

Formal Gold to Gold Transmetalation of an Alkynyl Group Mediated by Palladium: A Bisalkynyl Gold Complex as a Ligand to Palladium

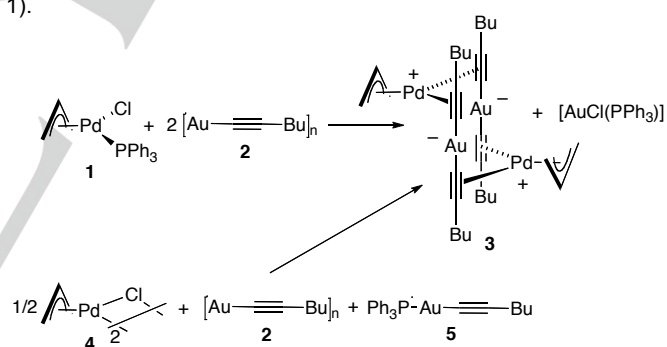
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Abstract: The reaction of $[\text{Au}(\text{C}\equiv\text{C}n\text{Bu})]_n$ with $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}(\text{PPh}_3)]$ results in a ligand and alkynyl rearrangement, and leads to the heterometallic complex $[\text{Pd}(\eta^3\text{-allyl})\{\text{Au}(\text{C}\equiv\text{C}n\text{Bu})_2\}]_2$ (**3**) with an unprecedented bridging bisalkynyl gold ligand coordinated to palladium. This is a formal gold to gold transmetalation that occurs through reversible alkynyl transmetalations between gold and palladium.

The exchange of organic groups between metals is at the core of many organometallic synthetic procedures and is a key step in catalytic C-C coupling reactions. Recently, the use of two transition metal complexes in catalytic reactions, the so called bimetallic catalysis, is opening new avenues for the synthesis of molecules.^[1-4] These processes rely on the efficient exchange of organic fragments between metal co-catalysts along with a fast and efficient final coupling step that drives the reaction to completion. Among the first examples, the coupling of alkynyl groups has used the cooperative role of two metals, generally a group 11 metal and palladium as, for example, in the Sonogashira reaction.^[5-7] The transmetalation of an alkynyl group between palladium and copper, or palladium and silver is a reversible reaction and this has been shown experimentally.^[8,9] After the transfer of the alkynyl group to palladium, the group 11 metal may remain coordinated to the Pd-alkynyl groups forming stable bimetallic intermediates.^[9] Both features are important since they influence the formation of the $[\text{Pd}(\text{alkynyl})\text{RL}_2]$ intermediate that eventually give, by reductive elimination, the coupling alkynyl-R derivative. We have previously studied the transmetalation reaction between copper or silver alkynyls and palladium allylic derivatives. The reluctance of the allylic fragment to undergo reductive elimination in a $[\text{Pd}(\text{alkynyl})(\text{allyl})\text{L}_2]$ compound hampers the otherwise preferred coupling process and allows the detection of bimetallic intermediate complexes.^[9] We report here the reaction of gold alkynyls with palladium allylic derivatives which turns out to be a complex process that involves multiple transmetalations between Au and Pd leading to a formal Au to Au alkynyl transfer. The impulse experienced by gold catalysis makes this metal an attractive candidate for the design of bimetallic catalysts,^[2,10] and this has been realized both in alkynyl coupling as in the gold cocatalyzed version of the Sonogashira reaction,^[11] or other Pd-

Au catalyzed reactions.^[12-17] In this context, it is important to gather information about the transmetalation processes between gold and palladium and the possible rearrangement events that can take place.

