ChemPubSoc Europe
DOI: 10.1002/chem.201600710
CHEMISTRY
A European Journal
Communication

Photoredox Catalysis

Alkyne Difunctionalization by Dual Gold/Photoredox Catalysis

Adrian Tlahuext-Aca, Matthew N. Hopkinson[+], R. Aleyda Garza-Sanchez[+], and Frank Glorius*[a]

Abstract: Highly selective tandem nucleophilic addition/cross-coupling reactions of alkynes have been developed using visible-light-promoted dual gold/photoredox catalysis. The simultaneous oxidation of Au^{I} and coordination of the coupling partner by photo-generated aryl radicals, and the use of catalytically inactive gold precatalysts allows for high levels of selectivity for the cross-coupled products without competing hydrofunctionalization or homocoupling. As demonstrated in representative arylative Meyer–Schuster and hydration reactions, this work expands the scope of dual gold/photoredox catalysis to the largest class of substrates for gold catalysts and benefits from the mild and environmentally attractive nature of visible-light activation.

Homogeneous gold catalysis has emerged as a powerful tool in organic synthesis during the last 16 years. This chemistry mostly relies on the use of Au^{I} or Au^{III} complexes as ligand-tunable soft, carbophilic Lewis acids, which are able to selectively activate unsaturated molecules, such as allenes, alkenes and, especially, alkynes towards nucleophilic attack.[1] Whereas a wide range of different intra- and intermolecular nucleophiles may be employed in these processes, in the vast majority of cases, the organogold species generated upon nucleophilic attack undergoes proto-demetalation leading to hydrofunctionalized products (Scheme 1 a).[2] A promising strategy to expand the scope of such reactions involves engaging the organogold intermediates in a cross-coupling process mediated by a Au^{I}/Au^{III} redox cycle.[3] The high potential of the Au^{I}/Au^{III} couple ($E_0 = +1.41$ V),[4] however, means that strong external oxidants, such as Selectfluor®, *t*BuOOH or hypervalent iodine species are generally required.

Ensuring high selectivity for the desired cross-coupled products in these reactions, however, remains a major challenge. In most cases, a Au^{I} precatalyst is converted under the reaction conditions to a coordinatively unsaturated cationic species, which then activates the π-system towards nucleophilic attack. In order for the resulting organogold(I) species (**A**) to selectively engage in coupling, the three-stage sequence of oxidation to Au^{III}, transmetalation of the coupling partner, and reductive elimination must outcompete conventional proto-demetalation (Scheme 1 b). As a result, most selective gold-catalyzed coupling reactions reported to date have focused on specific alkene[5a] or allenoate[5b] substrates, for which the corresponding organogold(I) species **A** are comparatively less prone to proto-demetalation.[5c,d] In particular, coupling reactions of alkynes, which represent the largest class of substrates for gold catalysis, are especially challenging with conventional hydrofunctionalization often dominating. Furthermore, independent oxidation and coordination steps can lead to low selectivity for cross-coupling over competing homodimerization.

As complementary strategy to access Au^{I}/Au^{III} redox cycles without strong external oxidants, our group disclosed a redox-neutral approach by merging gold and visible-light photoredox catalysis.[6] In our initial studies, aryldiazonium or diaryliodonium salts were employed as arylating reagents in intra- and intermolecular oxyarylation reactions of unactivated alkenes,[7a,b] while impressive applications of the concept to related arylative ring expansion and allenoate cyclization processes have since been reported by the groups of Toste[7c] and Shin,[7d] respectively. The same visible-light-promoted strategy has also led to the development of gold-catalyzed cross-coupling methodologies involving P–H[8a] and C(sp)–H bond functionalization.[8b,c]

