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Gold Redox Catalytic Cycles for the Oxidative Coupling of Alkynes

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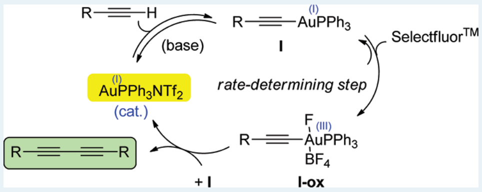
S Supporting Information

ABSTRACT: Au(I)/Au(III) catalytic cycles are catalytically competent to perform the oxidative coupling of alkynes in the homogeneous phase at room temperature and without any protecting atmosphere. Selectfluor as oxidant, wet acetonitrile as solvent, and sodium carbonate as base are the reagents of choice. Both aromatic and alkyl alkynes can be coupled, and mechanistic studies reveal that at least two gold species having different oxidation states are implicated in the key step of the coupling.



KEYWORDS: *gold catalysis, oxidative coupling of alkynes, redox chemistry, diynes, voltammetry*

■ INTRODUCTION

Gold, traditionally considered as the most inert of the noble metals, has emerged in the past years as a powerful catalyst in organic synthesis when used at the atomic level.[1−3] Paradoxically, part of this success is based on its inertness toward ambient conditions, since the high redox potential Au(I)/Au(III) prevents undesired changes in the oxidation state along the catalytic events.[4,5] However, it has been shown recently that the redox pathway can be reached with potent oxidizing agents such as selectfluor or peracids in the homogeneous phase, triggering redox gold catalytic cycles that ultimately leads to unexpected new reactions.[6−15]

Metal-catalyzed C−C coupling reactions are of great interest in organic synthesis. One representative example is the oxidative homocoupling of alkynes: Glaser discovered the copper-mediated oxidative homocoupling of alkynes in 1869, and, since then, a plethora of metal-based catalytic and non catalytic systems has been reported for the construction of di- and polyacetylenic compounds.[16,17] These products are an unique class of rigid, electron-rich compounds that play different roles in biological systems, and in industry.[18−21] Although other metals have been explored as possible catalysts, including palladium, cobalt, and titanium, copper is still the most active.[17] However, the use of high amounts of copper(II) salts (usually copper acetate) in dry pyridine (Eglinton procedure) to reoxidize the Cu(I) formed after the first catalytic cycle, or the use of additional amines as ligands for copper (Hay procedure), makes those systems less attractive from a practical and environmental point of view.

The superiority of copper lies in two facts: its ability to form acetylenic complexes and the accessibility to two different redox states, I and II, under reaction conditions. Although the first chemical property is common to the other two metals of group 11, silver and gold, the accessibility to higher oxidation states is restricted for those, and, to our knowledge, no examples of catalytic systems based on silver or gold for the homocoupling of alkynes have been reported. However, we envisaged that the in situ oxidation of Au(I) to Au(III) by F^+ in homogeneous systems could facilitate the C−C coupling of alkynes under gold-catalyzed conditions. Indeed, 1,4-diphenylbutadiyne **4** (Scheme 1, A) has been found as byproduct in the gold-catalyzed cascade cyclization-oxidative alkynylation of allenoates with selectfluor as oxidant[8] and, in addition, small amounts of **4** were also systematically found during the Sonogashira reaction of **1** with iodobenzene **5** when Au(III) complexes or gold-supported nanoparticles were used as catalysts (Scheme 1, B).[22−27]

■ RESULTS AND DISCUSSION

With these precedents in hand, we decided to investigate the oxidative homocoupling of alkynes under gold-catalyzed conditions in homogeneous phase. The homocoupling of phenylacetylene **1** was chosen as a test reaction, and the results obtained under different experimental conditions are shown in the Supporting Information, Table S1. The homocoupling does not proceed at all if no oxidant or base is present in the reaction medium (entries 1−10). However, if selectfluor[28−30] is added in stoichiometric amounts, small amounts of product **4** are observed for different gold catalysts (entries 11−18), $AuPPh_3NTf_2$ being the most active (40% after 20 h, entry 19). Addition of water (entry 20), other oxidizing agents milder than selectfluor,[31] and different solvents (entries 25−28) are detrimental for the reaction (entries 21−23), but a moderate increase is obtained when nondried acetonitrile is used as solvent. Full conversion of **1** was observed, which suggests that **1** and/or **4** are unstable under the high acidic conditions of the reaction medium. This problem is circumvented by the addition of K_3PO_4 (entry 29). Other bases were tried and, in general, those containing Na^+