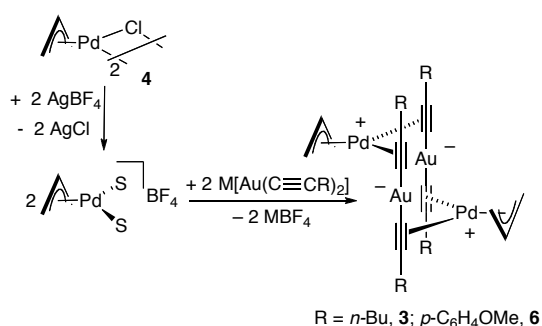
The reaction of $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}(\text{PPh}_3)]$ (**1**) with a twofold molar amount of $[\text{Au}(\text{C}\equiv\text{C}n\text{Bu})]_n$ (**2**) leads to the heterometallic Pd-Au complex **3** and $[\text{AuCl}(\text{PPh}_3)]$ as the only byproduct (Scheme 1). Complex **3** is a zwitterionic species that shows cationic palladium allyl units coordinated to anionic bridging $[\text{Au}(\text{C}\equiv\text{C}n\text{Bu})_2]^-$ fragments. The formation of **3** results from the reorganization of both the neutral ligands and the alkynyl fragments between metals. When the reaction is carried out using an equimolar amount of **1** and **2**, the reaction proceeds in the same fashion but only half of the starting **1** is transformed. A different combination of reagents having the same total number of atoms can also be used, i.e. a mixture of the dimeric allylic palladium complex **4** and the gold derivatives **2** and **5** (Scheme 1).



Scheme 1. Reactions leading to the formation of complex **3**.

The synthetic routes depicted in Scheme 1 are not convenient for the isolation of **3** since the separation of the gold byproduct $[\text{AuCl}(\text{PPh}_3)]$ from **3** is difficult. Besides, **3** decomposes in solution with a half life of about 1 h at room temperature. For this reason, a different reaction route was devised that involves the use of $[\text{Au}(\text{C}\equiv\text{C}R)_2]^-$ as reagent (either generated in situ for $R = n\text{Bu}$ or previously prepared for $R = \text{C}_6\text{H}_4\text{OMe-}p$) and its coordination to a preformed cationic palladium allyl (Scheme 2). In this way **3** ($R = n\text{Bu}$) was isolated and **6** ($R = \text{C}_6\text{H}_4\text{OMe-}p$) was detected. They were characterized by NMR spectroscopy, where both the ^1H and ^{13}C NMR spectra are quite simple reflecting the high symmetry of the complexes. A characteristic and revealing ABX_2 system is observed for the diastereotopic methylene hydrogens of the $\text{Au}-\text{C}\equiv\text{CCH}_2-\text{CH}_2-\text{Et}$ groups of complex **3** (see Supporting information).

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Scheme 2. Alternative synthesis of complexes **3** and **6**.

The molecular structure of **3**, determined by X-ray crystal diffraction at 120 K, shows a centrosymmetric derivative with two allylpalladium fragments, in a mutual trans arrangement, bridged by two [Au(C≡C*n*Bu)₂][−] complexes (Figure 1).¹⁸ The Au–C(alkynyl) bond lengths are in accordance with the literature data for other gold alkynyls.^[19,20] The C≡C bond also conforms to the values reported in the literature and it is not very sensitive to coordination to another metal.¹⁹ The bond distances and angles of the allylic fragments as well as the Pd–C(allyl) distances are within the range found for other palladium allyl complexes with ligands of moderate trans influence.^[21,22] The value of the Au–Au distance (3.255(10) Å) falls in the range found for aurophilic contacts.^[23] The Au–Pd distance (3.231(10) Å) is shorter than the sum of van der Waals radii (3.29 Å) and could indicate weak metalophilic interactions. The solid state structure is kept in solution and, besides the ¹H NMR pattern mentioned above, ¹H DOSY experiments give a hydrodynamic radius (*R*_H = 5.11 Å at 293 K) that is consistent with the radius determined from the X-ray molecular structure (*R*_{X-ray} = 4.86 Å).

