cycle highlights the need of the solution state catalysts and the cooperation of both the homo- and heterogeneous parts for the efficient synthesis of multi heteroaromatic structures.

This unprecedented hybrid homo-heterogeneous catalysis in the Pt-Au system differs from reported examples in mono metallic systems where either the homogenous switches to heterogeneous catalysis depending on the reaction conditions, or there is initially a supported heterogeneous catalyst with a catalytically active leached metal involved in a release and capture mechanism in the homogenous phase.[15]

Whether the metallic particles are just a reservoir releasing bimetallic ions in solution when needed or are truly heterogeneous catalysts of the reaction reported here, it is clear that both parts (homo and heterogeneous) are essential and needed at the same time for a more efficient process and can be consider hybrid catalysis. This type of hybrid catalysis could be more commonly operating in monometallic systems involving platinum or other metals than initially thought. Therefore, revisiting some known reactions catalysed by mono or bimetallic systems formerly believed to proceed only by homogeneous catalysis and asking the question of are they truly homogeneous or do they have a heterogeneous component? might bring new surprises to old systems and open new avenues for research in our laboratory and others.

Experimental Section

General experimental procedure: An oven-dried microwave vessel was charged with [bis(trifluoromethanesulfonyl)imidate](PPh$_3$)gold(I) (2:1) toluene adduct (2.5 mol%), platinum chloride (10 mol%), and the corresponding nucleophile (1-3 equivalents). Then, the vessel was purged with a stream of argon for 5 minutes, and solution of the corresponding **1a** in dry 1,4-dioxane was added via syringe (1 equivalent of allene, 0.2 M in dioxane), followed by addition of dry methanol (3 equivalents). The mixture was placed in a microwave apparatus and heated at 120 °C for the

indicated time. Then, reaction mixture was filtered through a path of Celite using DCM as eluent, and after evaporation under reduced pressure the resulting mixture was purified by column chromatography using mixtures of Petroleum ether/DCM/Ethyl acetate.

Cycles 3a and 3a':[22] ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 – 7.42 (m, 2H, **3a + 3a'**), 7.21– 6.92 (m, 6H, **3a + 3a'**), 6.59 (dt, *J* = 9.9, 1.8 Hz, 1H, **3a'**), 6.04 – 5.93 (m, 2H, **3a**), 5.92 – 5.86 (m, 1H, **3a'**), 4.53 (ddd, *J* = 6.7, 4.4, 2.7 Hz, 2H, **3a**), 3.98 (t, *J* = 6.9 Hz, 2H, **3a'**), 3.47 – 3.41 (m, 2H, **3a**), 2.58 – 2.52 (m, 2H, **3a'**) 2.24 (s, 3H, **3a'**), 2.19 (s, 3H, **3a**). ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.74 (C-**9'**), 135.3 (C, **3a**), 131.6 (C, **3a'**), 129.2 (C, **3a**), 129.2 (C, **3a'**), 128.5 (C, **3a'**), 122.9 (CH, **3a'**), 122.1 (CH, **3a**), 121.9 (CH, **3a** or **3a'**), 120.5 (CH, **3a**), 120.3 (CH, **3a** or **3a'**), 119.2 (CH, **3a** or **3a'**), 118.9 (CH, **3a** or **3a'**), 118.8 (CH, **3a** or **3a'**), 118.5 (CH, **3a'**), 117.8 (CH, **3a** or **3a'**), 108.5 (CH, **3a + 3a'**), 108.4 (CH, **3a + 3a'**), 107.5 (C, **3a'**), 104.5 (C, **3a**) 41.8 (CH$_2$, **3a**), 39.8 (CH$_2$, **3a'**), 24.4 (CH$_2$, **3a**), 22.8 (CH$_2$, **3a**), 8.3 (CH$_3$, **3a**), 8.1 (CH$_3$, **3a'**).

Product 4a:[22] ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.23 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 6.52 (s, 1H), 4.81 (t, *J* = 4.3 Hz, 1H), 4.34 – 4.25 (m, 1H), 3.94 (td, *J* = 11.1, 4.8 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.24 – 2.15 (m, 1H), 2.15 – 2.06 (m, 1H), 2.03 (s, 3H), 1.97 – 1.88 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.70 (C), 135.88 (C), 134.87 (C), 128.74 (C), 126.22 (C), 123.28 (CH), 121.94 (CH), 120.29 (CH, C), 119.34 (CH), 118.98 (CH), 118.78 (C), 118.05 (CH), 111.36 (CH), 108.65 (CH), 105.96 (C), 42.58 (CH$_2$), 30.42 (CH), 28.17 (CH$_2$), 19.56 (CH$_2$), 8.36 (CH, CH$_3$). M.P. 151-158 °C.