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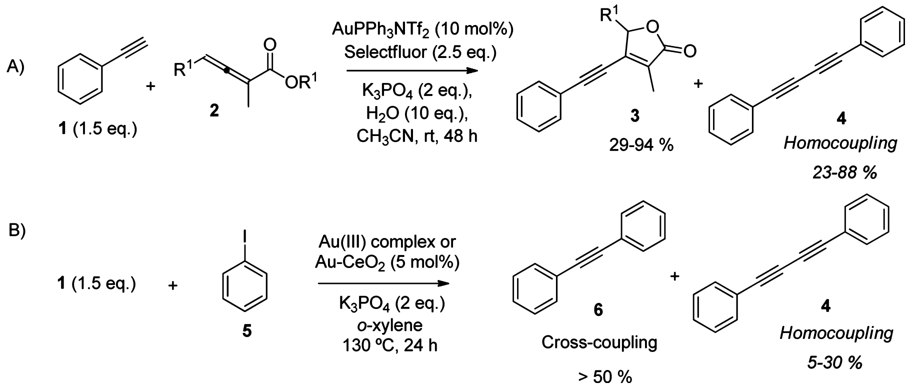
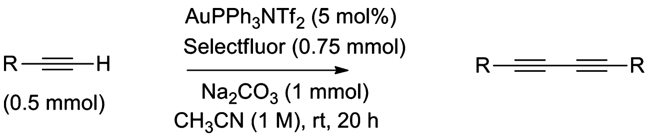
Scheme 1. Examples of Oxidative Homocoupling of Phenylacetylene 1 as Side Reaction in Gold-Catalyzed Processes



performed better than with K$^+$ or Cs$^+$ (compare entries 30−32 and 33−34), while weaker bases gave again uncompleted mass balances (entries 33−37) and an organic base is completely inactive (entry 38). Two other fluorine oxidizing agents instead of selectfluor and different gold phosphine complexes were tested under these basic conditions (entries 39−40, and 41−43 and 46−48, respectively) but little or no product was obtained. Silver triflimide (entry 44) and a gold carbene complex (entry 49) are not active either. However, AuPPh$_3$Cl was as good a catalyst as AuPPh$_3$NTf$_2$ under basic conditions (compare entries 45 and 50) and the use of BF$_4^-$ as counteranion gave also a good yield of **4** (entry 51). In summary, PPh$_3$-Au(I) complexes are active and selective catalysts for the oxidative homocoupling of **1** with selectfluor as oxidant and Na$_2$CO$_3$ as base in nondried acetonitrile.

Once the reaction conditions were selected, the scope of the reaction was examined (Scheme 2). Good yields are generally obtained for both aromatic (entries 1−8) and alkyl alkynes (entries 9−10) and experiments at 0.5 and 2 mmol scale gave similar results.

Scheme 2. Gold-Catalyzed Homocoupling of Aromatic Alkynes under Homogeneous Conditions



Run	R	Yield (%)[a]
1	Ph	80
2	*o*-Anisole	>99[b]
3	*m*-Anisole	>99[b]
4	*p*-Anisole	>99[b]
5	*o*-Tolyl	76 (64)[c]
6	*m*-Tolyl	47
7	o-Chlorophenyl	78 (59)[c]
8	o-Bromophenyl	75
9	butyl	>99[b]
10	hexyl	>99[b]

[a] Isolated yield. [b] GC yield. [c] 2 mmol scale.