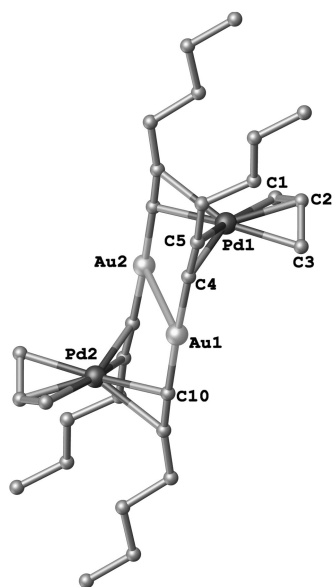


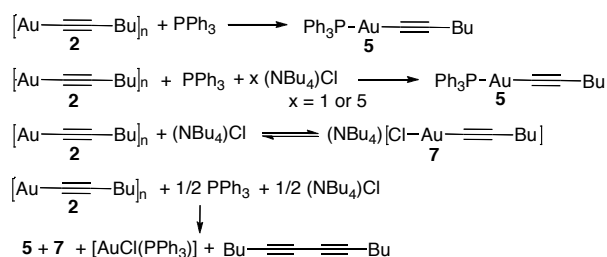
Figure 1. Molecular structure of **3**. Selected interatomic distances [Å] and angles [°]: Pd1–C1, 2.141(14); Pd1–C2, 2.115(13); Pd1–C3, 2.114(11); Pd1–C4, 2.270(13); Pd1–C5, 2.390(12); Au1–Au2, 3.255(10); Au1–C4, 2.005(12); Au1–

C10, 1.980(12); C4–C5, 1.202(16); Au1–C4–C5, 177.7(11); C4–Au1–C10, 177.2(5).

The structure of complexes **3** and **6** is unprecedented. Heterometallic platinum-gold alkynyl complexes are known, but most examples show the η² coordination of the triple bond of a platinum–alkynyl fragment to a gold atom. In some cases these complexes result from the reaction of a gold alkynyl complex with a platinum precursor so Au to Pt alkynyl transmetalation precedes the formation of the complex.^[24] Very few examples of [Au(C≡CR)₂][−] fragments acting as ligands have been reported. Most of them are heteronuclear alkynyl complexes combining several group 11 metals.^[25,26] As for palladium allyl fragments bound to two metal alkynyls, only a few examples of platinum alkynyls acting as ligands have been reported.^[22]

The formation of **3** in Scheme 1 involves an effective rearrangement of ligands and organometallic fragments. Complex **3** seems to act as a thermodynamic sink aided by the formation of the stable [AuClPPh₃]. A soluble gold alkynyl is also required since, the insoluble [Au(C≡CR)_n] (R = aryl) derivatives react too slowly to reach sufficient concentration of the bimetallic unstable complex. We carried out several experiments to find out how this rearrangement occurs.

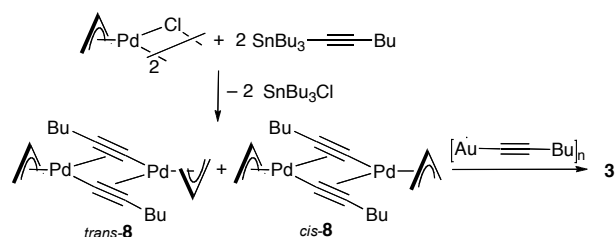
First of all, we analyzed the reactions of [Au(C≡C*n*Bu)_n] in the presence of the ligands provided by palladium in Scheme 1, i.e. PPh₃ and chloride. The results are collected in Scheme 3. The alkynyl gold complex **2** reacts with PPh₃ to give **5** and this occurs efficiently regardless the amount of chloride present in solution. The anionic complex **7** is the product of the reaction of **2** with chloride with an equilibrium constant *K*_(298 K) = [7]/[2][Cl[−]] = 32.6 ± 1.2, much lower than the equilibrium constant for the coordination of PPh₃ which should be *K* ≥ 10⁴, since both **2** and PPh₃ react completely, as shown by NMR. When both ligands are present in substoichiometric amounts, both **5** and **7** are formed along with small amounts of the dialkyne and [AuCl(PPh₃)] (5% and 10% mol respectively). No experiment showed the formation of [Au(C≡CR)₂][−] species.



