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On the Mechanism of the Digold(I) Hydroxide-Catalyzed Hydrophenoxylation of Alkynes

Adrián Gómez-Suárez,^[a] Yoshihiro Oonishi,^{[a],†} Anthony R. Martin,^{[a],‡} Sai V. C. Vummaleti,^[b] David J. Nelson,^{[a],§} David B. Cordes,^[a] Alexandra M. Z. Slawin,^[a] Luigi Cavallo,^{*,[b]} Steven P. Nolan,^{*,[a,c]} and Albert Poater^{*,[d]}

Dedicated to the memory of our friend and colleague Professor Tom Ziegler

Abstract: Herein we present a detailed investigation of the mechanistic aspects of the dual gold-catalysed hydrophenoxylation of alkynes, using both experimental and computational methods. The dissociation of $[\{Au(NHC)\}_2(\mu-OH)][BF_4]$ is essential to enter the catalytic cycle; this step is favored in the presence of bulky, non-coordinating counterions. Moreover, *in silico* studies confirmed that phenol does not only act as a reactant, but as a co-catalyst, lowering the energy barriers for several transition states. A gem-diaurated species might form during the reaction, but this lies deep within a potential energy well, and is likely to be an 'off-cycle' rather than an 'in-cycle' intermediate.

Introduction

The end of the 20th and the beginning of the 21st century saw the advent of a veritable "gold rush".^[1] With this was associated a sizeable number of publications dealing with the stoichiometric and catalytic reactivity of gold.^[2] The main driving force behind this modern gold fever was the discovery that gold salts and complexes could catalyse a wide range of chemical reactions, despite the longstanding dogma of inertness held throughout the ages.^[3] It has been

assumed that all gold-mediated transformations proceeded through the interaction of one gold centre with one substrate, until the seminal work of Toste and Houk in 2008.^[4] In this report, it was proposed that not one but two gold centres could interact with one substrate, thereby generating σ,π -digold acetylide or *gem*-diaurated species. Since then, several research groups have contributed to our understanding of these diaurated complexes and their role in catalysis,^[5] enabling the development of novel gold-catalysed transformations that require dual activation of the substrate by the gold catalyst. Specific catalysts for dual activation processes have also been developed as a result of this seminal work.^[6]

The Nolan group has reported the synthesis and reactivity studies of a series of diaurated complexes of the formula $[\{Au(NHC)\}_2(\mu-OH)][BF_4]$ (**1**- BF_4)^[7,8] and their use as catalysts for alkyne hydrophenoxylation.^[9] Phenols are more acidic than most aliphatic alcohols, and until recently the only protocol for their gold-catalysed addition to alkynes relied upon high catalyst loadings, temperatures and reaction times, and produced only moderate yields.^[10] In contrast, the addition of aliphatic alcohols to alkynes has been well-known for a number of years.^[11]

Digold hydroxides **1** can be considered as a combination of a Lewis acid $[Au(NHC)][BF_4]$ (**2**) and a Brønsted base $[Au(OH)(NHC)]$ (**3**).^[8] Preliminary mechanistic studies suggested that the hydrophenoxylation reaction proceeded via a dual activation mechanism, whereby the $[Au(NHC)][BF_4]$ (**2**) fragment coordinates to the alkyne (**4**) to form gold-alkyne π -complex **I** and $[Au(OH)(NHC)]$ (**3**) deprotonates the phenol (**5**) to generate gold phenoxide **II**^[12] (Scheme 1).^[13] The product is a *Z*-vinyl ether (**6**).