Once the generality of the catalytic method was confirmed and to have more information about the reaction pathway, we decided to prepare and compare the reactivity of the gold-tolylacetylide complex **7** and the corresponding free alkyne *o*-tolylphenylacetylene **8** in separated experiments, monitoring the reaction by in situ ^{1}H and ^{31}P NMR spectroscopy (Figure 1).

It was observed that the rate of formation of the oxidative homocoupling product **9** is higher when starting from the σ-gold(I) complex **7** than from the free alkyne **8** (compare curves C and D in Figure 1a) and that these reaction rates correlate with the conversion of selectfluor (compare curves A and B in Figure 2a). Interestingly, the conversion of Au(I)-phenylacetylide complex **7** is twice the conversion of selectfluor (compare curves C and A) and this indicates that *only one oxidative event [Au(I)→Au(III)] occurs per coupling of each two molecules of* **7**. To further check this observation, a second experiment using half the amount of selectfluor was carried out (Figure 2b). As it can be seen, a similar high yield of **9** is obtained when using 1 or 0.5 equiv of selectfluor (compare curves A and B in Figure 2b) and, moreover, the homocoupling completely stops after the oxidation of the Au(I) complex **7** is >40% (see curve C in Figure 2b). This indicates that further oxidation of the Au(I)-acetylide **7** to its corresponding oxidized form Au(III) is detrimental for the reaction, and we infer that both oxidation states (I) and (III) must be present for the homocoupling to occur. In a separate set of experiments, increasing amounts of selectfluor were added to the catalytic system using **8** as substrate. Then, when plotting the final yield of **9** as a function of the total selectfluor added, it can be seen that one mol of **9** *per* mol of selectfluor added is systematically obtained (Supporting Information, Figure S1). These results corroborate that one oxidation *per* homocoupling event occurs and, in principle, may discard the formation of the product on a monometallic Au(III) site by reductive elimination. This would nicely engage with the accepted bimetallic transition state for the copper-catalyzed Glaser coupling.[16,17] However, the possibility that one gold(I) center could be oxidized to gold(III), and, then, a transmetalation from another gold(I) could occur, followed by a monometallic Au(III) reductive elimination, cannot be excluded. To shed more light into the mechanism, a new experiment was designed (Scheme 3). According to the reaction pathway proposed, if phenylacetylene **1** is added to a catalytic system containing Au(I)-acetylide **7** as only substrate, the cross-coupling of alkynes should not proceed since coordination of **1** to the Au(III)-acetylide center **10** is not catalytically efficient (if occurs), and **9** should be the only product found. Alternatively, once the first catalytic cycle has finished, phenylacetylene **1** could coordinate to the in situ liberated AuPPh$_3$X catalyst and then compete with **7** for selectfluor, giving **4** as final product. In any case, the absence of the cross-coupled diyne would confirm the catalytic incompetence of single Au(III) sites to accommodate and couple two alkyne

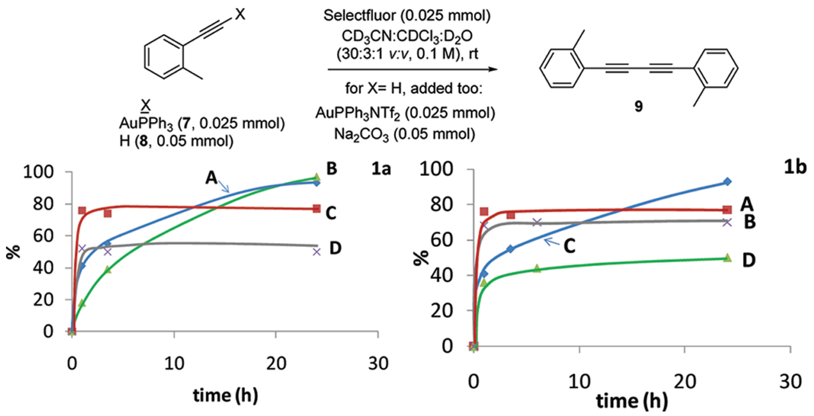


Figure 1. Plot-time yield for (1a) conversion of selectfluor for the homocoupling of **7** (curve A) or **8** (curve B) and yield of **9** from **7** (curve C) or **8** (curve D); (1b) yield of **9** from **7** with 1 equiv (curve A) or 0.5 equiv of selectfluor (curve B) and conversion of selectfluor when using 1 equiv (curve C) or 0.5 equiv (curve D).

