



Gold 2018

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# Enantioselective Gold(I)-Catalyzed Intermolecular [4+2] Annulation between Propiolates and Alkenes

Hanbyul Kim, Su Yeon Choi, Seunghoon Shin\*

Department of Chemistry and Center for New Directions in Organic Synthesis (CNOS), Hanyang University, Seoul 04763, Korea

The  $\alpha,\beta$ -unsaturated- $\delta$ -lactone scaffolds are found in a number of medicinal and natural compounds, displaying an array of significant biological activities.<sup>1</sup> Based on the powerful alkynophilic activation of homogeneous Au(I)-catalysis, we recently demonstrated that the dihydropyranones could be assembled in a single step from the intermolecular reaction of propiolates with alkenes.<sup>2</sup> However, achieving high level of stereocontrol has remained elusive in this case of intermolecular coupling.<sup>3</sup> The enantio-determining step involves discrimination of prochiral face of the alkene nucleophile, approaching away from the linearly coordinated Au(L\*) complex (Type I, Figure 1). Therefore, in the absence of a tether, intermolecular coupling presents a formidable challenge. Most successful examples of intermolecular enantioselective gold(I)-catalysis have involved face-selective coordination on the  $sp^2$ -alkenes/allenes or  $\sigma$ -bound Au(I) complexes. Herein, we demonstrated a highly enantioselective (upto 95 %ee) route toward the dihydropyranones for diverse alkene nucleophiles, utilizing a non-conventional counter-anion (SDS) in 1,1,2,2-tetrachloroethane as solvent (Scheme 1).<sup>4</sup>

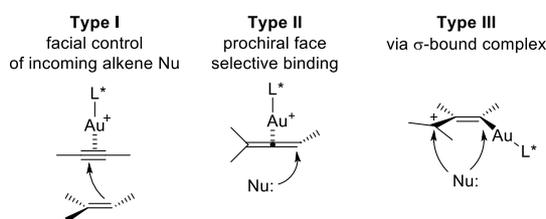
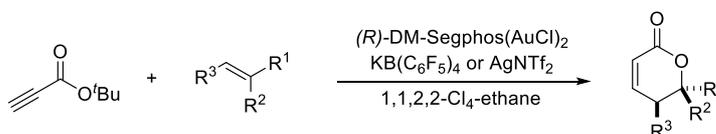


Figure 1. Types of enantio-determining step in intermolecular asymmetric Au(I)-catalysis



- intermolecular asymmetric Au(I) catalysis
- control of prochiral face of olefins by (L\*)Au-alkyne complex
- use of SDS in organic solvents to control selectivity
- 17 examples (70-95 %ee)
- tri-substituted and 1,2-disubstituted olefins & 1,3-dienes

Scheme 1. Enantioselective intermolecular [4+2] annulation

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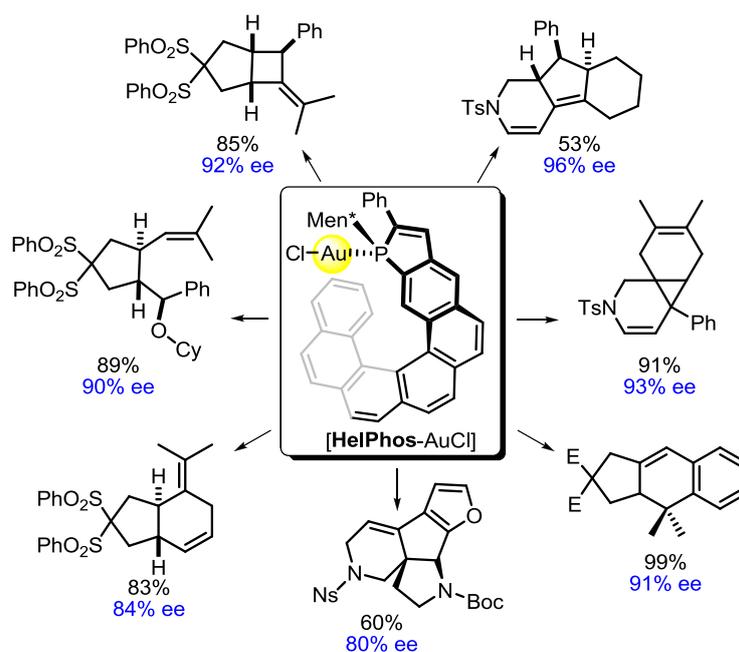
Corresponding author email: [sshin@hanyang.ac.kr](mailto:sshin@hanyang.ac.kr)

# Phospha[6]helicenes as Effective Ligands in Enantioselective Gold(I)-Catalysis

P. Aillard, K. Yavari, A. Marinetti, A. Voituriez

*Institut de Chimie des Substances Naturelles, ICSN - CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1, av. de la Terrasse, 91198 Gif-sur-Yvette, France.*

Over the past few years, helicenes have attracted considerable attention due to their wide potential, including in materials science.<sup>1a</sup> However, molecular scaffolds with helical chirality have been rarely used for building phosphorus ligands and catalysts.<sup>1b</sup> In this context, our purpose was to access unprecedented chiral auxiliaries for organometallic catalysis. We have synthesized new series of phosphahelicenes, where the phosphorus moiety is embedded at the end of the helical structure, following two strategies: the photochemical oxidative cyclization of diaryl olefins<sup>2</sup> and the [2+2+2] cyclootrimerization reaction.<sup>3</sup> The corresponding gold complexes of these phosphahelicenes were characterized and evaluated in enantioselective enyne, allen-ene and allene-diene cyclizations.<sup>2-4</sup> A short asymmetric total synthesis of (-)-rhazinilam, using a gold(I)-catalyzed cyclization, will be also presented.<sup>5</sup>



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*Corresponding author email: Arnaud.voituriez@cnr.fr*

# Evaluation of $\beta$ -cyclodextrin NHC-Gold(I) Complex in the Catalysis of Cycloisomerization and Alkoxy cyclization Reactions

N. Del Río<sup>1</sup>, N. Vanthuyne<sup>2</sup>, O. Bistri<sup>1</sup>, M. Sollogoub<sup>1</sup>, L. Fensterbank<sup>1</sup>, V. Mouriès-Mansuy<sup>1</sup>

(1) Sorbonne Université Science, UMR CNRS 8232, Institut Parisien de Chimie Moléculaire, 4 place Jussieu, 75005 Paris, France.

(2) Aix-Marseille Université, Centrale Marseille, CNRS, iSm2 UMR 7313, 13397 Marseille, France.

Nowadays, selectivity in chemical reactions is a must especially in atom-economical processes that are crucial for environmental concerns. Gold(I) catalysis has recently emerged as a very fecund and selective methodology in a wide range of reactions, and as allowed the development of new regio-<sup>1</sup> and enantioselective<sup>2</sup> chemical processes with high atom efficiency and low energy demand. Encapsulating a reactive center in a cavity with a defined and specific shape is an efficient way to promote selectivity in catalytic processes. This can result in reaction pathways that are different from those of the free catalyst, leading to remarkably enhanced selectivity of the caged catalysts compared to their non-encapsulated analogues. In this context, our groups have evaluated the cavity effect provided by  $\beta$ -cyclodextrin NHC-Gold(I) complex (figure 1) in terms of regioselectivity and asymmetric induction in a series of gold-catalyzed transformations.<sup>3</sup> The behavior of the catalyst in known reactions is indicative of strong  $\pi$ -acceptor properties.

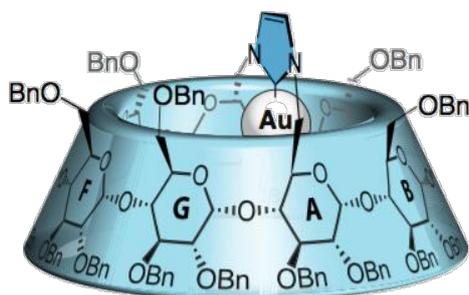


Figure 1.  $[\beta\text{-ICyDAuCl}]$  complex

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Corresponding author email: [natalia.del\\_rio\\_garcia@upmc.fr](mailto:natalia.del_rio_garcia@upmc.fr)

# Gold(I)-Catalyzed 1,3-O-Transposition of Ynone: Mechanism and Catalytic Acceleration with Electron-Rich Aldehydes

S. Aikonen<sup>1</sup>, M. Muuronen<sup>2\*</sup>, T. Wirtanen<sup>1</sup>, S. Heikkinen<sup>1</sup>, J. Musgreave<sup>3</sup>, J. Burés<sup>3\*</sup>, J. Helaja<sup>1\*</sup>

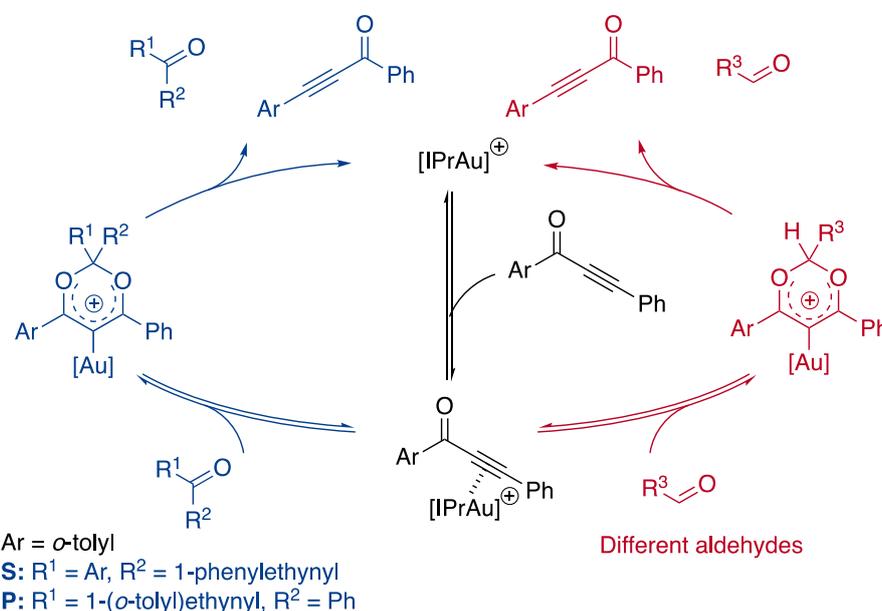
(1) Department of Chemistry, University of Helsinki, Helsinki, Finland

(2) Department of Chemistry, University of California Irvine, Irvine, United States

(3) The University of Manchester, School of Chemistry, Manchester, U.K.

Homogeneous gold-catalysis has proven to be a versatile and selective tool to activate alkynes for a range of nucleophilic additions.<sup>1</sup> Intramolecular C=O O-nucleophiles: aldehydes, ketones, esters and amides have been an important sub-class of nucleophiles yielding an access to various O-heterocycles and rearrangement products. Recently, gold(I)-catalysis was shown to mediate regioselective 1,3-O-transposition of ynone that is driven by sterical hindrance.<sup>2</sup> Thus far, the reaction mechanism has not been clarified in full detail. Our kinetic measurements<sup>3</sup> and computational reaction energy profiling together point out that the transposition of carbonyl is intermolecular (Scheme 1).<sup>4</sup> Kinetic analysis and theoretical calculations at DFT level suggest that the rate determining step in the reaction is the nucleophilic attack of substrate or product to gold activated alkyne.

Optionally, a notable acceleration of the transposition rate could be observed by addition of a catalytic amount of electron rich, i.e. nucleophilic, aromatic aldehyde. Experimentally measured relative reaction rates for different aldehydes were in agreement with the computational activation energy barrier differences for the studied aldehydes, and with <sup>18</sup>O labeling experiment the active site of the aldehyde could be pinpointed to be the C=O functionality.



Scheme 1. Suggested catalytic cycle for the reaction.