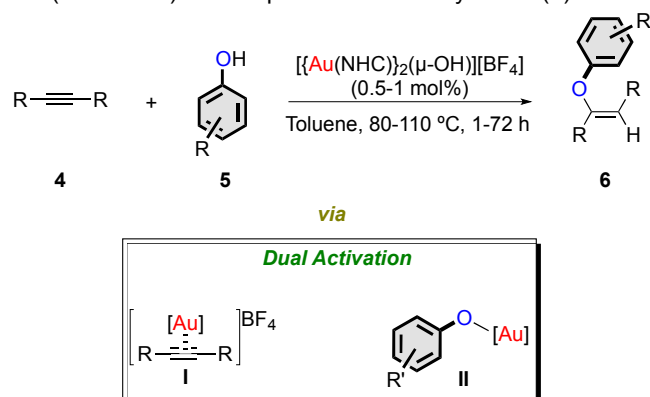
- [a] Dr. A. Gómez-Suárez, Dr. Y. Oonishi, Dr. A. R. Martin, Dr. D. J. Nelson, Dr. D. B. Cordes, Prof. A. M. Z. Slawin, Prof. Dr. S. P. Nolan*
EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, U.K.
E-mail: stevenp.nolan@gmail.com
- [b] Dr. S. V. C. Vummaleti, Prof. Dr. L. Cavallo*
KAUST Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
E-mail: luigi.cavallo@kaust.edu.sa
- [c] Prof. Dr. S. P. Nolan*
Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia.
- [d] Dr. A. Poater*
Institut de Química Computacional i Catàlisi and Departament de Química
Universitat de Girona
Campus Montilivi, 17071 Girona, Catalonia, Spain
E-mail: albert.poater@udg.edu

† Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan.

‡ Institut de Chimie de Nice, UMR 7272, Université de Nice Sophia Antipolis, CNRS, Parc Valrose, 06108 Nice cedex 2, France.

§ WestCHEM Department of Pure & Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL.

Supporting information for this article is given via a link at the end of the document, kinetic studies details, characterization data for all the compounds, computational details, and Cartesian coordinates.



Scheme 1. Hydrophenoxylation of alkynes via dual activation.

This reaction represents the first example of two gold centres interacting independently with two substrates to generate activated species that react in an intermolecular fashion.

The typical mechanistic scenario for the gold-catalysed addition of nucleophiles to alkynes involves activation of the alkyne by cationic gold followed by outer-sphere antiperiplanar attack of the alkyne by the nucleophile,^[14] with concomitant slippage of the gold centre to the other carbon atom.^[15,16] In contrast, our hydrophenoxylation reaction requires that the phenol nucleophile first be activated as a gold phenoxide complex, which then reacts with the gold-alkyne complex. The mechanism of these reactions was recently discussed in depth in a recent study by Maier and co-workers.^[16] They suggested that our protocol is a rare exception that does not follow the typical catalytic cycle previously investigated in the study of gold chemistry.^[17]

Therefore, we sought to explore the mechanistic aspects of this exciting and intriguing reaction, to fully understand the implications for gold catalysis. We have relied heavily on DFT calculations; while these were challenging to carry out on systems of this size, they have allowed previously unseen levels of insight into dual catalysis mechanism. Supporting experimental work was carried out to explore key steps and processes.

At the outset, answers to several key questions were sought:

- ❖ Does the reaction proceed via dissociation of the digold hydroxide species as suggested in Scheme 1?
- ❖ Is a digold phenoxide species (**III**) involved in the reaction?
- ❖ Are *gem*-di-aurated intermediates involved in this reaction?
- ❖ What is the role of water?

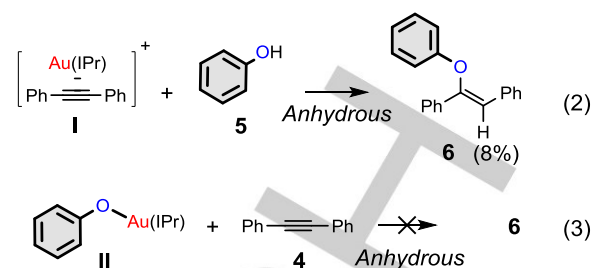
With these studies we have sought to contribute to the understanding of the interactions involved in dual-gold-catalysed reactions, and anticipate that this information will help design more efficient dual activation protocols.

Results and Discussion

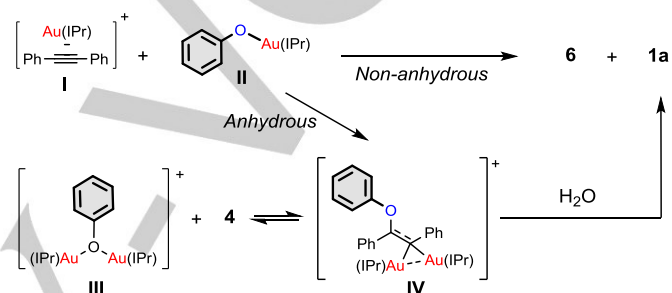
Initial studies^[9] confirmed that the dissociation/reassociation of **1** occurs rapidly. A mixture of $[\{\text{Au}(\text{IPr})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**1a**-BF₄) and $[\{\text{Au}(\text{SIPr})\}_2(\mu\text{-OH})][\text{BF}_4]$ (**1b**-BF₄) rapidly equilibrates to a 1:2:1 mixture of **1a**-BF₄, $[\{\text{Au}(\text{IPr})\}(\mu\text{-OH})\{\text{Au}(\text{SIPr})\}][\text{BF}_4]$ (**1c**-BF₄) and **1b**-BF₄ (eq. 1). Complexes **I** are poorly reactive with phenol,



and complexes **II** are poorly reactive with alkyne (eq. 2 and 3).