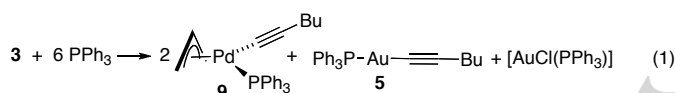
Scheme 3. Reactions of **2** with PPh₃ and chloride.

According to these results, palladium must play a direct role in the rearrangement, more important than a mere ligand source, and we believe that the formal gold to gold alkynyl transfer occurs through palladium. This is supported by several independent experiments that show that gold to palladium alkynyl transmetalation is reversible and can lead to complex **3**. First, we synthesized the new allyl alkynyl palladium complex **8**

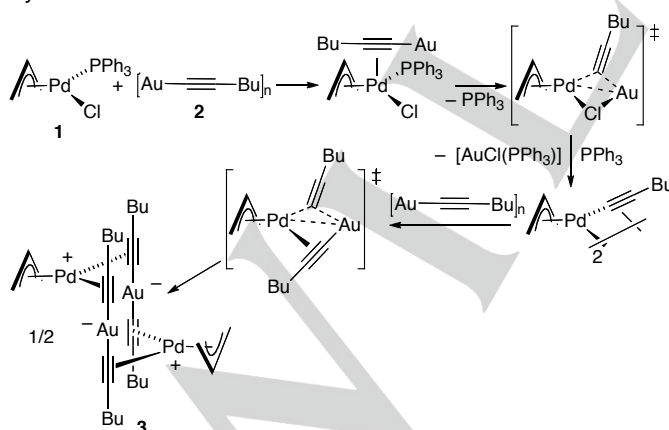
by the reaction of the allylic dimeric complex **4** and a slight excess of $\text{SnBu}_3(\text{C}\equiv\text{C}n\text{Bu})$ at 243 K. Consistent with its dimeric nature **8** is a mixture of cis and trans isomers, in a 1.2:1 ratio, as a result of the two different arrangements of both allylic moieties. The addition of an excess of $[\text{Au}(\text{C}\equiv\text{C}n\text{Bu})]_n$ to a solution of **8** at 243 K, produces the clean formation of the bimetallic complex **3** (Scheme 4). Thus, the formation of the bisalkynyl gold species $[\text{Au}(\text{C}\equiv\text{C}R)_2]^-$ occurs by transmetalation of the alkynyl moiety from palladium to gold. The reverse transmetalation, from gold to palladium, occurs by the addition of an excess of PPh_3 on complex **3**, which leads to the formation of the monoalkynyl allyl palladium complex **9**,^[9] and gold derivatives **5** and $[\text{AuCl}(\text{PPh}_3)]$ (Eq. 1).



Scheme 4. Transmetalation from Pd (**8**) to Au to form complex **3**.



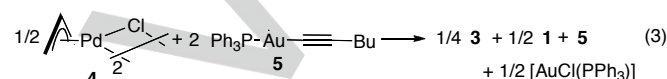
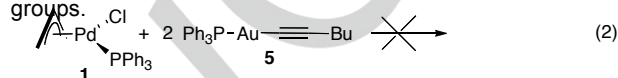
Thus, the transmetalation of the alkynyl group from gold to palladium is a reversible reaction that occurs in either direction depending on the presence of other ligands that influence the thermodynamics of the process. This has been observed before for the transmetalation of methyl and perfluorophenyl groups.^[27] In this case the solubility of $[\text{Au}(\text{C}\equiv\text{C}n\text{Bu})]_n$ and the formation of the stable $[\text{AuCl}(\text{PPh}_3)]$, which takes up all the ligands coordinated to palladium, drives the equilibrium to the formation and coordination of $[\text{Au}(\text{C}\equiv\text{C}R)_2]^-$. The above mentioned experiments support the route represented in Scheme 5 for the formation of **3** by reaction of **1** and **2** in Scheme 1.