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Corresponding author email: santeri.aikonen@helsinki.fi

# Gold(I)-Mediated Thiourea Organocatalyst Activation: A Synergic Effect for Asymmetric Catalysis

Anabel Izaga<sup>1</sup>, Juan V. Alegre-Requena<sup>1</sup>, Raquel P. Herrera<sup>2\*</sup>, M. Concepción Gimeno<sup>1\*</sup>

(1) Dpto. de Química Inorgánica. Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, E-50009, Spain

(2) Laboratorio de Organocatálisis Asimétrica. Dpto. de Química Orgánica. Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, E-50009, Spain

The unprecedented activation of thiourea organocatalysts through the coordination of a metallic Lewis acid is described (Figure 1). Coordination of the metal produces the consequent acidification of the thiourea protons achieving a better activity in terms of conversion and selectivity in the benchmark reaction of addition of indole to nitrostyrene.<sup>1,2</sup> Three thiourea organocatalysts **T1–T3** with different electronic and steric requirements were used to prepare several group 11 metal complexes. All the tested M–thiourea complexes provided better results than the thioureas alone, and the gold complexes [Au(thiourea)<sub>2</sub>]OTf were the best in terms of reactivity and selectivity.

After achieving the optimum experimental conditions a comparison of the activity of the thioureas *versus* the [Au(thiourea)<sub>2</sub>]OTf complexes in different catalysts loading were performed. As expected the higher values were achieved with thiourea **T3** and [Au(**T3**)<sub>2</sub>]OTf showing a great improvement in the reactivity and selectivity values of the metal thiourea complex compared with the thiourea alone. It was possible to reduce the catalyst loading to 1 mol% without a significant decrease of the activity, although optimum values are afforded with 3 mol% catalyst loading.

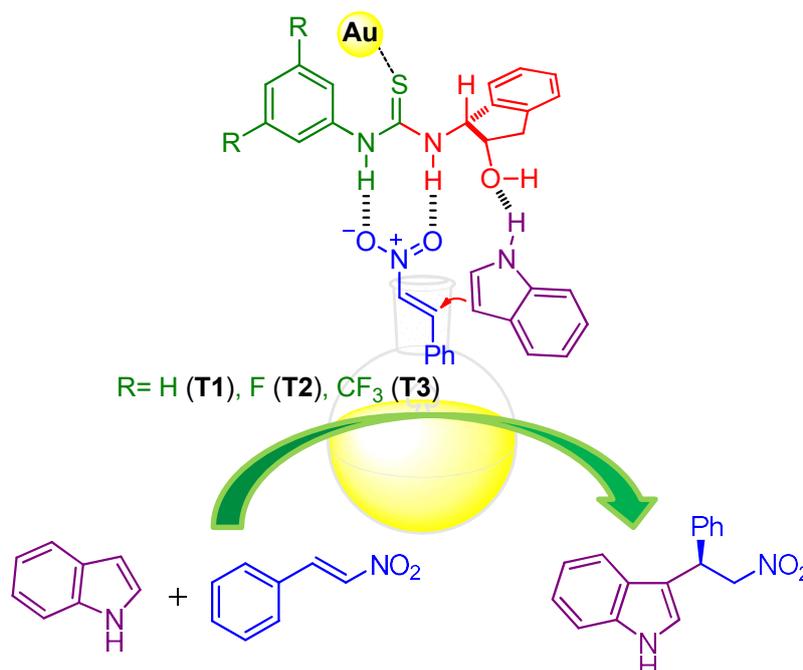


Figure 1. Pioneering idea

Computational calculations support this kind of activation mode. Thus, a new concept has been proved demonstrating the cooperative effect between a metallic Lewis acid and a thiourea catalyst providing metal complexes acting as organocatalysts.<sup>3</sup>

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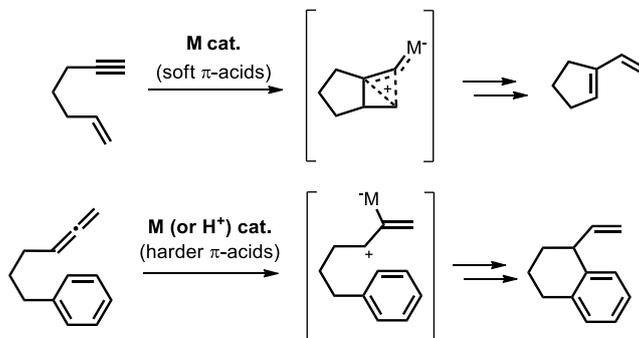
Corresponding author email: raquelph@unizar.es

# Revealing the Activity of $\pi$ -Acid Catalysts using a 7-Alkynyl Cycloheptatriene

M. Vayer<sup>1</sup>, C. Bour, V. Gandon

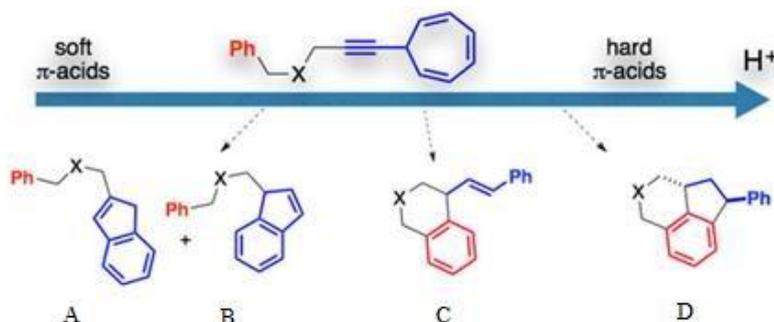
(1) ICMMO (UMR 8182), Univ. Paris-Sud, Université Paris-Saclay, 91405 Orsay cedex, France

Nucleophilic attacks onto C-C  $\pi$ -bonds are commonly catalyzed by metal complexes referred as soft  $\pi$ -Lewis acids. For instance, the softest  $\pi$ -acids of the gold series are relevant choices to catalyze cycloisomerizations of 1, $n$ -enynes. Such reactions involve the formation of a “soft” highly delocalized nonclassical carbocation.<sup>1</sup> On the other hand, hydroarylations of allenes usually require “harder” soft  $\pi$ -acids that can still be found in the gold series, provided strongly  $\pi$ -acidic ligands are used. Moreover, even Brønsted acids can be used to perform hydroarylations of allenes (Scheme 1).<sup>1</sup>



**Scheme 1.** Prototypical examples of reactions catalyzed by  $\pi$ -acids

The border between softer and harder  $\pi$ -acids is thin and many factors can influence the reactivity. Besides, in many cases, the active species is actually generated from a two-component mixture, each of which having a potential activity as  $\pi$ -acid. For instance, gold cations can be obtained from a gold chloride and a silver salt, so it can be hard to distinguish which of the two metals is the active one.<sup>3</sup> Lastly, the use of a  $\pi$ -acid can generate protons in the reaction mixture, which are also potent catalysts. In order to predict the general activity pattern of  $\pi$ -acids, and to distinguish between two metals when a two-component mixture is used, or if adventitious protons compete as the true catalyst, we have designed a substrate containing a 7-alkynyl cycloheptatriene moiety, which combines the chemistry of enynes and the hydroarylation of allenes. Whereas soft  $\pi$ -Lewis acids trigger a nonclassical carbocation rearrangement to generate two regioisomeric indenenes **A** and **B**, harder ones rather give the hydroarylation product **C** or the polycyclic compound **D** as a consequence of two sequential hydroarylation steps (Scheme 2).<sup>4</sup>



**Scheme 2.** Divergent pathways depending on the nature of the  $\pi$ -acids used

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Corresponding author email: [marie.vayer@u-psud.fr](mailto:marie.vayer@u-psud.fr)

# $\alpha$ -Iminocarbene Gold(I) Intermediates from Nitrogen Heterocycles

Z. Zeng<sup>1</sup>, H. Jin<sup>1</sup>, A. Stephen K. Hashmi<sup>1\*</sup>

(1) Organisch-Chemisches Institut, Heidelberg University, Heidelberg, Germany

Starting from the first papers<sup>1,2</sup> which demonstrated the potential of gold catalysis for organic transformations with a high increase of molecular complexity, homogeneous gold catalysis has emerged to a precious, frequently used tool in organic synthesis.<sup>3,4</sup> Among the many new methods and reactivity patterns developed in the last 18 years in the field, a highly useful and versatile aspect was the in situ generation and synthetic exploitation of  $\alpha$ -ketocarbene gold(I) intermediates from alkynes and pyridine-*N*-oxides as reagents by Liming Zhang.<sup>5,6</sup> These innovative methods have also been used<sup>7</sup> and further developed by our group.<sup>8,9</sup>

Now we were interested in the use of the corresponding  $\alpha$ -iminocarbene gold(I) intermediates for complex organic conversions. Instead of an *O*-transfer reagent, now an *N*-transfer reagent will be needed.<sup>10</sup> This indeed can be achieved by a number of different nitrogen heterocycles as building blocks for different types complex and highly functionalized products (for examples, see Figure 1).

Furthermore, even a selective access to specific quinoxaline *N*-oxides, which are not selectively accessible by oxidation of quinoxalines, can be opened by such methods. This is quite remarkable, as usually such *N*-oxides in transition metal catalysis are reactive reagents rather than isolable products.

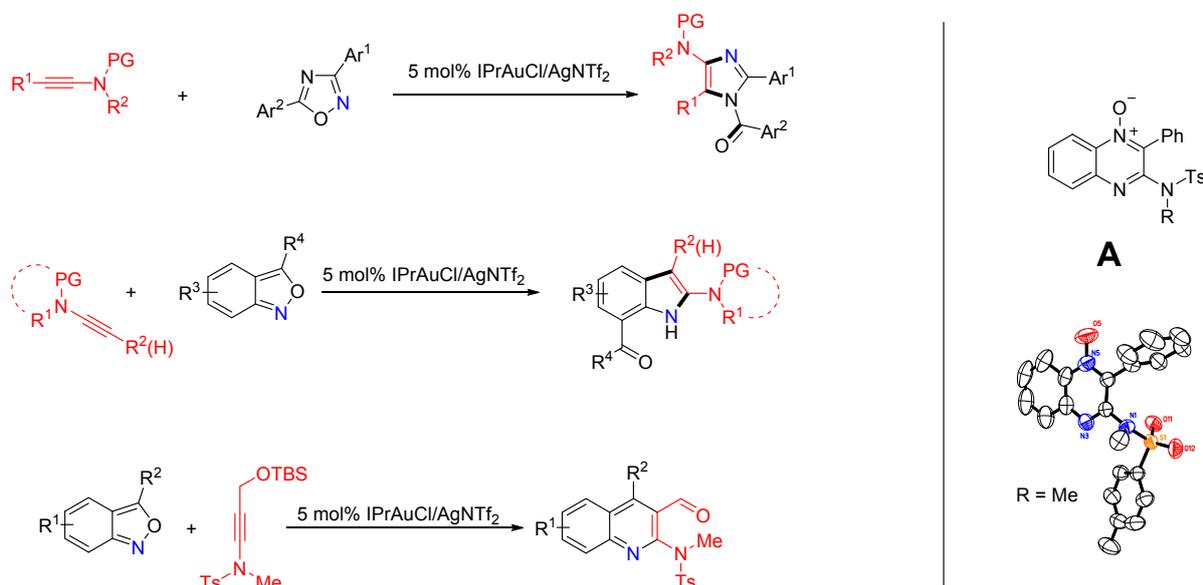


Figure 1. New reactivity patterns involving  $\alpha$ -iminocarbene gold(I) intermediates (PG = protecting group)

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Corresponding author email: hashmi@hashmi.de

# Gold(I)-Catalyzed Carboaminations of Tetrahydro- $\beta$ -carbolines to Allenes

V. Gobé<sup>1</sup>, M. Dousset,<sup>1</sup> X. Guinchard<sup>1\*</sup>

(1) Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1 av. de la Terrasse, 91198 Gif-sur-Yvette, France

The indoloquinolizine or indolizinoindole patterns are widely found in natural products possessing interesting pharmacological properties.<sup>1</sup> Over the last few years, we have been looking for new routes to these scaffolds via metalcatalyzed cyclizations of conveniently functionalized tetrahydro- $\beta$ -carbolines<sup>2</sup> allowing the ring-closure of the cycle D.