Moreover, **I** and **II** successfully react to re-form **1** and deliver the product (Scheme 2).^[9] However, a *gem*-di-aurated species (**IV**) was observed by NMR spectroscopy when this was carried out under anhydrous conditions.



Scheme 2. Preliminary mechanistic studies.

With these initial results in mind, it was then logical to expect that an inner-sphere counterion (such as OTf or NTf₂) might reduce reactivity compared to more weakly coordinating counter-ions such as BF₄, FABA and SbF₆ (FABA = tetrakis(pentafluorophenyl)borate). Kinetic experiments conducted using a model reaction (the hydrophenoxylation of diphenylacetylene with phenol; monitored by GC-FID) confirmed that the reactivity of $[\{\text{Au}(\text{IPr})\}_2(\mu\text{-OH})][\text{X}]$ decreased in the order X = SbF₆ ≈ BF₄ ≈ FABA > OTf >> NTf₂, supporting our hypothesis (see the Supporting Information for profiles).^[18] This is in direct contrast with recent reports on the counterion effect on gold-catalysed hydroalkoxylation of alkynes. There the counterion plays a crucial role in stabilizing key intermediates and aiding the protodeauration step, acting as a proton shuttle. This supports the hypothesis that our reaction does not follow a prototypical gold catalytic cycle, and instead proceeds *via* the reaction of phenoxide **II** with gold-alkyne complex **I**.^[19] These results are supported by DFT calculations that show that the dissociation of BF₄ from the cationic moiety [Au]⁺ is facile, bearing in mind the binding energy of NTf₂ is 17.6 kcal/mol stronger.

Previous studies have shown that **1a** reacts with phenol to form $[\{\text{Au}(\text{IPr})\}_2(\mu\text{-OPh})]$ (**III**).^[9] The need for a dissociative pathway raises questions regarding the possible involvement of a digold phenoxide complex, particularly as the reaction proceeds in the presence of a large excess of phenol with respect to **1**. Complex **III** could be prepared and isolated under rigorously anhydrous conditions, and was characterised by NMR spectroscopy, elemental analysis, and crystallographic methods (see