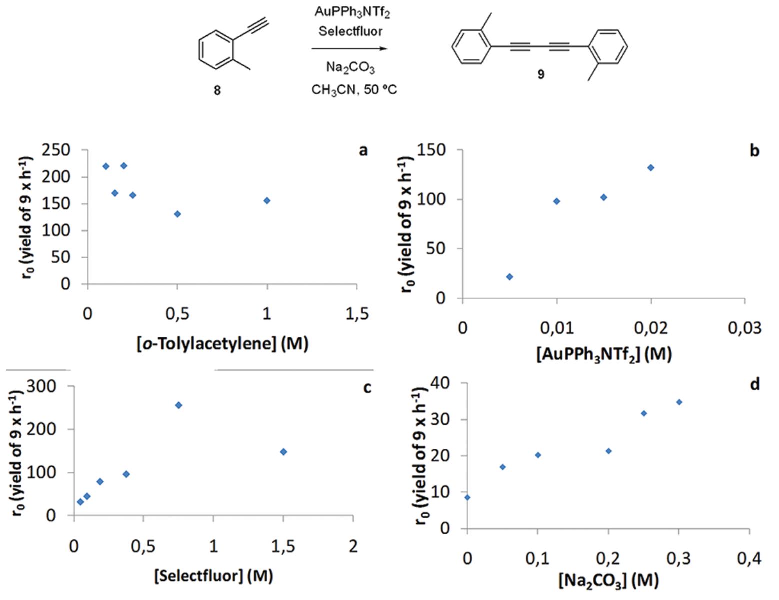
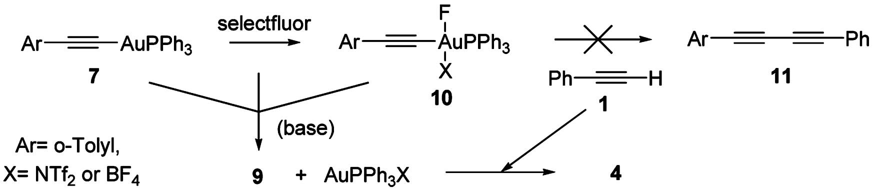


Figure 2. Plot-concentration initial rate for (a) ortho-tolylacetylene **8**, (b) $AuPPh_3NTf_2$, (c) selectfluor, and (d) Na_2CO_3.

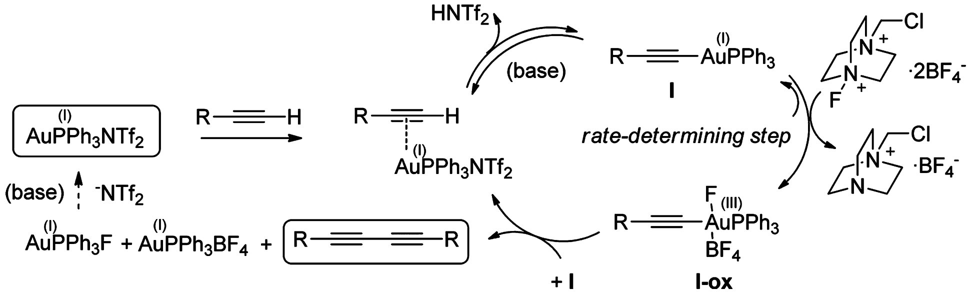
molecules. As expected, the results showed that **9** and **4** are the main products of the reaction, and **11** is not formed.