In this context, we have developed the synthesis of novel compounds from chiral *N*-allyl tetrahydro- $\beta$ -carbolines bearing an allene function, resulting from an asymmetric Pictet-Spengler reactions<sup>3</sup> catalyzed by chiral phosphoric acids between *N*-allyl tryptamines and allenaldehydes. Our first strategies relied on palladium-catalyzed tandem reactions of deprotection/ cyclization affording polycyclic compound *via* a formal hydroamination.<sup>4</sup> In this process, the allyl protecting group was lost. More recently,<sup>5</sup> we found that Au(I) catalysts promote carboaminations which result in both the ring closure and a transfer of the allyl group to the allene function. The allyl protecting group is then converted into a useful three carbon synthon. The regioselectivity of this reaction diverges depending on the substituent R<sup>2</sup>.

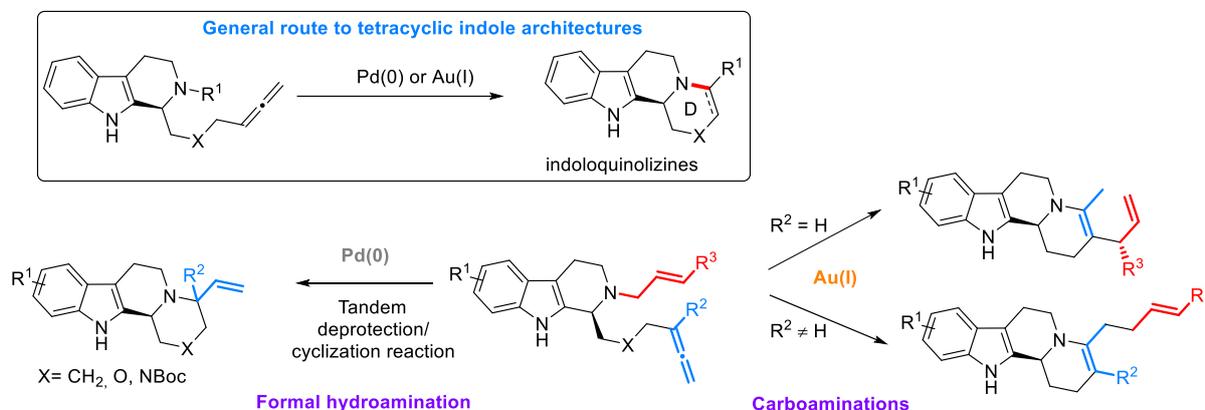


Figure 1. Au(I)-catalyzed spirocyclizations

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Corresponding author email: xavier.guinchard@cnrns.fr

# Gold(I)-Catalyzed Cascades via Ammoniumation Reactions: towards Functionalized Azacyclic Derivatives

Romain Pertschi<sup>(1)</sup>, Patrick Pale<sup>\*(1)</sup> and Aurélien Blanc<sup>\*(1)</sup>

(1) *Laboratoire de Synthèse, Réactivité Organiques et Catalyse, Institut de Chimie, UMR 7177, Strasbourg, France*

Nitrogen-containing heterocycles have always retained the attention of organic chemists considering their potent biological properties as well as their large occurrence in natural product structures.<sup>1</sup> In the past decade, the strong development of metalcatalyzed reactions using  $\pi$ -acidic metals such as platinum, palladium and especially gold, provided powerful tools toward the elaboration of complex azacyclic structures.<sup>2</sup>

In regards to the continual enthusiasm for gold-catalyzed reactions as well as the important class of azacyclic derivatives, we are developing new synthetic methods based on ammoniumation<sup>3</sup> of alkynes to gain access to five and seven-membered rings via a unique scaffold: the 2-propargylic sulfonyl azetidine derivatives **1**<sup>4</sup> (Figure 1). Depending on the external or internal nucleophilic partner used as well as the functionalization of the substrate, the key intermediate **2** can undergo to a selective ring-opening or ring-expansion of the azetidine moiety leading, respectively, to pyrroles **3**<sup>5</sup> or to tetrahydroazepine derivatives **4**, **5**, **6**.

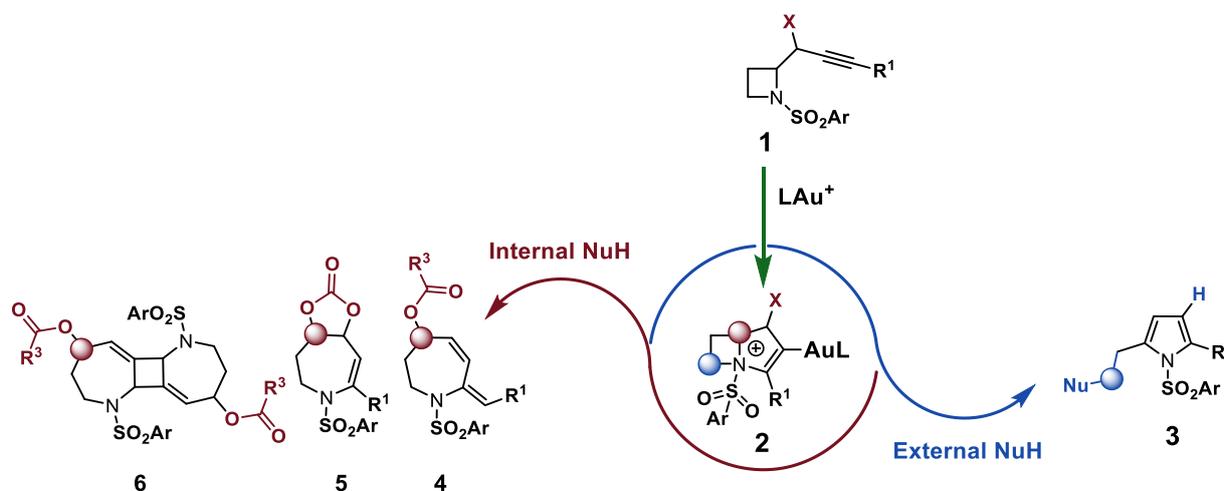


Figure 1. Gold(I)-Catalyzed Formation of Pyrroles **3** and Tetrahydroazepine Derivatives **4**, **5**, **6** from Sulfonyl Azetidine Derivatives **1**

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email: [rpertschi@unistra.fr](mailto:rpertschi@unistra.fr)

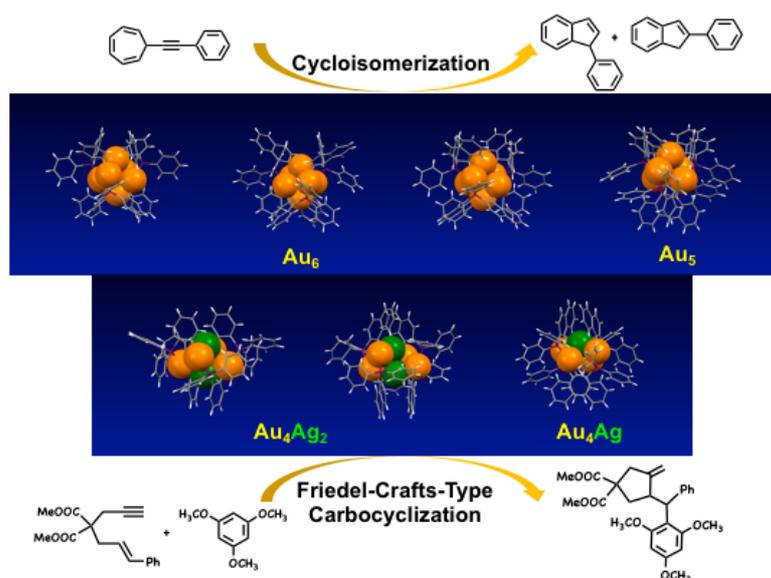
# Phosphine-Stabilized Small Gold & Gold-Silver Clusters

X.-L. Pei<sup>1</sup>, E. S. Smirnova<sup>1</sup>, A. Pereira<sup>1</sup>, A. M. Echavarren<sup>1,2\*</sup>

(1) Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, Tarragona, Spain

(2) Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Tarragona, Spain

Gold or heterometallic gold-silver systems, especially metal clusters and nanoparticles, have attracted widely research interests in these decades, due to their potential application in catalysis, sensors, bio-image and etc.<sup>1,2</sup> The increasing research work revealed that the optical properties, catalytic activity and stability are closely related with the structures.<sup>3</sup> Particularly inspired by the highly efficient catalytic activities of very small sized gold clusters in organic transformations,<sup>4,5</sup> we anticipated that small gold(I)/gold(I)-silver(I) clusters might be rationally designed by Au<sup>I</sup>/Ag<sup>I</sup> transmetalation with potentially hemilabile phosphines (*ortho*-silylphosphine ligands), based on the previous studies in hexagold clusters.<sup>6</sup> Herein, we report the successful isolation of a family of small gold and gold-silver clusters, and show their interesting structure-related activities in the activation of internal and terminal alkynes with two representative Au-catalyzed transformations: the cycloisomerization of 7-alkynyl cycloheptatriene and the tandem Friedel-Crafts-type carbocyclization of 1,6-enyne reactions. The unique structures of small gold and gold-silver clusters may provide new insights in discovering new gold or gold-silver catalysts, and also a better understanding of structure-depended catalytic activities in gold catalyzed transformations.



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Corresponding author email: xpei@icIQ.es

# Building on the Gold Catalysed Rautenstrauch Rearrangement of 1,*n*-Enyne Esters

Philip Wai Hong Chan<sup>1,2\*</sup>

(1) School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

(2) Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

In this presentation, we will disclose our recent contributions toward developing gold(I)-catalysed methodologies that are practical and of potential use in natural products and functional materials synthesis.<sup>1,2</sup> The talk will cover the current results of an on-going program focused on realising new and efficient synthetic routes to carbocycles and heterocycles from the cycloisomerisation of 1,*n*-enyne esters initiated by a Rautenstrauch rearrangement or followed by further functionalisation by a remaining pendant group.<sup>2a</sup> For example, we will present a synthetic method to prepare tricyclic bridged heptenones and hexenones from gold(I)-catalysed double cycloisomerisation of 1,11-dien-3,9-diyne benzoates. A divergence in product selectivity was achieved by fine-tuning the steric nature of the ligand of the Au(I) catalyst. In the presence of [MeCNAu(JohnPhos)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (JohnPhos = (1,1'-biphenyl-2-yl)-di-*tert*-butylphosphine) as the catalyst, tandem Rautenstrauch rearrangement/1,6-enyne addition/Cope rearrangement of the substrate was found to selectively occur to afford the bridged heptenone adduct. In contrast, changing the Au(I) catalyst to [MeCNAu(Me<sub>4</sub>*t*BuXPhos)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (Me<sub>4</sub>*t*BuXPhos = di-*tert*-butyl(2',4',6'-triisopropyl-3,4,5,6-tetramethyl-[1,1'-biphenyl]-2-yl)phosphine) was observed to result in the 1,11-dien-3,9-diyne benzoate undergoing a more rapid tandem Rautenstrauch rearrangement/[4 + 2]-cyclisation pathway to give the bridged hexenone derivative.