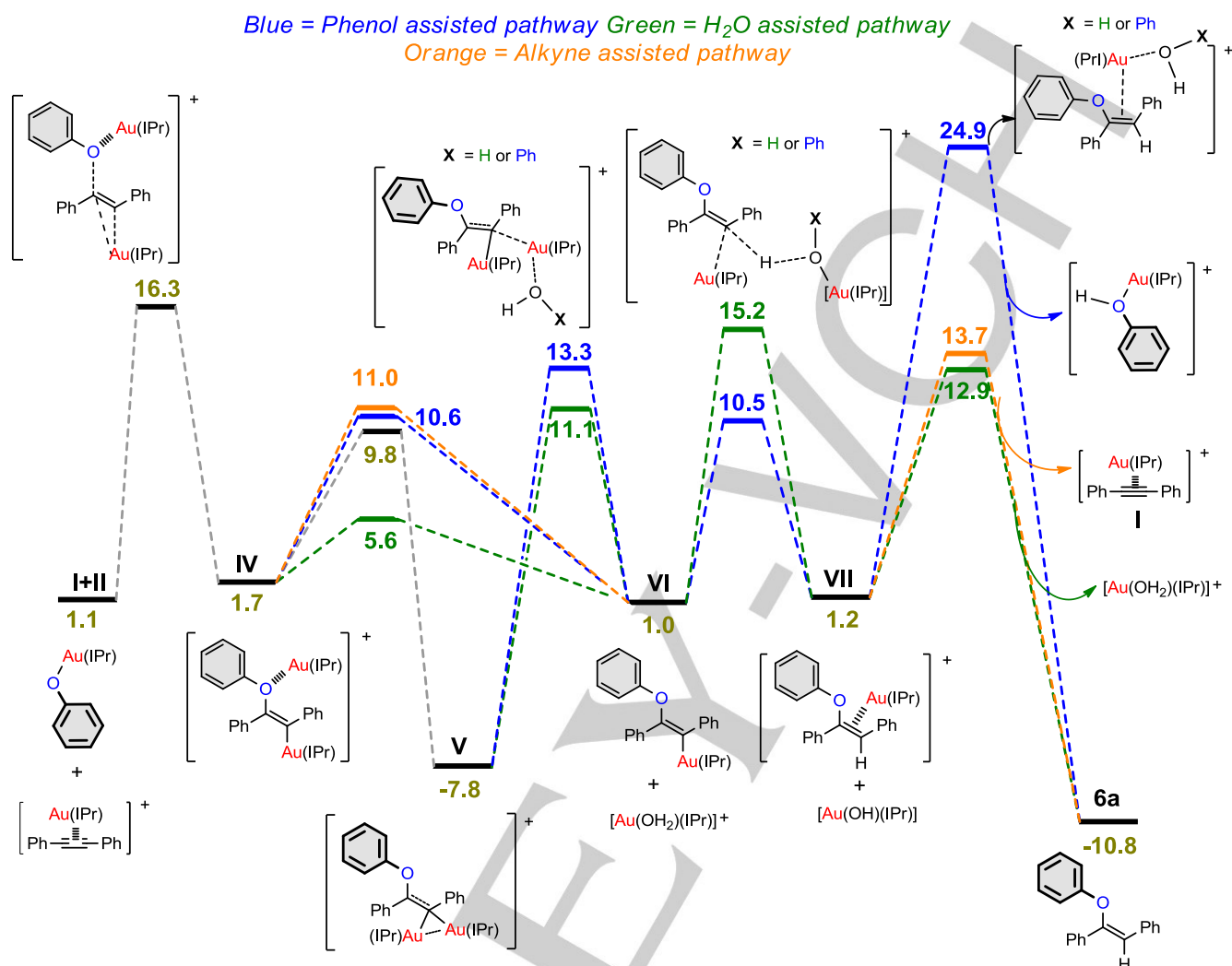


Figure 3. a) Computed stationary points for the dual-gold-catalyzed hydrophenoxylation using **4** as a substrate, **5** as a nucleophile, from the metal catalytic combination **I+II** (Gibbs free energies are given in kcal/mol).

Subsequent protodeauration, assisted by phenol, delivers the enol-ether species **VII** and regenerates gold-phenoxide **I**; if water were to perform this role the barrier is higher and the corresponding hydroxide would be produced, which can re-enter the cycle by reaction with phenol. The final decomplexation of the gold in **VII** can be achieved by reaction with alkyne or water. The former will directly regenerate gold-alkyne complex **I**, while the latter will form a gold-aqua complex that would react with **II** forming digold-phenoxide **III** overcoming a barrier of 9.2 kcal/mol, and then dissociate in the presence of alkyne requiring 10.7 kcal/mol to deliver **I** + **II** and thus re-enter the catalytic cycle (see Figure 2).

For the sake of a broader analysis and to unravel why experimentally the hydrophenoxylation of **4a** gives only the trans-product **6**, we explored the possible reaction pathway to generate the cis-isomer **6cis**. However, our results showed that this pathway contains intermediates that are either endothermic in nature or they are connected by high-energy barriers (see

Figure S1 in the Supporting Information). The main results can be summarized as follows: the predicted barriers for the formation of intermediates **IVcis** and **Vcis** are 6.5 and 27.6 kcal/mol higher in energy (respectively) when compared to the barriers for their trans counterparts (intermediate **IV** and **V**) given in Figure 3a.