Cyclic Voltammetry Experiments. The results (Supporting Information, Figure S2) show the progressive formation of homocoupling products **4** and **9** (curves C–E) together with the selectfluor conversion (curves A–B), and, as expected, the absence of any cross-coupled bisalkyne **11** in significant amounts (curve F). At this point, we decided to confirm the feasibility of this Au(I)/Au(III)-based reaction pathway and the electronics of the process by cyclic voltammetry (Supporting Information, Figure S3). Electrochemical data support the idea that the phenylacetylene gold complex **7** can be in both oxidation states and also plays a crucial role in the catalytic homocoupling process. Cyclic voltammograms for solutions of $AuPPh_3NTf_2$ and **7** plus a stochiometric amount of selectfluor are compared with that for $AuPPh_3NTf_2$ plus selectfluor after adding free alkyne, all in 0.10 M Bu_4NPF_6/MeCN solution. As shown (curve a), the $AuPPh_3NTf_2$ plus selectfluor solution displays two reduction processes at −0.90 (C_2) and −1.80 V (C_3) which can be described by eqs 1 and 2, whereas the organogold(I) complex **7** plus selectfluor solution (curve b) yields two reduction processes at potentials of −1.15 (C_4) and −1.80 V (C_5, eqs 4 and 5). Interestingly, if

Scheme 3. Plausible Reaction Pathway for the Homocoupling of 7 and Predicted Effect after Addition of 1 (Ar = *o*-Tolyl)



Scheme 4. Plausible Mechanism for the Gold-Catalyzed Oxidative Homocoupling of Terminal Alkynes



o-phenylacetylene **8** is added to the $AuPPh_3NTf_2$ plus selectfluor solution, peaks C_2 and C_3 are diminished and accompanied by peaks C_4 and C_5 (curve c), thus denoting the formation of gold(III) complex **10** from $AuPPh_3NTf_2$ and free alkyne **8** in the presence of selectfluor. Both Au(III)→Au(I) reductions are low potential, single $2e^-$ processes, accessible to their participation in Au(I)/Au(III) catalytic cycles.

Another point to clarify is if the oxidation event Au(I)→Au(III) occurs on the free catalyst $AuPPh_3NTf_2$ as well as on the corresponding organogold(I) complex, since the corresponding potentials (see Supporting Information, Figure S3) allow both processes to occur. If this is so, the free alkyne would coordinate to the Au(I) or to the Au(III) phosphine complex independently before the reductive coupling. However, an additional experiment shows that the oxidation of gold is catalytically competent only if it occurs on the organogold complex 7 rather than on $Au^{III}FPPh_3NTf_2BF_4$ (Supporting Information, Scheme S1), suggesting that the acetylide gold complex **10** exclusively comes from the corresponding Au(I) complex 7.

Kinetic Model for the *ortho*-Tolylacetylene Homocoupling Reaction. To have deeper information on the kinetics of the homocoupling, the different initial rates for the gold-catalyzed oxidative homocoupling of *ortho*-tolylacetylene **8** as a function of the concentration of each component, at 50 °C, were measured (Figure 2, for the whole kinetic curves see Supporting Information, Figure S4−S7).

While alkyne **8** shows dispersed values that roughly fit a zero order kinetic model (Figure 2a), the other three components, the catalyst $AuPPh_3NTf_2$ (Figure 2b), the oxidant selectfluor (Figure 2c), and the base Na_2CO_3 (Figure 2d), show a first order equation at low concentrations. It is noteworthy that the effect of increasing the amount of base is much lower than increasing the catalyst or the oxidant (70 times *per* mol of base, while 7000 *per* mol of catalyst and 340 *per* mol of oxidant). Taking this into account, we have proceeded to develop the kinetic rate equation for the homocoupling of *ortho*-tolylacetylene **8**. Thus, if we define the gold-catalyzed oxidative homocoupling of **8** as follows,

$$2\cdot\mathbf{8} + \text{Select-F} + 2\text{B} \underset{k_{-1}}{\overset{\overset{\text{Cat}}{k_1}}{\rightleftharpoons}} \mathbf{9} + \text{Select-noF} + 2\cdot\text{BH}$$

$$(\text{Cat:AuPPh}_3\text{NTf}_2\text{,Select-F:Selectfluor,B=Na}_2\text{Co}_3) \qquad (1)$$

the general kinetics of the gold-catalyzed homocoupling of alkynes (see Supporting Information, Scheme S2 for calculations and development) can be described as

$$\mathbf{r} = k_4[\text{Cat}]_{\text{total}}[\text{Select-F}]\left(\frac{1}{\left(1 + \frac{[\text{BH}]}{\text{Keq}'_3[\text{B}]}\right)}\right) \qquad (2)$$