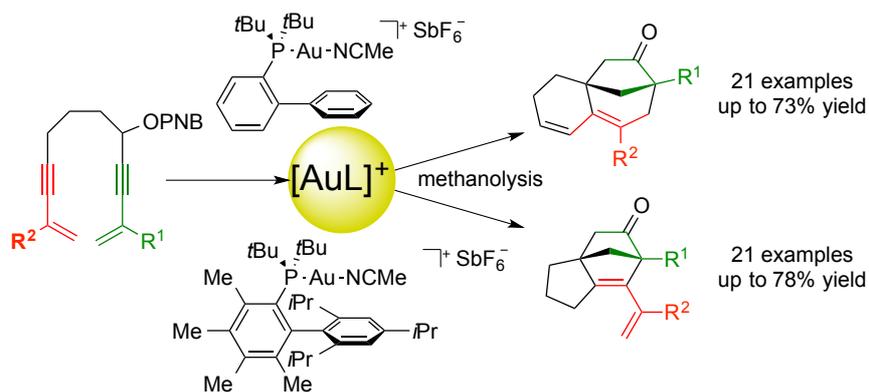


Figure 1. Ligand-Controlled Product Selectivity in Gold-Catalysed Double Cycloisomerisation of 1,11-Dien-3,9-Diyne Benzoates

## References

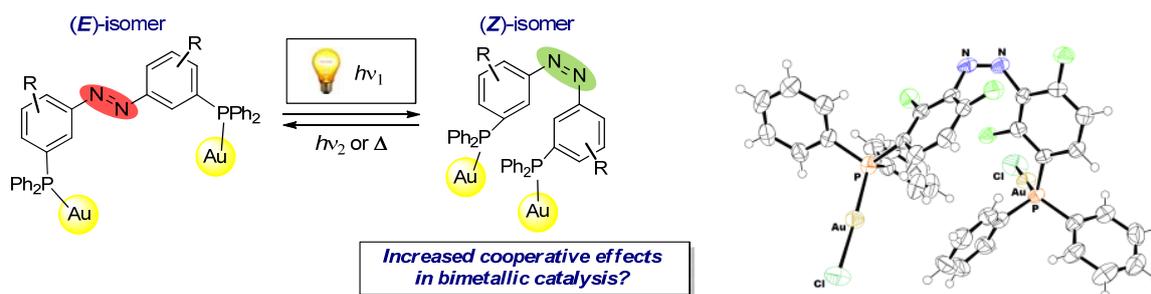
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Corresponding author email: : [phil.chan@monash.edu](mailto:phil.chan@monash.edu); [p.w.h.chan@warwick.ac.uk](mailto:p.w.h.chan@warwick.ac.uk)

# Bimetallic gold complexes of photoswitchable diphosphines

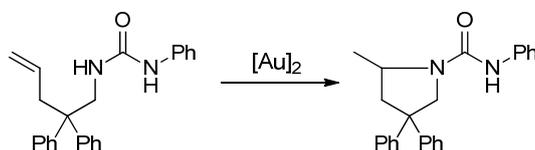
T. Arif,<sup>1</sup> J. Xie,<sup>2</sup> R. Métivier,<sup>2</sup> N. Bogliotti,<sup>2</sup> A. Voituriez,<sup>\*1</sup> A. Marinetti<sup>\*1</sup>  
(1) ICSN, CNRS UPR 2301, 1, av de la Terrasse, 91198 Gif-sur-Yvette, France  
(2) PPSM, ENS Paris-Saclay, 94235 Cachan, France

In organometallic catalysis, photoswitch phenomena have been investigated in processes involving monometallic complexes with photoswitchable ligands,<sup>1</sup> while bimetallic catalysts haven't been considered so far. Our studies proceed from the assumption that ligands photoswitch might have a particularly marked effect in catalytic reactions which involve cooperative effects between two metals. In these reactions indeed, the catalytic activity should increase when a light-induced switch between different spatial arrangements of the catalyst will bring the metals closer to each other.



## *Bimetallic gold complexes of photoresponsive, azobenzene-derived diphosphines*

The first photoresponsive bimetallic gold catalysts based on an azobenzene backbone have been prepared, their photochromic properties have been studied and the catalytic behavior has been investigated notably in an intramolecular hydroamination reaction. The reaction rate proved to be dependent on the E- or Z-configuration of the catalyst, with the Z-isomer being significantly more active.



## *Gold catalyzed intramolecular hydroamination reaction*

These preliminary results suggest that cooperative effects between the two metals might operate here, e.g. double activation of the substrate by coordination of gold(I) to both the olefin and the carbonyl groups.

The experiments above as well as additional examples of bimetallic photoswitch catalysis will be presented here.

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Corresponding author email: [angela.marinetti@cnr.fr](mailto:angela.marinetti@cnr.fr)

# Elementary Organometallic Steps at a 2,2'-Bipyridyl Ligated Gold Center

Matthew J. Harper, John F. Bower and Christopher A. Russell  
School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom

In contrast to the reactivity of Pd(0), Au(I) is reluctant to undergo oxidative addition into aryl halide bonds. This has largely precluded gold from partaking in classical  $M^{x/x+2}$  redox processes such as catalytic cross-couplings (Suzuki, Negishi, Hiyama ect.). The development of such processes is highly desirable due to the inherent lower toxicity of gold vs. palladium.

A common strategy to circumvent the “redox gold problem” is the use of external oxidants to give access the Au(I)/(III) redox couple.<sup>1,2</sup> However, this approach is not ideal as the oxidants involved (usually  $F^+$  or I(III) based) are often both expensive and highly reactive, in addition to introducing an additional waste stream.

In this work, we report that facile and reversible oxidative addition of aryl iodides to Au(I) can be achieved using the cheap and readily available 2,2'-bipyridyl (bipy) ligand.<sup>3</sup> The resulting Au(III) complexes undergo transmetalation to give bis-aryl-Au(III) complexes, which upon heating reductively eliminate to give biaryl products. This represents significant progress towards the development of oxidant free gold-catalyzed cross-coupling.

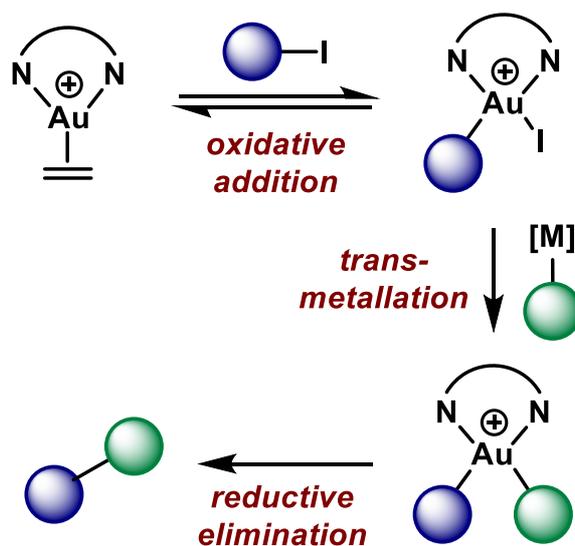


Figure 1. Oxidative addition, transmetalation and reductive elimination at a gold center.

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Corresponding author email: mh8483@bristol.ac.uk

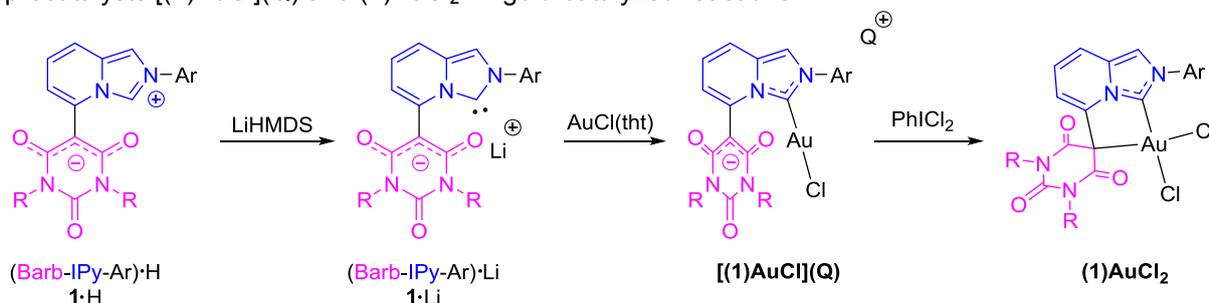
# 5-Barb-imidazo[1,5-*a*]pyridin-3-ylidene (Barb-IPy)<sup>-</sup> : A novel class of anionic, L-shape (chiral) N-Heterocyclic Carbenes for (asymmetric) gold(I) and gold(III) catalysis

Idir Benaissa,\* Mathieu Huynh, Marie-Emilie Morantin, Noël Lugan, Stéphanie Bastin, Vincent César  
*Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077, Toulouse, France*

Over the last two decades, gold catalysis has gained a considerable significance in the field of organic synthesis since it comprises atom-economic and highly efficient processes for the transformation of relatively simple substrates into valuable, highly complex molecular architectures.<sup>1</sup>

More recently, the use of hemilabile bidentate ligands based on (P,N) or (NHC-N) ligands have been introduced and appeared as a very promising strategy to access new reactivities by stabilizing highly reactive intermediates or by allowing elementary Au(I)/Au(III) redox processes.<sup>2,3,4</sup> In this context, we were interested in the development of the new class of anionic, L-shape N-Heterocyclic Carbenes **1**·Li, based on the rigid imidazo[1,5-*a*]pyridin-3-ylidene (IPy) platform and exhibiting an anionic, potentially coordinating malonate unit in close proximity to the gold center. This specific design would favor electronic interactions between the anionic heterocycle and the gold center, to a net formation of carbon-gold coordination bond, in the case of a highly electron-demanding gold center.

In this communication, we report the highly modular synthesis towards the (chiral) precursors 5-barb-imidazo[1,5-*a*]pyridinium (**1**·H), the generation of the free, stable and anionic carbenes **1**·Li and their coordination chemistry towards gold(I) and gold(III) centers, as well as the implementation of the precatalysts [(**1**)AuCl](Q) and (**1**)AuCl<sub>2</sub> in gold-catalyzed reactions.



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Corresponding author email: [idir.benaissa@lcc-toulouse.fr](mailto:idir.benaissa@lcc-toulouse.fr)

# Photoreducible Au(III) Complexes and Homogeneous Catalysis

Z. Cao<sup>1</sup>, C. Mongin<sup>1</sup>, D. M. Bassani<sup>1</sup>, B. Bibal<sup>1\*</sup>

(1) Université de Bordeaux, Institut des Sciences Moléculaires UMR 5255, Talence, France

We report a series of catalyst **L1-L4** (see Figure 1) composed of one or two lipophilic thioether side-chains that binds gold(III) chloride. Upon excitation using visible light, the Au<sup>III</sup> ions are smoothly reduced to Au<sup>I</sup>. The mechanism of reductive elimination was studied as well as the thermal reduction of these complexes.

The complexes of Au(III) and Au(I) were evaluated in classical catalysis (cyclization of propargylic amides) and in a new cascade reaction towards a fused N-heterocyclic polyaromatic compound.

When photoreduction of complex **L1** is achieved in the presence of water, crystalline gold nanoparticles of 20-50 nm diameter are obtained. Using a biphasic reactor, the photocatalyst shows average turnover numbers of 150 atoms of Au<sup>III</sup> reduced to Au<sup>0</sup> per molecule of photocatalyst.

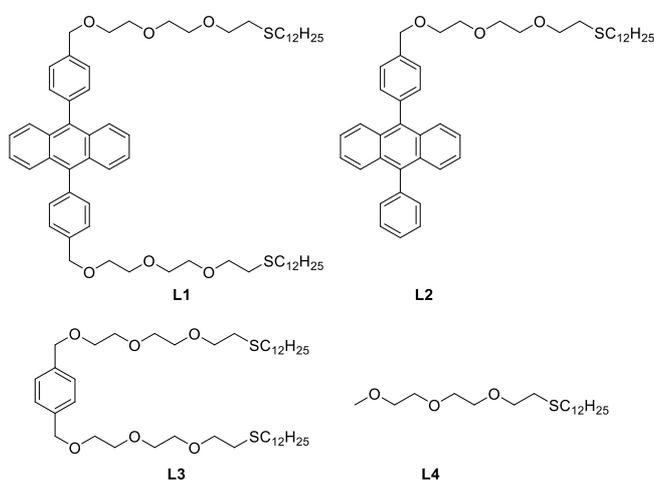


Figure 1. Thioether ligands for Gold homogeneous catalysis

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Corresponding author email: [brigitte.bibal@u-bordeaux.fr](mailto:brigitte.bibal@u-bordeaux.fr)

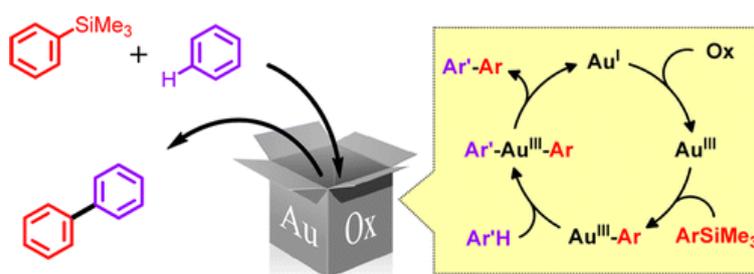
# Homogeneous gold catalysed oxidative direct arylation

LT Ball,<sup>1</sup> MH Harper,<sup>1</sup> GC Lloyd-Jones<sup>2</sup> and CA Russell,<sup>1\*</sup>

(1) School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK.