A key question is this: why do not mono-gold catalysts mediate this reaction? To explore this, calculations were also carried out to unravel any potential mono-gold reaction pathway. The most preferred one displays a barrier for the C...O bond formation between the alkyne and the phenoxide moieties placed at 42.8 kcal/mol above **1a**, to be compared with the barrier described by the transition state **I+II**→**IV**, which is 26.5 kcal/mol lower in energy (see Figure 3), and pointing out that this monogold alternative pathway would not drive to the **6**, but to the **6-cis**. The high barriers that a monogold-catalysed process would have to overcome are evident from, and consistent with, the very forcing conditions that Sahoo and co-workers required to conduct this reaction with AuCl₃.^[10]

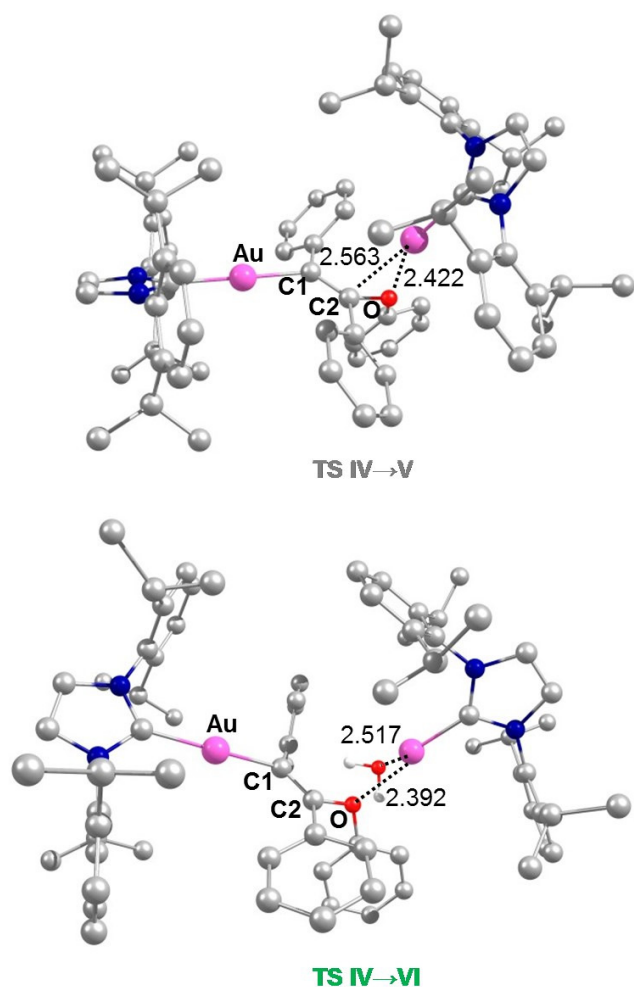


Figure 4. Molecular structures of computed transition states linking intermediates IV with V and VI. Selected distances are indicated in Å.