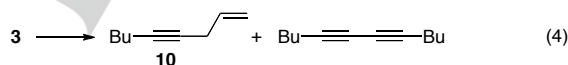
Scheme 5. Plausible route for the formation of **3**.

The substitution of the PPh_3 by a gold alkynyl must be the first step of the reaction. This may be an actual decoordination,

as depicted in Scheme 5, or a concerted process that leads to PPh_3 coordination to gold, and takes place along with the transmetalation of the alkynyl group. In any case, available coordination sites are needed either on palladium or in the gold center, so the later can trap the PPh_3 . The presence of PPh_3 in both metal centers is detrimental for the alkynyl transfer as shown by the lack of reaction between complexes **1** and **5** in Eq. 2. On the other hand, the chloro-bridged palladium complex **4** does react with **5** to give **3** albeit in low yield since the PPh_3 present inhibits further reaction (Eq. 3). It is noteworthy that no shift of the allyl ligand from an η^3 to a σ coordination seems to occur. The transmetalation transition states depicted in Scheme 5 are analogous to those proposed by Espinet et al.^[27b] and Hashmi et al.^[28] for the Au-Pd transmetalation of aryl and vinyl groups.



The decomposition of complex **3** leads to a mixture of the allyl-alkynyl coupling product **10** and the dialkyne in a 2:1 molar ratio (Eq. 4). The formation of **10** is a result of reductive elimination on a $[\text{Pd}(\text{alkynyl})(\text{allyl})\text{L}_2]$ intermediate, so the presence of this compound shows again that the transmetalation from the bisalkynyl gold moiety to palladium takes place.



In conclusion, a formal gold to gold transfer of an alkynyl fragment occurs by sequential gold to palladium and palladium to gold transmetalations. Thus, palladium acts as a mediator in the rearrangement of the alkynyl gold complex. It is interesting to note that gold shows a distinct behaviour when compared to the other group 11 members. In the latter cases alkynyl transmetalation to palladium takes place when $[\text{M}(\text{alkynyl})]_n$ ($\text{M} = \text{Cu}, \text{Ag}$) are reacted with **1**, and M remains η^2 -coordinated to the Pd-alkynyl fragment leading to heterometallic complexes $[\{\text{Pd}(\eta^3\text{-allyl})(\text{alkynyl})\text{L}\}_2\text{CuCl}]_2$ and $[\{\text{Pd}(\eta^3\text{-allyl})(\text{alkynyl})\text{L}\}_2\text{AgCl}]$ where σ -alkynyl-Pd and η^2 -alkynyl-M coordination modes can be found. In the analogous reaction gold forms no complex of that type but acts as a ligand scavenger, forming $[\text{AuCl}(\text{PPh}_3)]$, and undergo more facile transmetalation processes showing a preference for the σ -alkynyl-Au coordination mode, present in complexes **3** and **6**, leaving palladium coordinated in a η^2 -alkynyl-Pd fashion.

Experimental Section

Synthesis of **3**.

Method A: A 5 mm NMR tube was charged with $[\text{Pd}(\eta^3\text{-C}_6\text{H}_5)\text{Cl}(\text{PPh}_3)]$ (0.024 g, 0.054 mmol) and $[\text{Au}(\text{C}\equiv\text{C}n\text{Bu})]_n$ (0.030 g, 0.108 mmol). Then, CDCl_3 (0.6 mL) was added under nitrogen at room temperature. A yellow solution was obtained and it slowly turned dark brown. After 15 minutes,

the solution was cooled at 243 K and then characterized by NMR. Equimolar amounts of **3** and $[\text{AuCl}(\text{PPh}_3)]^{29}$ were formed in solution.