(2) School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh EH9 3JJ, U.K

Synthetic routes to industrially-important biaryls are dominated by the palladium-catalysed cross-coupling of preactivated partners. We have accessed such molecules using a homogeneous gold-catalysed oxidative coupling of arylsilanes<sup>[1,2]</sup> and simple arenes, which occurs with high selectivity and in the presence of functional groups incompatible with traditional approaches. The reaction proceeds under remarkably mild conditions – at room temperature, without the exclusion of air or moisture. The first generation systems employ non-toxic iodine(III) oxidants; advances in control of the electronic structure of the gold centres allowed development of a new set of catalysts that do not require exogenous oxidants.



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Corresponding author email: [chris.russell@bristol.ac.uk](mailto:chris.russell@bristol.ac.uk)

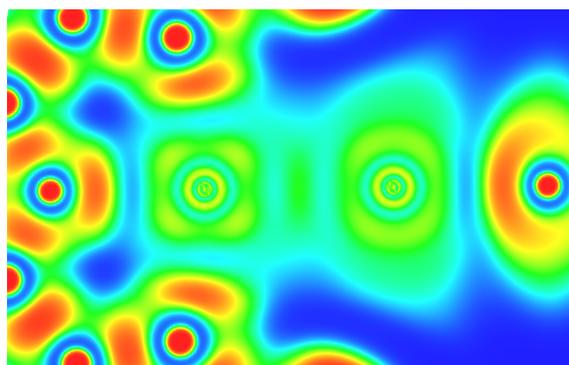
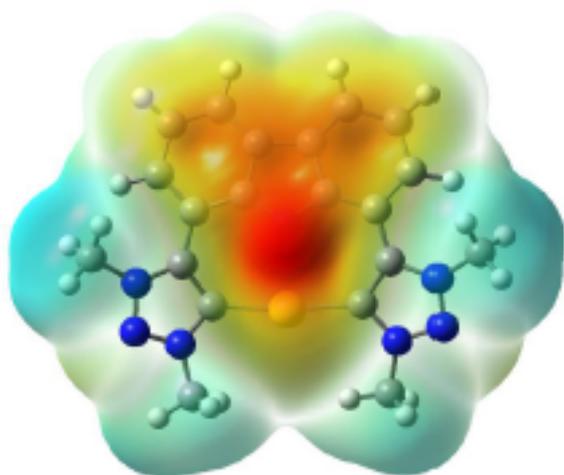
# When Gold Meets Relativity

Peter Schwerdtfeger,<sup>1</sup> Paul Jerabek,<sup>1</sup> Beatriz von der Esch,<sup>1</sup> Lisa Vondung,<sup>1</sup> and Hubert Schmidbaur<sup>2</sup>

<sup>1</sup> Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, Auckland, New Zealand.

<sup>2</sup> Department Chemie, Technische Universität München, 85747 Garching, Germany.

Gold is a rather unusual element. In spite of the similarity in the electronic structure ( $d^{10}s^1$ ) between the Group 11 elements, there are only few resemblances between these elements. Gold has an unusually large ionization potential and electron affinity reflected in the high electronegativity, gold-ligand bonds have unusually large force constants and small interatomic bond distances, dinuclear gold compounds show strong dispersive type of interactions (termed aurophilic interactions), gold halides crystallize in unusual chain structures, and gold shows interesting catalytic activities at the nano-scale range, which resulted in a new “gold rush”. Only in the past three decades has it become clear that relativistic effects are responsible for these anomalies. This talk will show typical anomalies in the chemistry of gold and will discuss relativistic effects in detail with some emphasis on gold coordination chemistry. Predictions for physical properties of the next Group 11 element with nuclear charge  $Z=111$  (Röntgenium), discovered by the GSI group in Darmstadt, are also mentioned.



# **Design and application of chelating sulfur-based ligands for selective extraction of gold using a simultaneous leaching and solvent extraction system**

S. R. Foley, H. Salimi, L. Moradi

*Department of Chemistry, University of Saskatchewan, Saskatoon, Canada*

For more than a century most of the world's gold has been recovered using the cyanide process. More effective extractants with higher selectivities are highly desirable for both environmental and economic concerns. We are interested in developing processes for the selective recovery of gold from both primary and secondary sources. In this regard, we have developed a family of chelating sulfur-based ligands which can be used in a simultaneous leaching and solvent extraction system resulting in a gold extraction process that is fast and efficient. The ligand system was found to be highly selective for gold even in the presence of huge excesses of transition metal impurities; so much so that further purification steps are not necessary to recover the gold. The key step in this process is the application of a simultaneous leaching and solvent extraction system which allows for very low acid concentrations. The process and metal-ligand coordination chemistry will be discussed in detail along with some interesting catalytic activities observed along the way.

*Corresponding author email: [stephen.foley@usask.ca](mailto:stephen.foley@usask.ca)*

# Experimental measurement of [LAuCO]<sup>+</sup> dissociation energy to probe ligand electronic effect

D. Gatineau<sup>1,2</sup>, D. Lesage<sup>2</sup>, H Clavier<sup>3</sup>, H. Dossmann<sup>2</sup>, A. Milet<sup>1</sup>, and Y. Gimbert<sup>1</sup>

(1) Univ Grenoble Alpes and CNRS, DCM (UMR 5250) BP 53, Grenoble Cedex9 France

(2) Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, 75005 Paris France

(3) Aix Marseille Univ. and CNRS, Centrale Marseille, iSm2, Marseille France.

Homogenous gold(I) catalyzed reactions are known to achieve a perfect control of chemo-, regio- and stereoselectivity in a very broad range of chemical reactions.<sup>1,2</sup> To control this selectivity, the choice of the ligand bound to the gold center is a key parameter.<sup>3</sup> Predicting the ligand electronic and/or steric influence is thus of most importance to access a very fine tuning of the reaction pathway. Well known experimental approaches developed to evaluate these effects (such as Tolman Electronic Parameter) fail nevertheless mostly in the case of Gold(I) complexes. Recently, several theoretical works succeeded in the interpretation of this particular behavior and could evidence the ability of gold to transmit electronic effects.<sup>4</sup> To strengthen these findings, experimental indication of the capability of Gold to transmit electronic effect from a ligand to another one was highly desirable. In this context, a mass-spectrometry (MS)-based work was undertaken to determine experimentally the M-CO bond dissociation energies of 16 [L-Au-CO]<sup>+</sup> complexes bearing ligands widely used in gold catalysis. Coupled to DFT calculations, this approach enables first to observe well-defined ligand effects considering the LAu-CO bond strength. Quantitative interpretation of the LAu-CO bond is further also made possible via an energy decomposition analysis (EDA).

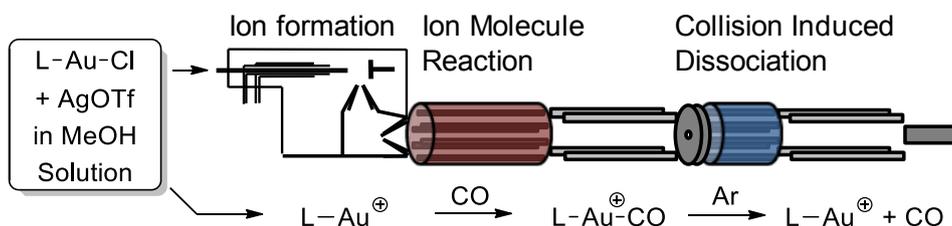


Figure 1. [L-Au-CO]<sup>+</sup> formation and dissociation inside a tandem mass spectrometer.

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Corresponding author email: [david.gatineau@univ-grenoble-alpes.fr](mailto:david.gatineau@univ-grenoble-alpes.fr)

# Gold and Hydrogen Bonding: Myth or Reality?

M. Rigoulet<sup>1</sup>, E.D. Sosa Carrizo<sup>2</sup>, K. Miqueu<sup>2</sup>, A. Amgoune<sup>1</sup>, D. Bourissou<sup>1</sup>

(1) CNRS, Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR 5069), Toulouse, France

(2) Université de Pau et des Pays de l'Adour, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (UMR 5254), Pau, Cedex 09, France

Hydrogen bonds involving transition metal centers as proton acceptors have attracted considerable attention over the last three decades. Besides their fundamental interest in terms of chemical bonding, they are also relevant to several organometallic transformations (such as the simple formation of metal hydrides by protonation). In contrast to the other transition metals,<sup>1</sup> there is so far no clear evidence for hydrogen bond to gold. A number of close Au...H contacts have been reported in crystal structures of aurides, gold(I) or gold(III) complexes, but no spectroscopic evidence for attractive Au...H interactions in solution have been reported and nothing substantiates unequivocally the presence of hydrogen bonds.<sup>2</sup> However, theoretical studies on model compounds suggest that hydrogen bonding to gold is indeed possible and actually favored energetically when an electron-rich gold(I) center bears a chelating ligand that positions a proton in close proximity to the metal.<sup>3</sup> Starting from chelating ligands, we have prepared and thoroughly characterized cationic gold(I) complexes of type **A**. The presence of N-H...Au hydrogen bonds has been unambiguously demonstrated by experimental means (NMR, IR, D-labeling...) and theoretical calculations. These data will be presented and discussed.

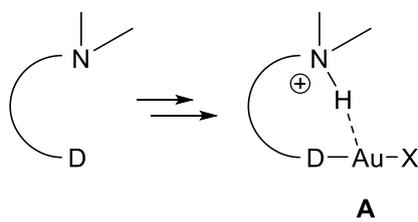


Figure 1. Schematic representation of gold complex displaying N-H...Au gold-hydrogen bonding.

