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Additional Information

## **Electrochemical monitoring of the oxidative coupling of alkynes catalyzed by triphenylphosphine gold complexes**

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**Abstract.** Electrochemical monitoring of the oxidative coupling of alkynes in the homogeneous phase through catalytic cycles involving triphenylphosphine gold complexes and selectfluor as oxidant reveals that at least two gold species in +3 and +1 oxidation states are implicated. Electrochemically driven homocoupling of terminal alkynes using molecular oxygen as the oxidant can be performed using such catalysts.

**Keywords.** Gold catalysis; oxidative coupling of alkynes; oxygen; voltammetry.

## 1. Introduction

Homocoupling of alkynes for obtaining di- and polyacetylenic compounds, electron-rich compounds that play different roles in biological systems and in industry [1], are reactions of considerable interest in organic synthesis [2]. The reaction can be catalyzed by a variety of metal-based catalytic systems [3]. Recently, gold, in spite of its inertness towards ambient conditions, has emerged as a powerful catalytic agent [4-6] when combined with oxidizing agents such as selectfluor (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)) or peracids in homogeneous phase [7-12].

The formation of 1,4-diphenylbutadiyne as by-product in the cascade cyclization-oxidative alkylation of allenolates with selectfluor catalyzed by gold complexes [13] as well as in the Sonogashira reaction catalyzed gold-supported nanoparticles [14-19] are recent examples for the use of gold-based catalyst. In a prior report, we have described the catalytic effect of a series of  $\text{PPh}_3\text{-Au(I)}$  complexes on the oxidative homocoupling of terminal alkyl and aryl alkynes using selectfluor as oxidant and  $\text{Na}_2\text{CO}_3$  as base in non-dried acetonitrile [20]. Monitoring the reaction by *in-situ*  $^1\text{H}$  and  $^{31}\text{P}$ -NMR spectroscopy and with the support of preliminary electrochemical data [20], it was suggested that the reaction can be achieved with gold catalysts at room temperature and indicated that both oxidation states (I) and (III) could be involved. The presence of a base allows to neutralize the two protons liberated from the terminal alkyne and to form the corresponding final salt of  $\text{BF}_4^-$  or  $\text{F}^-$ . Here, we report an electrochemical study devoted to: i) monitoring the catalytic effect exerted by  $\text{AuPPh}_3\text{NTf}_2$  (**1**) and two different phenylacetylene gold complexes  $\text{R-Ar-CC-Au(I)-PPh}_3$  ( $\text{Ar} = o\text{-tolyl}$  or  $p\text{-tolyl}$ , **2** and **3** respectively) on the oxidative homocoupling reactions, and, ii) explore the possibility of using dissolved  $\text{O}_2$  as the oxidant.

## 2. Experimental

Voltammetry and electrolysis experiments were performed at 298 K in MeCN (Carlo Erba) solutions of the Au(I) complexes and *o*-phenylacetylene using  $\text{Bu}_4\text{NPF}_6$  (Fluka) as a supporting electrolyte using glassy carbon working electrode (GCE) and a Pt-wire

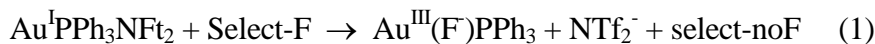
counterelectrode in a frit-separated compartment. To reproduce conditions used in ‘chemical’ experiments [20], the solvent contained 1-5 mM water. Chemicals were prepared as already described [20].

### 3. Results and discussion

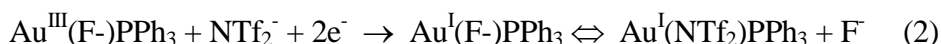
Figure 1a shows the cyclic voltammetric response for a 0.5 mM solution of **1** in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN. A main oxidation peak at +1.35 V vs. Fc<sup>+</sup>/Fc, attributable to the Au(I) to Au(III) oxidation of the metal complex, appears, in agreement with the high redox potential expected for the Au(III)/Au(I) couple in these complexes. This is accompanied by weaker signals at -1.25 V (cathodic, C<sub>1</sub>) and +1.0 V. The second can be identified as a typical adsorption-based pre-peak whereas the C<sub>1</sub> shoulder could correspond to the reduction of gold species resulting from the partial dissociation of the complex, as suggested by blank experiments for solutions of NaAuCl<sub>4</sub>·2H<sub>2</sub>O in the same electrolyte. Similar responses were obtained for complexes **2** and **3**. This electrochemistry separates from those reported for gold complexes with dithiolate and dithiolene ligands [21,22] and porphyrins [23,24], among others [25].