Method B: A solution of *n*-butyl lithium (0.49 mL, 1.6 M in hexane, 0.79 mmol) in dry THF (5 mL) was added dropwise under nitrogen to a stirred solution of 1-hexyne (0.091 mL, 0.79 mmol) in dry THF (5 mL) at $-40\text{ }^\circ\text{C}$. After 90 min at this temperature, $[\text{Au}(\text{C}\equiv\text{C}n\text{Bu})]_n$ (0.22 g, 0.79 mmol) was added under nitrogen and the solution stirred at $-40\text{ }^\circ\text{C}$ for 3 hours. In other Schlenk tube $[\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)]_2$ (144.5 mg, 0.395 mmol) was added to a solution of AgBF_4 (153.8 mg, 0.79 mmol) in dry THF (5 mL). The mixture was stirred for 15 min protected from light and the yellow solution was removed with a syringe and added to the first solution with the preformed gold derivative at $-40\text{ }^\circ\text{C}$. A light orange solution was obtained and after 30 min the solvent was removed in vacuum at $-20\text{ }^\circ\text{C}$. The brownish residue was extracted with CH_2Cl_2 (3 x 5 mL), filtered under nitrogen and then, the filtrate evaporated to dryness. The light brown residue was triturated with dry cold hexane (5 mL) in a bath at $-80\text{ }^\circ\text{C}$. The resulting solid was filtered, and dried in vacuo (227 mg; 56.7% yield). This complex was stored at $-30\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, δ , CDCl_3 , 243 K): 5.62 (m, 2H, H^2 allyl), 4.12 (d, $J = 7.1\text{ Hz}$, 4H; H^1_{syn} , H^3_{syn} allyl), 3.41 (d, $J = 12.5\text{ Hz}$, 4H; H^1_{anti} , H^3_{anti} allyl), 2.26, 2.15 (ABX₂ system, $J_{\text{AB}} = 16.4$, $J_{\text{AX}} = J_{\text{BX}} = 7.7\text{ Hz}$, 8H, $\text{C}\equiv\text{C}-\text{CH}_2$), 1.48 (m, 8H; $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.33 (m, 8H; CH_2-CH_3), 0.83 (t, $J = 7.3\text{ Hz}$, 12H; CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, δ , CDCl_3): 112.01 (s, C^2 allyl), 100.8 (s, $\text{Au}-\text{C}\equiv\text{C}$), 90.8 (s, $\text{Au}-\text{C}\equiv\text{C}$), 67.1 (s, C^1 , C^3 allyl), 31.85 (s, $\text{CH}_2\text{CH}_2\text{CH}_3$), 22.15 (s, CH_2CH_3), 21.84 (s, $\text{C}\equiv\text{CCH}_2$), 13.97 (s, CH_3). MS (ESI-TOF, dichloromethane, m/z): 1037.09 ($\text{M}+\text{Na}^+$) (Na^+ comes from HCOONa used for calibration). The hydrodynamic radius determined by ^1H DOSY is $R_{\text{H}} = 5.11\text{ \AA}$ (293 K).

Acknowledgements

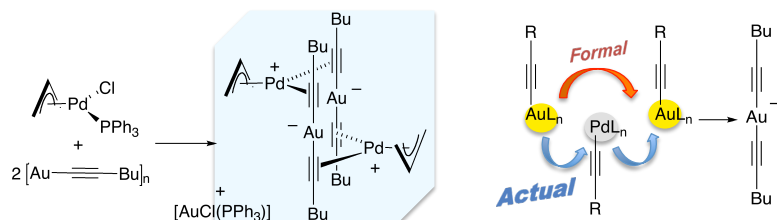
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Keywords: Palladium • gold • transmetalation • bimetallic • ligand exchange

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COMMUNICATION



Back and forth! Direct gold to palladium and reverse palladium to gold alkynyl transmetalations effectively produce a deceptively simple gold to gold transfer. The resulting bisalkynyl gold complexes act as bridging ligands to palladium atoms in an unprecedented structure motive (see scheme).

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Formal Gold to Gold Transmetalation of an Alkynyl Group Mediated by Palladium: A Bisalkynyl Gold Complex as a Ligand to Palladium