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Corresponding author email: [rigoulet@chimie.ups-tlse.fr](mailto:rigoulet@chimie.ups-tlse.fr)

## Stimuli-responsive water soluble Au(I) complexes

Elisabet Aguiló,<sup>1</sup> Artur J. Moro,<sup>2</sup> Raquel Gavara,<sup>1</sup> João Carlos Lima<sup>2</sup> and Laura Rodríguez.<sup>1</sup>

(1) *Departament de Química Inorgànica i Orgànica. Secció de Química Inorgànica. Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain. Tel.: +34 934039130. e-mail:*

*laura.rodriguez@qi.ub.es*

(2) *LAQV-REQUIMTE, Departamento de Química, CQFB, Universidade Nova de Lisboa, Monte de Caparica, Portugal.*

Self-assembly of small molecules by the establishment of non-covalent interactions has received great attention in the past decade as a way to build supramolecular structures with a large number of specific functions and morphologies.<sup>1</sup> As a result, supramolecular chemistry has matured from a conceptually marvelous scientific curiosity to a technologically relevant science encompassing a broad area of advanced materials. Within this field, gold(I) complexes represent an emerging area of investigation in the last years, as they show weak Au(I)···Au(I) interactions which can modulate and govern the resulting assemblies and properties in very different potential applications.<sup>2,3</sup>

An important goal, rarely explored, is the control over the aggregation motifs in order to obtain on/off aggregated/disaggregated systems. In this work we extend the development of these small molecules by adding a chelating unit able to trigger the assembly/disassembly process by external stimuli (e.g. cations and chelating molecules). At the same time, the increase in the number of aromatic rings, will allow a change in the balance between Au···Au and  $\pi$ ··· $\pi$  interactions, which will impact on the stability of the aggregates. The complexation with cations will significantly change the electrostatic balance of the assemblies leading to dissociation. The disassembly can be reversed by the addition of molecules that compete for the metal cation, leading to reassemble of the nanostructures. Spectroscopical characterization by means of NMR, absorption, emission, optical and fluorescence microscopy, SAXS and theoretical calculations have been very useful to understand the systems.<sup>4</sup>

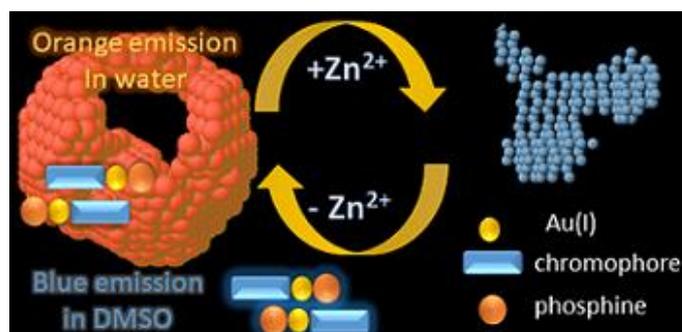


Figure 1. Schematic representation of the on/off aggregation/disaggregation motifs

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Corresponding author email: [laura.rodriguez@qi.ub.es](mailto:laura.rodriguez@qi.ub.es)

## Small-molecule functionalisation chemistry at Au(III)

M. S. M. Holmsen<sup>1</sup>, A. Nova<sup>1</sup>, M. Tilset<sup>1\*</sup>  
(1) *University of Oslo, Oslo, Norway*

Our efficient synthesis of Au(III) complexes with cyclometalated N–C ligands<sup>1</sup> paved the way to studies of small-molecule reactivity at Au(III)<sup>2–5</sup>, including the isolation and structural characterisation<sup>2</sup> of the cationic Au(III) alkene complex Me<sub>2</sub>Au(cod)<sup>+</sup>.

In this contribution, we will focus on mechanistic issues concerning the stoichiometric and catalytic reactivity of ethylene and acetylene at the Au(III) complex (tpy)Au(OAc<sup>F</sup>)<sub>2</sub> and derivatives (see Figure 1). In particular, the importance and consequences of trans effects in the reactivity of (tpy)Au(OAc<sup>F</sup>)<sub>2</sub> and its derivatives will be discussed.

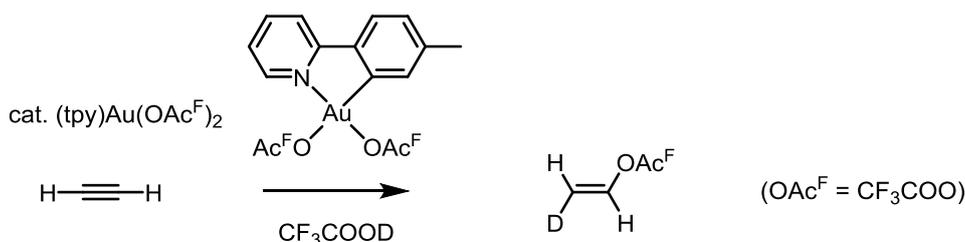


Figure 1. Catalytic functionalization of acetylene at Au(III)

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Corresponding author email: [mats.tilset@kjemi.uio.no](mailto:mats.tilset@kjemi.uio.no)

# Cyanoaurate-based Coordination Polymers as Advanced Optical Materials

D.B. Leznoff

Dept. of Chemistry, Simon Fraser University, Burnaby, Canada

My group uses cyanometallates to target coordination polymers with vapochromic, birefringent, luminescent, magnetic, negative-thermal expansion and other properties. In particular, neglected linear  $d^{10}$   $[\text{Au}(\text{CN})_2]$  units harness attractive aurophilic interactions to increase structural dimensionality.<sup>1</sup> Several property-based vignettes will be presented: simple "mineral-like"  $\text{M}[\text{Au}(\text{CN})_2]_2$  with unusual vapochromic properties;<sup>2</sup> luminescent  $\text{Cu}[\text{Au}(\text{CN})_2]$ -based thioether and related ammonia sensors,<sup>3</sup> and tunable-light emitting materials using  $\text{Ln}/\text{Au}$ <sup>4</sup> and  $\text{Cu}/\text{Au}$  systems.<sup>5</sup> Time permitting, the criteria for designing the world's most birefringent crystalline materials<sup>6</sup> will also be discussed.

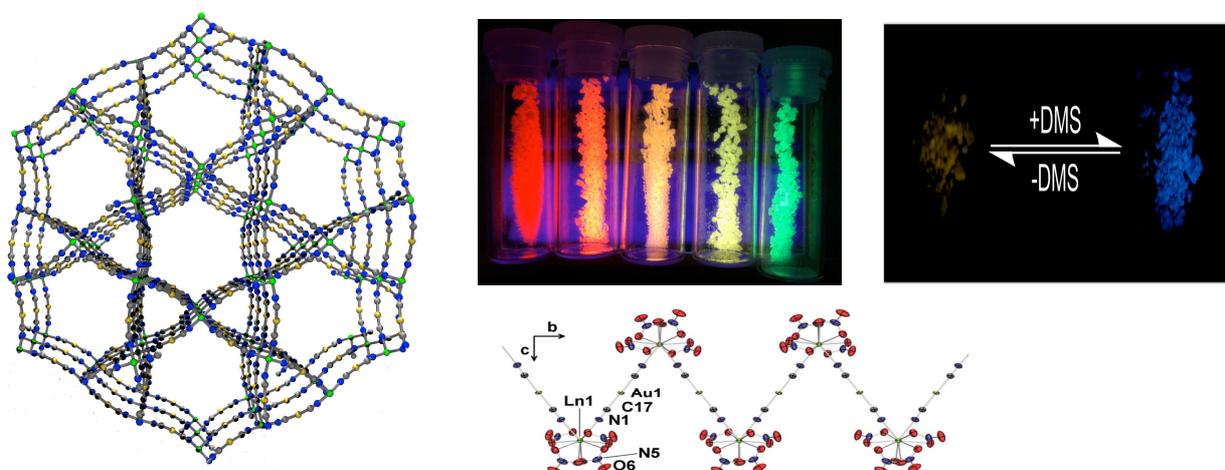


Figure (Left): Hexagonal quartz-type  $\text{Zn}[\text{Au}(\text{CN})_2]_2$  is an ammonia-sensing material. (Middle): Tuning the Ln-component of a  $\text{Ln}/\text{Au}(\text{CN})_2$ -based 1-D chain coordination polymer allows for control of the emission colour. (Right): Response of a vapoluminescent dimethylsulfide  $\text{Me}_2\text{S}$  (DMS)-sensing  $\text{Cu}/\text{Au}(\text{CN})_2$ -based material under a UV-lamp.

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Corresponding author email: [dleznoff@sfu.ca](mailto:dleznoff@sfu.ca)

# Carbene Gold Carbazole Dendrimer Complexes for the Development of the Solution-Processable Flexible OLEDs

A.S. Romanov<sup>\*1</sup>, D. Di<sup>2</sup>, L. Yang<sup>2</sup>, S. Jones<sup>2</sup>, R. Friend<sup>2</sup>, M. Linnolahti<sup>3</sup>, D. Credgington<sup>2</sup>, M. Bochmann<sup>1</sup>

(1) School of Chemistry, University of East Anglia, Earlham Road, Norwich, NR4 7TJ, United Kingdom

(2) Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge, CB3 0HE, United Kingdom

(3) Department of Chemistry, University of Eastern Finland, Joensuu Campus, FI-80101 Joensuu, Finland

Materials design becomes very important for the successful incorporation of the coinage metal complexes into organic light-emitting diodes (OLEDs) to achieve not only high efficiency and brightness but also flexibility of the OLED devices. We have recently designed numerous linear Au(I) complexes with efficient photo- and electroluminescent properties.<sup>1,2</sup> We designed highly efficient emitters based on substituted carbazoles and carbene ligands linked by a gold atom for application in the rigid and flexible OLEDs. Rotation about the gold-amide bond allows to tune the energy gap between singlet and triplet excited states ( $\Delta E(S_1-T_1)$ ) close to zero. When the gap is close to zero, facile intersystem crossing is possible which enables efficient singlet and triplet excited state harvesting (Figure 1).

Here, we present various gold complexes based on carbazole derivatives and dendrons (G0, G1 and G2). The zero generation materials are largely crystalline and possess exceptionally high external quantum efficiencies (>28% EQE) in both solution-processed and vacuum-deposited OLEDs.<sup>3</sup> Power and current efficiencies are comparable to or exceeding state-of-the-art phosphorescent OLEDs and quantum dot LEDs. First and second generation dendrimers are not only amorphous materials, which is important towards higher flexibility of the emitting layer, but also possess short excited state lifetime (100-300 ns) for the delayed emission which is important for the fabrication of the highly stable and flexible displays.

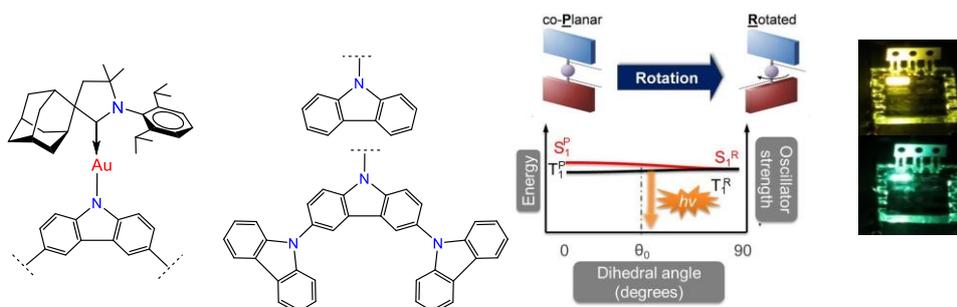


Figure 1. Gold complexes, energy diagram and OLEDs

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Corresponding author email: [asromanov5@gmail.com](mailto:asromanov5@gmail.com)

# Effect of the bis-cyclometallation ligand and temperature on luminescence of gold(III) complexes

Hayat Ayache<sup>1,2</sup>, Dalila Hammoutène<sup>2\*</sup>, Aziz Elkechai<sup>1</sup>, Camille Latouche<sup>3</sup>, Abdou Boucekine<sup>4</sup>

(1) *Laboratoire de Physique et Chimie Quantique, Université Mouloud Mammeri (UMMTO), Tizi-Ouzou, Algérie*

(2) *Laboratoire de Thermodynamique et Modélisation Moléculaire, Faculté de Chimie, USTHB, Alger, Algérie*

(3) *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, Nantes, France*

(4) *Laboratoire de Sciences Chimiques, UMR-CNRS 6226, Université de Rennes 1, Rennes, France*

A novel class of luminescent cyclometallated gold(III) alkynyl complexes has been demonstrated to possess electroluminescence (EL) properties and has been employed in the roles of electrophosphorescent emitters or dopants of organic light-emitting diodes (OLEDs) with high brightness and efficiency<sup>[1-3]</sup>.

This work focuses on the effect of the bis-cyclometallation ligand in order to investigate how ligand affects the luminescence properties of the resulting gold (III) complexes<sup>[4]</sup>. Our complexes include a diphenyl-pyridine metallacycle with a terminal R1 group and an alkynyl ligand bearing a radical R2, namely  $[\text{Au}(\text{HC}^{\wedge}\text{N}(\text{R}1)^{\wedge}\text{CH})(\text{C}\equiv\text{CR}2)]$ . Absorption and emission properties of our compounds were performed by density functional theory (DFT) and TD-DFT calculations, using the hybrid functional PBE0 associated with a double zeta basis of atomic orbitals, in addition with the polarization functions LANL2DZ, as implemented in the Gaussian 09 package.

Obtained results show that the nature of the ligands influences greatly the geometry and the molecular orbital borders. In addition, the phosphorescence wavelength of these complexes was estimated. It appears to be dependent on both the surrounding environment and the nature of the R1 and R2 end groups. Temperature effects have been considered to improve the simulated spectrum, when is taken into account, the simulated and observed spectra fit much better.