Product 4b:[14] ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.99 (s, 1H,), 7.56 (m, *J* = 7.8 Hz, 1H), 7.47 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.34 (m, 2H,), 7.23 (t, *J* = 7.1 Hz,1H), 7.15 (t, *J* = 7.1 Hz, 1H), 6.50 (s, 1H), 4.77 (m, 1H), 4.29 (m, CH$_2$), 3.90 (m, 1H), 3.67 (s, 3H), 2.51 (m, 2H), 2.00 (s, 3H), 1.97 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ: 138.9 (C), 135.9 (C), 133.9 (C), 130.3 (CH), 128.6 (C), 126.3 (C), 124.7 (CH), 124.5 (CH), 120.9 (C), 120.6 (CH), 119.2 (CH), 118.6 (C), 118.1 (CH), 110.3 (CH), 108.8 (CH), 106.1 (C), 101.9 (CN), 42.5 (CH$_2$), 32.9 (CH), 30.0 (Me), 28.3 (CH$_2$), 19.4 (CH$_2$), 8.4 (Me). HRMS (FTMS + p NSI) ((DCM) / MeOH + NH$_4$OAc): Calc. for C$_{23}$H$_{22}$N$_3$ [M+H]$^+$ 340.1814: Found: 340.1810.

Products 4c + 5c:[14] ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.61 (br s, 1H, **5c + 4c**), 7.56 (d, *J* = 7.7 Hz, 1H, **5c + 4c**), 7.45 (d, *J* = 2.4 Hz, 1H, **5c**), 7.35 (d, *J* = 8.2 Hz, 1H, **4c**), 7.27 (m,1H, **5c + 4c**), 7.18 (m, 2H, **5c + 4c**), 7.02 (br s, 1H, **4c**), 6.29 (br s, 1H, **5c**), 6.16 (br s, 1H, **4c**), 5.88 (t, *J* = 4.0 Hz,1H, **4c**), 4.76 (m, 1H, **5c**), 4.31 (m, 1H, **4c**), 4.20 (m, 1H, **5c**), 4.04 (m, 1H, **5c**), 3.91 (1H, m, **4c**), 3.51 (m, 1H, **5c**), 3.34 (m, 1H, **5c**), 2.62 (m, 3H, **5c** (2H) + **4c** (1H)), 2.20 (m, 1H, **4c**), 2.28 (s, 3H, **5c**), 2.09 (s, 3H, **4c**), 1.97 (m, 2H, **4c**). ^{13}C NMR (126 MHz, CDCl$_3$) δ: 139.6 (CH, **4c**), 139.4 (CH, **5c**), 136.3 (C, **4c**), 135.9 (C, **4c**), 130.0 (C, **5c**), 128.9 (C, **5c**), 128.8 (CH, **4c**), 128.5 (C, **4c**), 128.1 (C, **4c**), 127.3 (CH, **5c**), 122.1 (CH, **4c**), 120.9 (CH, **5c**), 119.6 (CH, **4c**), 119.4 (CH, **5c**), 119.0 (CH, **4c**), 118.2 (CH, **5c**), 109.9 (C, **4c**), 109.2 (CH, **4c**), 108.7 (CH, **5c**), 106.3 (C, **5c**), 105.5 (CH, **5c**), 104.8 (CH, **4c**), 56.0 (CH, **5c**), 53.9 (CH, **4c**), 42.3 (CH$_2$, **4c**), 40.5 (CH$_2$, **5c**), 30.0 (CH$_2$, **5c**), 29.3 (CH$_2$, **5c**), 28.9 (CH$_2$, **4c**), 18.7 (CH$_2$, **4c**), 8.2 (CH$_3$, **5c**), 7.9 (CH$_3$, **4c**). HRMS (FTMS + p NSI) ((DCM) / MeOH + NH$_4$OAc): Calc. for C$_{16}$H$_{18}$N$_3$ [M+H]$^+$: 252.1495. Found: 252.1495.

Experiments in the presence of Hg: All the experiments were carried out following the general reported procedure, adding the indicated amount of Hg (0) to the reaction mixture. Yields were estimated by NMR using dimethyl sulfone as internal reference.

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Reactivity of complex 1F from indolyl allene 1a: An oven dried vessel was charged with **Complex 1F** (6 mg) and indole (9 mg, 0.08 mmol) and purged with Ar for 5 minutes. Then, allene **1a** (15 mg, 0.08 mmol) was added in dioxane (1 mL) via syringe, followed by MeOH (9 mL). The mixture was heated at 120 °C for 3h. After that time, the reaction mixture was filtrated trough a celite path and washed with DCM. After evaporation of the solvent, the crude was analysed by NMR. NMR yields calculated using dimethylsulfone as internal reference.

Reactivity of complexes 1 from cyclic alkene 3a: All experiments were carried out using starting material **3a** (15 mg, 0.08 mmol), CN-indole (13 mg, 0.08mmol) or pyrazole (16 mg, 0.24 mmol), MeOH (9 mL) and **complexes 1** (6 mg) as catalyst, in dioxane (1 mL), stirring for 3h at 120 °C under mw irradiation. NMR yields calculated using dimethylsulfone as internal reference.

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Keywords: • hybrid catalysis • homogeneous • heterogeneous • platinum • gold

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We report here our efforts towards understanding the catalytic species involved in a novel Pt/Au heterobimetallic system capable of catalyse the tandem cyclisation/C-X coupling reaction of heteroarylallenes with nucleophiles. Homogeneous Au-catalysis is first involved to generate an intermediate that enters the second catalytic cycle where hybrid homogeneous-heterogeneous catalysis by [Pt-Au] clusters seems to be responsible for the high efficiency of the process.

*José Miguel Alonso and María Paz Muñoz**

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Evidences of hybrid homo-heterogeneous catalysis in a Pt/Au heterobimetallic system