Equation 2 represents the whole equation rate for the homocoupling of **8** under gold-catalyzed conditions (see eq 1). This model fits the experimental results well, reproducing the reaction orders given in the kinetics for the alkyne, the catalyst, and the oxidant. In addition, the secondary role of the base is also explained through this equation since its influence is restricted to a fraction of 1.

Taking together the kinetics and spectroscopic evidence shown, we can propose a mechanism for the gold-catalyzed homocoupling of alkynes in homogeneous phase as given in Scheme 4.

In a first step, the gold(I) catalyst forms the π-coordinated alkyne adduct that subsequently transforms into the corresponding σ-acetylide gold(I) complex (**I**). Then, oxidation of (**I**) by selectfluor occurs to give the gold(III) adduct (**II**) which, as soon as is formed, reacts with a second molecule of **I** to give the product and the corresponding gold(I) salts. The fluoride gold(I) bond is extremely weak and spontaneously breaks to regenerate a second active species.[32,33] The final formation of two different gold(I)-phosphine complexes was confirmed by cyclic voltammetry (Supporting Information, Figure S3) and their catalytic activity was also checked (Supporting Information, Table S1, entries 45 and 51). These species can be general in selectfluor-mediated gold(I)-catalyzed processes and must be taken into account. The presence of a base in all these processes allows to neutralize the two protons liberated from the terminal alkyne as $HNTf_2$ and to form the corresponding final salts of BF_4^- and F^-. The hard character of the fluoride anion suggests that hard cations such as Na^+ would allow a better removal of fluoride from the catalytic cycle, and this could explain the better activity observed for sodium when compared to potassium or cesium bases. However, it has been shown that the homocoupling may proceed without base in the reaction medium. This implies that the σ-organogold(I) complex (**I**) must be formed from the corresponding π-adduct via a slippage mechanism. In a previous work[34] we have shown that this mechanism operates for gold(I) in the presence of electrophiles (as well as nucleophiles), as is the case of selectfluor. Interestingly, when deuterated phenylacetylene was used as substrate, an inverse kinetic isotopic effect was observed (see Supporting Information, Figures S8−S9), that indicates the formation of an intermediate metal-H bond,[35] which would fit into the slippage pathway for the formation of **I**. Finally, a Au(II)−Au(II) mechanism, recently proposed by Toste, Goddard, and co-workers for C−C couplings[36] and which in turn operates for copper-catalyzed homocoupling of alkynes, must be inoperative in our case since B−F stabilization[36] is not possible here and, accordingly, electronics show a single 2e$^-$ reduction process from Au(III) (Supporting Information, Figure S3).[37]

In conclusion, the oxidative homocoupling of terminal alkyl and aryl alkynes can be achieved with gold catalysts at room temperature in homogeneous conditions.[38−43] Mechanistic studies show that at least two different Au$^{\delta+}$-alkyne complexes are needed for the homocoupling to proceed and that the key step of the reaction is the oxidation of the gold(I)-acetylide complex.