The addition of selectfluor promotes significant changes in the voltammetric response. This can be seen in Fig. 1, where cyclic voltammograms for selectfluor (b) and the oxidizing agent plus **1** in stoichiometric concentrations (c) can be compared. The selectfluor reagent is reduced at -0.35 V vs. Fc<sup>+</sup>/Fc, the cathodic peak (C<sub>F</sub>) displaying electrochemical parameters corresponding to a two-electron process accompanied by fast follow-up reactions. In the presence of a stoichiometric concentration of the complexes, the peak C<sub>F</sub> vanishes and is replaced by a cathodic signal at -0.90 V (C<sub>2</sub>), followed by a reduction wave at ca. -1.8 V (C<sub>3</sub>) accompanied, as can be seen in Fig. 1c, by two oxidation peaks at -1.0 (A<sub>2</sub><sup>\*</sup>) and -0.88 V (A<sub>2</sub><sup>\*\*</sup>). This voltammetric response can be rationalized by assuming that selectfluor reacts quantitatively with the Parent Au(I) complex to form a Au(III) fluorinated complex which is reduced, stepwise, to Au(I) and Au(0). The variation of the voltammetric parameters for peak C<sub>2</sub> and its anodic counterparts A<sub>2</sub><sup>\*</sup> and A<sub>2</sub><sup>\*\*</sup> with the potential scan rate suggests that the C<sub>2</sub> reduction process can be described in terms of a essentially reversible reduction preceded

by a fast chemical reaction (CE mechanism) which can be represented, prior chemical reactivity data [20] as:



The reductive step is followed by follow-up reactions yielding two different Au(I) products in equilibrium. This equilibrium can be attributed to the loss of the fluoride unit, replaced by the solvent or the triflimide unit:

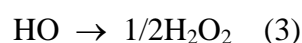
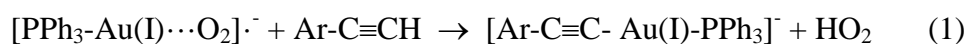


So that the processes  $A_2^*$  and  $A_2^{**}$  can be attributed to the oxidation of such Au(I) complexes to analogue Au(III) ones.

This can be seen in Fig. 2, where voltammograms for solutions of **1** and **2** plus a stoichiometric amount of selectfluor are compared with that for a **1** plus selectfluor solution after adding *o*-phenylacetylene, all in 0.10 M  $\text{Bu}_4\text{NPF}_6/\text{MeCN}$ . The **1** plus selectfluor solution displays two reduction processes at -0.90 ( $C_2$ ) and -1.80 V ( $C_3$ ) whereas the **2** plus selectfluor solution yields two reduction processes at potentials of -1.15 ( $C_4^*$ ) V and -1.80 V ( $C_5$ ). Interestingly, if *o*-phenylacetylene is added to the **1** plus selectfluor solution, peaks  $C_2$  and  $C_3$  are diminished and accompanied by peaks at -0.80 ( $C_4^*$ ) and -1.70 V ( $C_5^*$ ) (see Fig. 2c). This voltammetric pattern can be rationalized on assuming that the complex **1**,  $\text{Au}^{\text{I}}\text{PPh}_3\text{NFt}_2$ , in the presence of selectfluor, reacts to some extent with the alkyne to produce the *o*-tolylacetylene gold complex similar to complex **2** (*o*-tolyl)-CC-Au(I)-PPh<sub>3</sub>.

In order to explore the possibility of using  $\text{O}_2$  as oxidizing agent, voltammetric experiments were performed in air-saturated, water-containing MeCN solutions. It should be noted, however, that variants of copper-catalyzed homocouplings of alkynes use oxygen as the oxidant with no need of electrochemical activation [3]. Under our experimental conditions, the voltammetric response of dissolved oxygen is close to that described in literature [26-28], consisting of an one-electron reversible couple ( $C_{\text{ox}}/A_{\text{ox}}$ ), at ca. -1.2 V, accompanied by an irreversible wave at ca. -1.7 V. As can be seen in Fig.