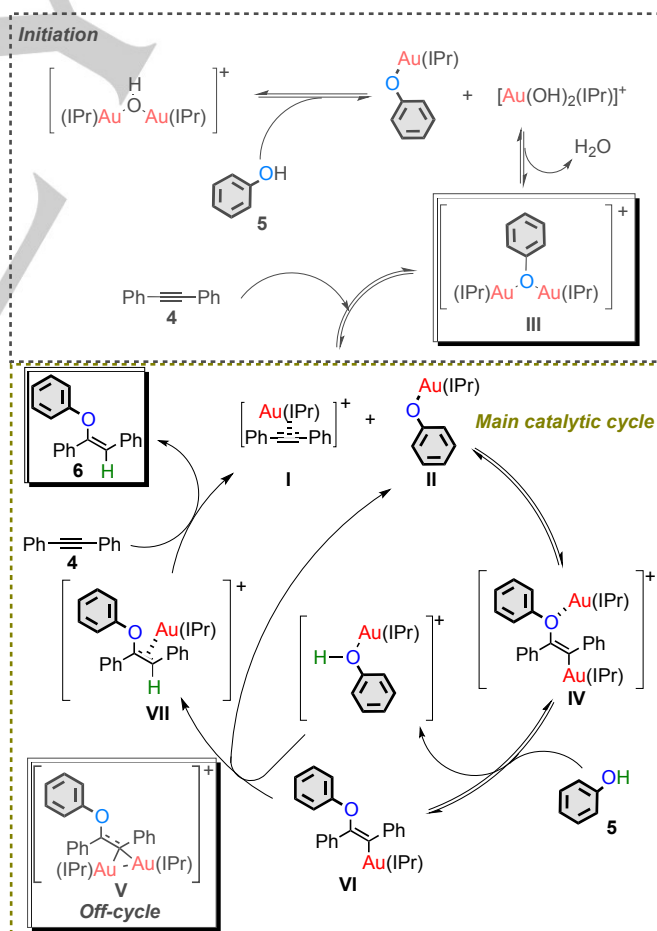
Computational Details

All the DFT static calculations have been performed at the GGA level with the Gaussian09 set of programs,^[27] using the BP86 functional of Becke and Perdew.^[28] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, and O (SVP keyword in Gaussian).^[29] For Au we used the quasi-relativistic Stuttgart/Dresden effective core potential, with the associated valence basis set (standard SDD keywords in Gaussian).^[30] The geometry optimizations were carried out without symmetry constraints, and the characterization of the stationary points was performed by analytical frequency calculations. Single point calculations on the BP86 optimized geometries were performed using the M06 functional^[31] with the triple- ζ basis set of Ahlrichs for main-group atoms (TZVP keyword in Gaussian),^[32] while for Au the SDD basis set has been employed. These single point calculations also used the polarizable continuous model PCM to model the solvent effects, using toluene as a solvent.^[33] The

reported free energies in this work include energies obtained at the M06/TZVP level corrected with zero-point energies, thermal corrections and entropy effects evaluated at 298 K and 1354 atm^[34] with the BP86/SVP method in the gas phase.

Conclusions

In conclusion, a series of *in silico* studies, supported by experimental work, have been carried out to further elucidate mechanistic aspects of the hydrophenoxylation of alkynes. The results suggest that the synergic cooperation of two monogold species facilitates this process, while analogous mono-gold species are not capable of mediating this reaction. All insights, both experimental and theoretical, support the proposed dual activation pathway for this transformation (see Scheme 3). There is a considerable counter-ion effect, with more coordinating counter-ions reducing the rate of reaction. The dissociation of the digold species via three possible mechanisms (alkyne, water, phenol) confirming that this process is essential to enter the catalytic cycle. Even though the digold-phenoxide species III only has an active role before the catalytic cycle, it is a sine qua non precursor of the active catalytic species.



Scheme 3. Hydrophenoxylation of alkynes via dual gold activation catalysis.

However, the oft-mentioned gem-diaurated species are unlikely to play a role in this reaction; competing processes mediated by water, phenol and alkyne serve to disfavour the formation of such a complex, which lies in a very deep potential energy well and is unlikely to contribute to productive catalysis. Finally, water is shown to have a key role.

With these studies we have sought to explore and explain the most likely interactions involved in dual-gold-catalysed reactions, and anticipate that this information will help in the design of more efficient dual activation protocols. We are currently studying the use of digold hydroxide species in other dual-gold-catalysed reactions and these results will be published in due course.

Acknowledgements

The ERC (Advanced Investigator Award-FUNCAT), EPSRC and Syngenta are gratefully acknowledged for support. Umicore AG is acknowledged for their generous gift of materials. S.P.N. and L.C. thank King Abdullah University of Science and Technology (CCF project) for support. Y.O. thanks the Uehara Memorial Foundation for a Research Fellowship. A.P. thanks the Spanish MINECO for a project CTQ2014-59832-JIN, FEDER grant UNGI10-4E-801, and European Commission for a Career Integration Grant (CIG09-GA-2011-293900).

Abbreviations: NHC, N-heterocyclic carbene; FABA, tetrakis(pentafluorophenyl)borate; IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; SIPr, 1,3-bis(2,6-diisopropylphenyl)imidazolidine

Keywords: homogeneous catalysis • kinetic studies • DFT calculations • dual catalysis • gold catalysis • alkyne • hydrophenoxylation

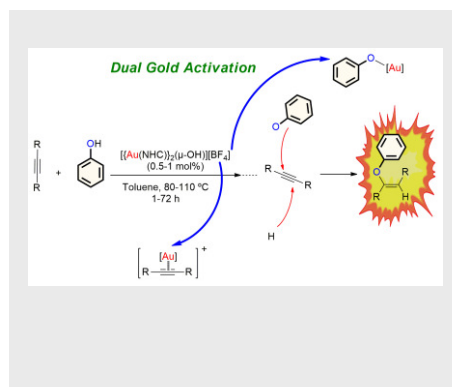
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COMMUNICATION

Hydroarylation of alkynes mediated by gold centers occurs via a bimetallic cooperative mechanism.



A. Gómez-Suárez, Y. Oonishi, A. R. Martín, S. V. C. Vummaleti, D. J. Nelson, D. B. Cordes, A. M. Z. Slawin, L. Cavallo,* S. P. Nolan,* and A. Poater*

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