EXPERIMENTAL SECTION

Catalyst Screening, Selectivity Studies, and Scope (Supporting Information, Table S1 and Scheme 2). The catalyst (0.025 mmol) and, if needed, the oxidant (0.75 mmol) and the base (1 mmol) were placed in a 2 mL vial equipped with a magnetic stir bar. The corresponding solvent (0.5 mL) and phenylacetylene **1** (55 μL, 0.5 mmol) were added, the vial was sealed, and the resulting mixture was magnetically stirred for 5−20 h at room temperature. Then, the reaction mixture was poured into diethyl ether (4.5 mL), dodecane (22.4 μL, 0.2 mmol) was added as external standard, and 1.5 mL from this mixture was passed through a filter syringe and submitted to GC and GC-MS analysis. For isolation of the product, the whole mixture was submitted to flash column chromatography to give, after removal of the solvents, the corresponding product in pure form. Compound **9** (white solid): R_f (*n*-hexane): 0.51. MS (*m*/*z*, relative intensity): 230 (M$^{+\cdot}$, 100), 229 (100), 228 (100), 215 (60), 202 (40), 115 (97), 101 (20). IR (υ, cm^{-1}): 2947, 1595, 1455. ^{1}H NMR (δ, ppm; *J*, Hz): 7.51 (aromatic C*H*, 2H, dmult, *J* = 7.8), 7.27 (aromatic C*H*, 2H, td, *J* = 7.7, 1.4), 7.22 (aromatic C*H*, 2H, dmult, *J* = 7.6), 7.14 (aromatic C*H*, 2H, tmult, *J* = 7.5), 2.51 (C*H*$_3$, 6H, s). ^{13}C NMR (δ, ppm): 141.6 (aromatic, 2C), 132.9 (aromatic, 2CH), 129.5 (aromatic, 2CH), 129.1 (aromatic, 2CH), 125.6 (aromatic, 2CH), 121.7 (aromatic, 2C), 81.1 (alkyne, 2C), 77.5 (alkyne, 2C), 20.7 (methyl, 2CH$_3$).

In Situ NMR Experiments (Figures 1 and Supporting Information, Figure S2). The corresponding metal complex **7** (14.3 mg, 0.025 mmol) or *o*-tolylphenylacetylene **8** (6.3 μL, 0.05 mmol), selectfluor (8.8 mg, 0.25 mmol) and, when it corresponds, AuPPh$_3$NTf$_2$ (19.8 mg, 0.025 mmol) or phenylacetylene **1** (2.75 μL, 0.025 mmol) were dissolved in a mixture of CD$_3$CN:CDCl$_3$ (0.75:0.075 mL) and then H$_2$O (25 μL) was added. The solution was transferred to an NMR tube containing Na$_2$CO$_3$ (2.65−5.3 mg, 0.025−0.05 mmol) if needed. The reaction mixture was followed by ^{1}H and ^{31}P NMR spectroscopy at a temperature of 20 °C.

Kinetics (Figure 2 and Supporting Information, Figures S4−S7). AuPPh$_3$NTf$_2$, selectfluor, and Na$_2$CO$_3$ were placed in a 10 mL round-bottomed flask equipped with a magnetic bar. CH$_3$CN (4 mL) and *o*-tolylphenylacetylene **8** were added, a septum rubber was fitted, and the reaction mixture was magnetically stirred in a preheated oil bath at 50 °C for the indicated time. Aliquots (100−200 μL) were periodically taken, poured into dichloromethane (1 mL), filtered, and submitted to GC analysis after addition of dodecane (5.6 μL, 0.05 mmol) as external standard.

Cyclic Voltammetry. Electrochemical experiments were performed in 0.1−1.0 mM solutions of the Au(I) complexes in MeCN (Carlo Erba) using Bu$_4$NPF$_6$ (Fluka) as a supporting electrolyte in 0.10 M concentration. Measurements were carried out, unless stated, after previous degasification by bubbling Ar during 15 min and maintaining the cell thermostatted under an Ar atmosphere at 298 ± 1 K. A conventional three-electrode electrochemical cell was used with a AgCl (3 M NaCl)/Ag reference electrode separated from the bulk solution by a salt bridge, a glassy carbon working electrode (BAS MF 2012, geometrical area 0.071 cm^2), and a platinum mesh auxiliary electrode. Cyclic and square wave voltammetry were used as detection modes. Potentials were referred to the Fc$^+$/Fc couple after adding ferrocene (Fluka) until a 0.5 mM concentration.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, additional schemes, figures and tables, and compound characterization including NMR copies. This material is available free of charge via the Internet at http://pubs.acs.org.

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