3a for **2**, in complex-containing solutions the cathodic signal  $C_{ox}$  becomes broader and the peak  $A_{ox}$  vanishes. In the second and successive scans, an additional Au(III)/Au(I) couple appears at potentials of -0.25 ( $A_6$ ) and -0.70 V ( $C_6$ ). The process  $C_6$  is entirely absent in initial cathodic scan voltammograms, thus denoting that a direct oxidation of the parent Au(I) complex by the dissolved oxygen does not occur. These features can be rationalized by assuming the occurrence of a reaction between the electrochemically generated superoxide ion with the parent Au(I) complex to give an oxygen-containing oxidized species. In the presence of o-tolylacetylene (see Fig. 3b), an additional oxidation process appears at 0.0 V ( $A_7$ ). This process can be attributed to the oxidation of the hydrogen peroxide generated, as denoted by blank experiments in  $H_2O_2$  solutions in air-saturated 0.10 M  $Bu_4NPF_6/MeCN$ . The possibility of performing the electrochemically driven homocoupling reaction under our experimental conditions using  $O_2$  as the oxidant was confirmed by electrolysis experiments at -1.5 V where the FTIR band at  $2240\text{ cm}^{-1}$ , characteristic of the terminal alkyne, disappears progressively (see Fig. 3c,d), the entire spectra retaining all other alkyne features in agreement with homocoupling features [20]. The process would be electrochemically driven by the generation of  $O_2^{\cdot-}$  in the process  $C_{ox}$ , followed by the formation of a superoxide-Au(I) adduct, as described for copper-superoxide adducts [29,30] which could act as intermediate for the reaction with the alkyne. A plausible reaction scheme would be:



Scheme 1 summarizes a tentative scheme for the overall electrochemical pathway.

#### 4. Conclusions

Electrochemical data reveal that the studied Au(I) complexes react with selectfluor to yield the corresponding Au(III) fluorinated complexes which possess a reduction potential accessible to their participation in Au(III)/Au(I) catalytic cycles.

Electrochemical data are consistent with the reaction scheme proposed to occur under 'chemical' conditions. Here, the catalytic cycle is initiated by the formation of a Au(I)- $\pi$ -coordinated alkyne adduct that subsequently transforms into the corresponding  $\sigma$ -acetylide gold(I) complex whose oxidation by selectfluor yields an fluorinated phenylacetylene Au(III) adduct which, as soon as is formed, reacts with a second molecule of acetylide gold(I) complex or, in much lesser extent, of alkyne to yield the coupling product. A comparable reaction scheme occurs in the presence of O<sub>2</sub>. In this case, the catalytic cycle has to be initiated electrochemically via generation of the superoxide radical anion and involves, presumably, intermediate Au(III)/Au(I) metal-oxo and superoxo complexes.

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## Figures

**Figure 1.** Cyclic voltammograms at GCE for: a) 0.5 mM solution of **1**, b) 0.5 mM selectfluor, and c) 0.5 mM **1** plus 0.5 mM selectfluor, all in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN. Potential scan rate 50 mV/s.

**Figure 2.** Square wave voltammograms for: a) 0.2 mM **1** + 0.2 mM selectfluor; b) 0.1 mM **2** + 0.2 mM selectfluor; c) 0.2 mM **1** + 0.2 mM selectfluor; + 0.2 mM *o*-alkyne solutions in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 10 Hz..

**Figure 3.** Cyclic voltammograms at glassy carbon electrode for: a) air-saturated 5 mM water plus 0.5 mM **2** plus 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN solution; b) id. plus 0.2 mM *o*-tolylacetylene. Potential scan rate 500 mV/s. Insets: FTIR spectra for a 5 mM *p*-tolylacetylene plus 0.5 mM **3** in air-saturated 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/MeCN c) before and d) after electrolysis at -1.5 V during 30 min.

**Scheme 1.** Scheme proposed for the electrochemically-driven homocoupling of alkynes catalyzed by Au(I) complexes in this study using dissolved O<sub>2</sub> as the oxidant.