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Corresponding author email: [dhammoutene@yahoo.fr](mailto:dhammoutene@yahoo.fr)

# Self-assembly of gold(I) alkynyl phosphine: impact on the photophysical pathways

Artur Moro<sup>1</sup>, Elisabet Aguiló<sup>2</sup>, João Pina,<sup>3</sup> Sérgio Seixas de Melo,<sup>3</sup> Laura Rodríguez<sup>2</sup>, J.C. Lima<sup>1\*</sup>

<sup>1</sup>REQUIMTE-LAQV, Chemistry Department, School of Science and Technology, University NOVA de Lisboa, 2829 516 Campus da Caparica, Lisboa, Portugal.

<sup>2</sup>Department of Inorganic and Organic Chemistry. Inorganic Chemistry section., Universitat de Barcelona, c/Martí i Franquès, 1-11, 08028 Barcelona, Spain.

<sup>3</sup>Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal

\*e-mail: lima@fct.unl.pt

Gold(I) complexes exhibit interesting emissive properties that usually are modulated by the presence of aurophilic (Au...Au) interactions.[1-4] These interactions are a consequence of the strong relativistic effects displayed by gold atoms and their energy can range from 29-46 kJ/mol[5] which is comparable to that of strong hydrogen bonds.[6] We demonstrated for a series of dinuclear [(diphos){(4-pyridyl)ethynyl gold(I)}<sub>2</sub>] complexes that the occurrence of aurophilic interactions in the solids produced and enhancement of the radiative rate constant and emission quantum yield due to the favoured intersystem crossing to the ground state, promoted by the approaching of the gold(I) atoms and the subsequent increasing of the spin-orbit-coupling.

Our recent results on the formation of hydrogels from small organometallic complexes containing Au(I)-alkynyl moieties,[7-9] prompted us to go one step further in the design and synthesis of supramolecular nanostructures constituted by self-assembly of small molecules, where the supramolecular packing is modulated by Au...Au interactions. The aim of the present work is to analyze the effect of the Au...Au interactions on the photophysical properties of these supramolecular nanostructures, through the use of femtosecond time resolved spectroscopy.

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# 1D and 2D Gold(I)-Thiophenolate-based Coordination Polymers, a Rich Palette of Photophysical Properties

O. Veselska,<sup>1</sup> N. Guillou,<sup>2</sup> G. Ledoux,<sup>3</sup> A. Fateeva,<sup>4</sup> A. Demessence<sup>1\*</sup>

(1) IRCELYON, UMR CNRS 5256, Université Claude Bernard Lyon 1, Villeurbanne, France.

(2) ILV, UMR CNRS 8180, Université de Versailles Saint-Quentin-en-Yvelines, Versailles, France.

(3) ILM, UMR CNRS 5306, Université Claude Bernard Lyon 1, Villeurbanne, France.

(4) LMI, UMR CNRS 5615, Université Claude Bernard Lyon 1, Villeurbanne, France.

Hybrid Au(I) compounds exhibit a large domain of applications such as electronic devices, contrast agents, sensors or photocatalysts. These applications are related to the ability of gold(I) to form aurophilic interactions implying self-assembly and luminescence.<sup>1</sup> Among them, gold(I) thiolates are an important class of materials, due to the soft-soft interaction between Au(I) and thiolates, and their potential to form self-assembled monolayers, to protect and functionalize gold clusters and nanoparticles and to generate oligomeric or polymeric species, used for a long time as antiarthritic agents. However due to the fast precipitation and the insolubility of these solids, a little is known about their structure making the origin of the photoluminescence difficult to rationalized.<sup>2</sup> Here, we present the syntheses and the first structure resolutions, by powder X-Ray diffraction, of series of gold(I)-thiophenolate-based coordination polymers,  $[\text{Au}(\text{SPhR})]_n$ . Depending on the substituent and its position, different chain-like and lamellar structures are obtained (Fig. 1).<sup>3</sup> The photophysical properties of these hybrid materials are analyzed in solid-state and coupled with DFT calculations. These studies show different origins of the charge transfers depending on the electrophilicity of the thiolate molecules coupled with the participation or not of the aurophilic interactions. Among those coordination polymers, some exhibit high quantum yield around 70 % at room temperature and in the solid state,<sup>3b</sup> another one shows an rare switch ON of the emission with a thermally induced solid-state phase change from amorphous to crystalline.<sup>3a</sup> When the mercaptobenzoic acids are used in *ortho* and *para* positions, the structures of the resulting  $[\text{Au}(\text{SPhCO}_2\text{H})]_n$  coordination polymers are 1D and 2D, respectively. Thus their photoluminescent properties are distinct,  $[\text{Au}(\text{o-SPhCO}_2\text{H})]_n$  presents thermally induced delayed fluorescence (TADF) phenomenon and in the case of the  $[\text{Au}(\text{p-SPhCO}_2\text{H})]_n$ , its dual emission, associated with luminescence thermochromism was highlighted as intrinsic and ratiometric optical temperature sensor.<sup>3c</sup> These different examples shed light on the great potential of gold thiolate coordination polymers as emerging hybrid materials for diverse optical applications.

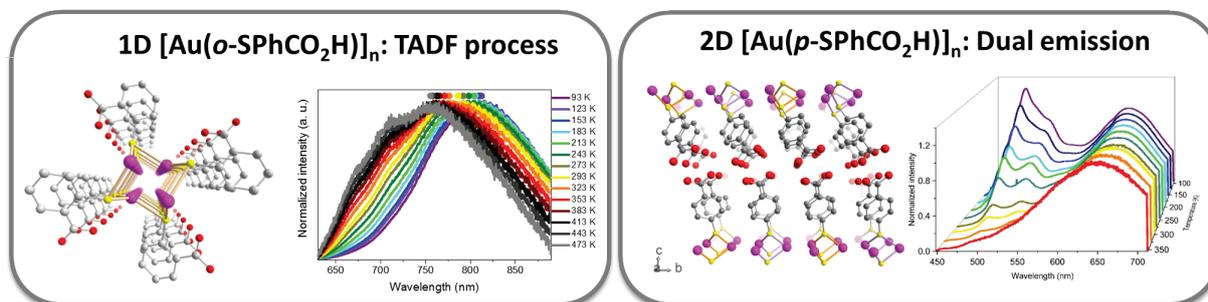


Figure 1. Structures and photoluminescent properties in the solid state of  $[\text{Au}(\text{o-SPhCO}_2\text{H})]_n$  and  $[\text{Au}(\text{p-SPhCO}_2\text{H})]_n$ .

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Corresponding author email: [aude.demessence@ircelyon.univ-lyon1.fr](mailto:aude.demessence@ircelyon.univ-lyon1.fr)

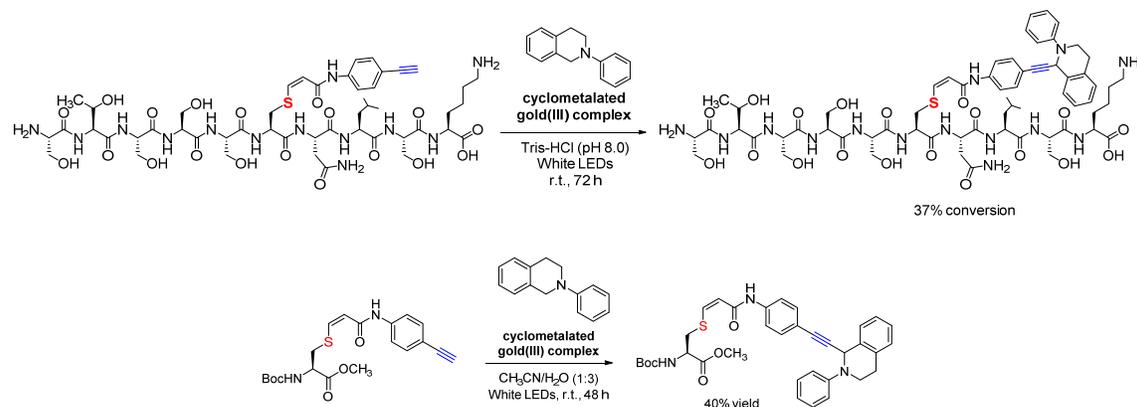
# Gold-Catalyzed Photooxidative Alkynylation of Tetrahydroisoquinolines using Visible Light

Man Kin Wong,\* Jie-Ren Deng, and Rui Tang

State Key Laboratory of Chirosciences and Department of Applied Biology and Chemical Technology,  
The Hong Kong Polytechnic University, Hung Hum, Hong Kong, China

Gold catalysis has contributed to a variety of conceptually new synthetic methods greatly facilitating organic synthesis with excellent reactivity, selectivity, and operational simplicity. Visible light photoredox catalysis providing efficient pathways for selective functionalization of organic compounds has emerged as a fast expanding research area in organic chemistry. Combining the unique strengths from the two areas, synergistic use of gold and visible light photoredox catalysis would provide green, efficient, and sustainable synthetic technologies for selective chemical synthesis that would not be possible by employing either one of the catalysis approaches.

We have developed a diversity-oriented synthesis of a new class of fluorescent quinolizinium compounds *via* a photosensitizer-free visible light-mediated gold-catalyzed *cis*-difunctionalization of silyl-substituted alkynes.<sup>[1]</sup> Spectroscopic experiments revealed that the fluorescent quinoliziniums exhibit full color tunable emission properties in visible light region ( $\lambda_{em} = 450$  to  $640$  nm) and large Stokes shifts (up to  $6,797$   $\text{cm}^{-1}$ ). Built upon this work, we set out to explore the combination of gold and visible light photoredox catalysis for alkylation of tetrahydroisoquinolines. We found that treatment of tetrahydroisoquinolines with terminal alkynes and a catalytic amount of cyclometalated gold(III) complexes afforded alkynylated products with up to 73% isolated yields under irradiation (White, LEDs 5W) in 48 h under air at room temperature. Interestingly, the product distribution varied with substituents on the terminal alkynes. More favorable alkylation was found by using electron-donating 4-ethynylanisole. In addition, we have employed the newly developed gold and visible light photoredox catalysis for multifunctional modification of peptides and proteins in aqueous medium.



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Corresponding author email: [mankin.wong@polyu.edu.hk](mailto:mankin.wong@polyu.edu.hk)

# A One "Click" Synthesis to Supramolecular Metallopeptide-Based Amphiphiles and Their pH-Responsive Self-Assembly in Water

V. Lewe\* and P. Besenius

Johannes Gutenberg-University, Organic Chemistry Institute, Duesbergweg 10-14, 55128 Mainz and Graduate School Materials Science in Mainz, Staudingerweg 9, 55128 Mainz.

The promising properties of peptide-based supramolecular materials in water rely on their stimuli-responsiveness to manipulate the self-assembling process.<sup>[1]</sup> The synthesis of water-soluble Au(I)-metallopeptides is a challenging task and has gained increased attention as Au(I) provides interesting material properties. Beyond water-soluble alkynyl-Au(I) complexes for post-functionalisation with biomacromolecules,<sup>[2a]</sup> Besenius and coworkers reported the synthesis of peptidic Au(I)-phosphane complexes for kinetically controlled stepwise self-assembly in water<sup>[2b]</sup> or the charge regulated supramolecular aggregation leading to a variety of nanostructured morphologies.<sup>[2c]</sup>

Herein we introduce a facile synthetic access to supramolecular (bio)organic-inorganic Au(I)-hybrid materials based on copper(I) mediated alkyne-azide 1,3-cycloaddition as keystone. The presented synthetic strategy of the late introduction of Au(I) was realised with N-heterocyclic carbenes known for strong  $\sigma$ -donor ligand properties and their tunable and planar structure. This modular approach led to a small library of Au(I)-peptide building blocks with selected amino acid sequences from hydrophobic to charge containing side chains in water. Their supramolecular self-assembly into nanorods was investigated with circular dichroism (CD) spectroscopy and transmission electron microscopy (TEM) showing pH and ionic-strength dependent aggregation.

In a future perspective, the peptidic Au(I)-hybrid materials are envisaged to allow intermolecular shortened Au(I)···Au(I) interactions and resultant photoluminescent properties will be investigated.

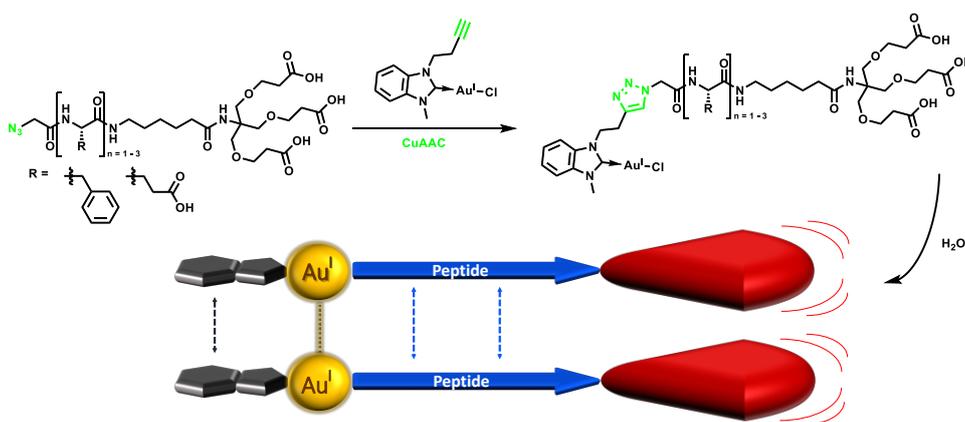


Figure 1. Preparation synthesis route with a copper(I) mediated alkyne-azide 1,3-cycloaddition as final step to Au(I)-metalloamphiphiles.

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Corresponding author email: vlewe@uni-mainz.de

# Pyrazine-based cyclometalated ( $C^{\wedge}N^{PZ^{\wedge}}C$ )Au(III) complexes: from simple NHC complexes to bioconjugates

B. Bertrand,<sup>\*1</sup> M. Williams,<sup>1</sup> A. I. Green,<sup>1</sup> J. Fernandez-Cestau,<sup>1</sup> M. Searcey,<sup>1,2</sup> Z. A. E. Waller,<sup>2</sup> M. A. O'Connell,<sup>2</sup> M. Bochmann<sup>1</sup>

(1) School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, UK

(2) School of Pharmacy, University of East Anglia, Norwich, NR4 7TJ, UK

Gold complexes are widely studied as potential new anti-cancer agents.<sup>1,2</sup> Biscyclometalated Au(III) complexes are particularly known for their stability under physiological conditions and their promising cytotoxic properties.<sup>3</sup> We have demonstrated the potential of a pyrazine-based ( $C^{\wedge}N^{PZ^{\wedge}}C$ )Au(NHC) complex (A figure 1) as anticancer treatment. However, the compound suffered from a certain lack of selectivity for cancer cells.<sup>4</sup> We thus explored various strategies to conjugate our known pharmacophore to different biovectors to improve the selectivity of the drug. We have investigated the possibility to attach some amino acid derivatives to the ( $C^{\wedge}N^{PZ^{\wedge}}C$ )Au(III) scaffold via an open chain carbene ligand.<sup>5</sup> We have also explored the synthesis of a ( $C^{\wedge}N^{PZ^{\wedge}}C$ )Au(NHC) platform bearing a pentafluorophenyl ester moiety for the conjugation with several vectors including biotin and estradiol derivatives. We measured the cytotoxicity of the complexes against a panel of different human cancer cell lines. We could assess the targeting ability of the vectors by ICP-MS as well as their impact on the interaction of the ( $C^{\wedge}N^{PZ^{\wedge}}C$ )Au(NHC) core with an example of potential intracellular target.

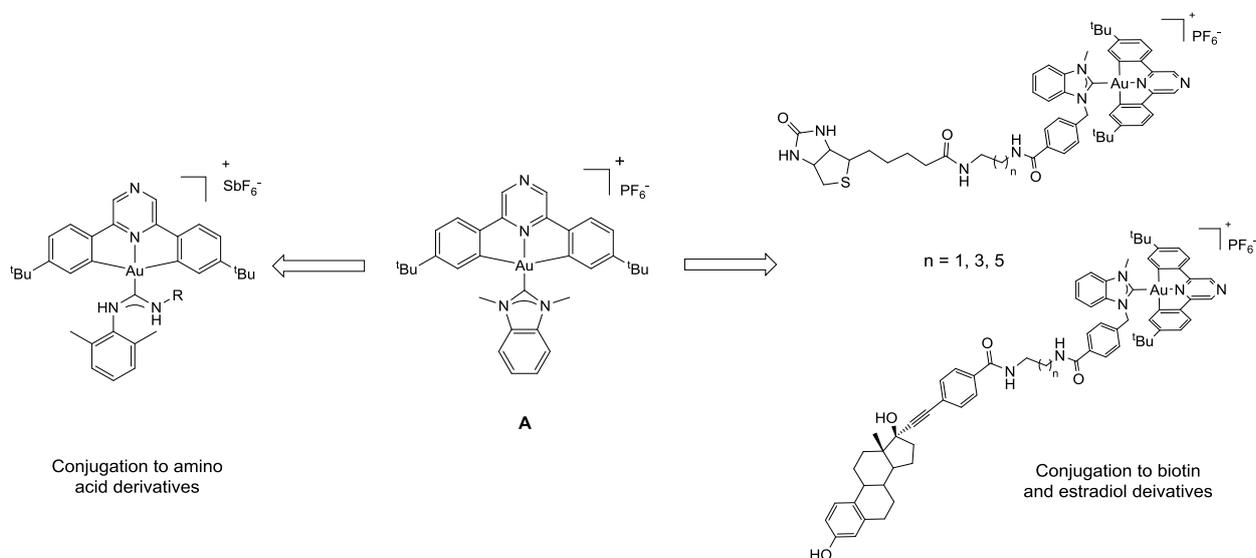


Figure 1. Scheme of the bioconjugated ( $C^{\wedge}N^{PZ^{\wedge}}C$ )Au(III) carbene complexes.

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Corresponding author email: benoit.bertrand1988@gmail.com

# Application of Mono- and Dinuclear Gold Complexes in Photochemistry

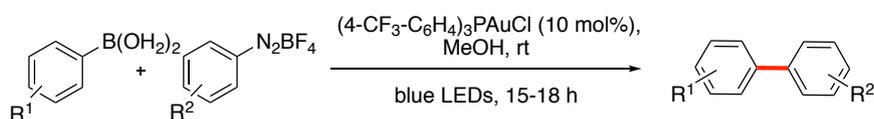
S. Witzel<sup>1,\*</sup>, J. Xie<sup>2</sup>, A. S. K. Hashmi<sup>1</sup>

(1) Institute of Organic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

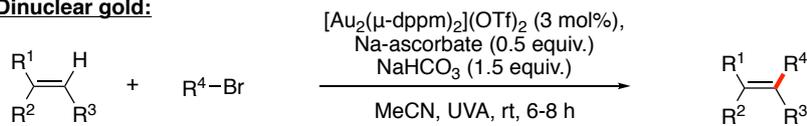
(2) School of Chemistry and Chemical Engineering, Nanjing University, Hankou Road 22, 210093 Nanjing, China

Visible light photoredox catalysis has recently experienced a revival and today functions as a versatile tool in organic chemistry, allowing alternative strategies towards synthetically useful scaffolds.<sup>1,2</sup> In these systems, photoactive complexes, such as ruthenium or iridium, or organic dyes are employed to initiate organic reactions.<sup>3,4</sup> These photosensitizers are often combined with a second catalyst, which completes the coupling or cyclization. Hashmi *et al.* have focused their efforts on developing novel photoredox methodologies only mediated by a gold catalyst (see Scheme 1).<sup>5-8</sup>

## Mononuclear gold:



## Dinuclear gold:



Scheme 1. Selected “gold-only”-catalysed photoredox reactions with mono- and dinuclear gold complexes.

The reactions proceed under very mild reaction conditions and show a broad functional group tolerance.

The latest applications of the photosensitizer-free cross-coupling catalysed by a mononuclear gold complex as well as novel photoredox catalytic systems using dinuclear gold complexes will be presented.

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Corresponding author email: [sina.witzel@oci.uni-heidelberg.de](mailto:sina.witzel@oci.uni-heidelberg.de)

# Gold(I) Catalysis Under Visible Light

Z. Xia\*, L. Fensterbank, V. Mouriès-Mansuy, C. Ollivier

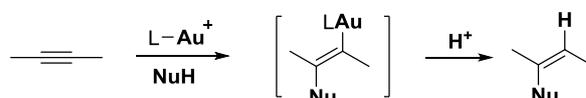
Institut Parisien de Chimie Moléculaire, (UMR 8232) Sorbonne Université, 4 place Jussieu, 75005 Paris, France

Homogeneous gold catalysis has received great attention over the last decade.<sup>1</sup> The selective activation of the carbon-carbon multiple bond by the gold complex generally constitutes the preliminary triggering event of the catalytic cycle.<sup>2</sup> In the vast majority of cases, the organogold species generated upon nucleophilic attack undergoes protodemetalation leading to hydrofunctionalized products (Figure 1a).

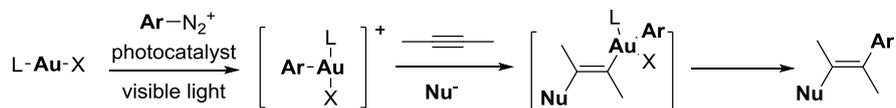
Recently, the groups of Glorius, Toste and Hashmi<sup>3</sup> reported a dual gold and photoredox catalytic difunctionalization of alkynes. In these transformations, the aryldiazonium salts deliver aryl radicals under the visible light irradiation, then these radicals add to the gold catalyst, coordinate to alkynes and give the arylated compound rather than the hydrofunctionalized products (Figure 1b).

In 2016, we reported a dual photoredox/gold catalysis arylation cyclization of *ortho*-alkynylphenols with aryl diazonium salts: a flexible synthesis of benzofurans (Figure 1c-i).<sup>4</sup> In our latest work, we developed a new method for the synthesis of valuable alkynyl benzofuran derivatives devised from *o*-alkynylphenols and iodoalkynes in the presence of a catalytic mixture of Au(I) and Ir(III) under blue LED irradiation (Figure 1c-ii).<sup>5</sup> The mechanism of these transformation is actively studied and the different results along these lines will be presented.

a) Gold-catalyzed nucleophilic addition to alkynes



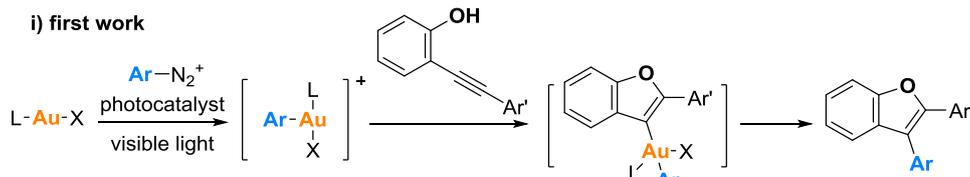
b) Dual Au and photoredox catalytic difunctionalization of alkynes



Glorius (2013), Toste (2014), Hashmi (2016)

c) Our work: gold(I) catalysis under visible light

i) first work



Fensterbank, et al. (2016)

ii) second work

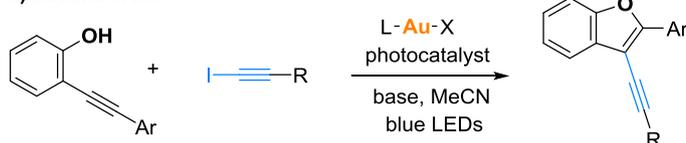


Figure 1. Gold-Catalyzed Additions to Alkynes

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Corresponding author email: zhonghua.xia@sorbonne-universite.fr