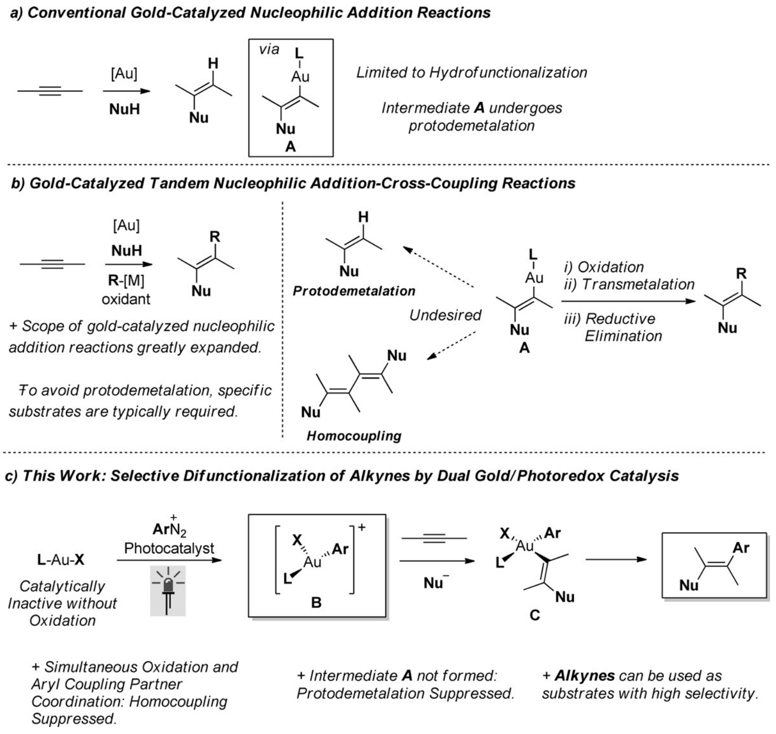
Several features of dual gold/photoredox catalysis indicate that this approach may be inherently better suited to imparting high selectivities for difunctionalized, cross-coupled products in gold-catalyzed tandem nucleophilic addition reactions (Scheme 1 c). In this system, Au^{I} is oxidized in a stepwise fashion by photo-generated aryl radicals leading to cationic Au^{III} species **B**, which already bears the aryl coupling partner. Coordination of the π-system then leads selectively to the cross-coupling product via intermediate **C**, without competing homodimerization. Furthermore, coordinatively-saturated Au^{I} complexes, such as [Ph_3PAuCl], which themselves are not catalytically-active, can be successfully employed without preactivation. As such, organogold(I) species **A**, which are prone to proto-demetalation, are not formed with coordination to the π-system taking place only once photo-mediated oxidation to the arylgold(III) species **B** has occurred. Indeed, previous studies by Toste and co-workers have shown that arylative ring expansion can be favored with reactive allenes,[7c] whereas no diyne homocoupling products were observed during our stud-

---

[a] *A. Tlahuext-Aca, Dr. M. N. Hopkinson,[+] R. A. Garza-Sanchez,[+]
Prof. Dr. F. Glorius
NRW Graduate School of Chemistry, Organisch-Chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstraße 40, 48149 Münster (Germany)
E-mail: glorius@uni-muenster.de*

[+] *These authors contributed equally to this work.*

Supporting information and the ORCID identification number for the author of this article can be found under http://dx.doi.org/10.1002/chem.201600710.

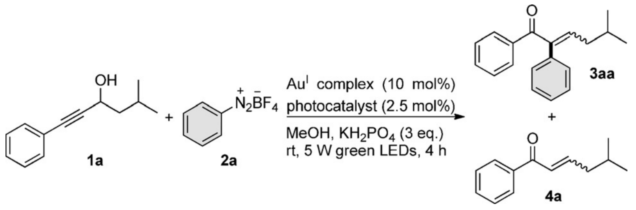


Scheme 1. Mechanistic pathways accessible to gold catalysts during tandem nucleophilic addition/cross-coupling reactions with π-systems.

ies on the dual gold/photoredox-catalyzed Sonogashira–Hagihara reaction.[8b] Herein, we report the successful application of these concepts in challenging tandem nucleophilic addition/arylation reactions of alkynes. Focusing on two benchmark gold-catalyzed transformations, the Meyer–Schuster rearrangement of propargyl alcohols and the hydration of simple alkynes, dual gold/photoredox catalysis delivered the cross-coupled, arylated products with high selectivity without competing homodimerization or hydrofunctionalization typically observed with these substrates.

As an initial study, the well-established Meyer–Schuster rearrangement of easily prepared propargyl alcohols **1** was selected as a representative alkyne nucleophilic addition reaction. This formal 1,3-hydroxyl migration process has attracted widespread attention as a powerful method to access enone compounds, which are feedstocks for synthetically important processes, such as Diels–Alder cycloadditions, Michael additions, and catalytic hydrogenations.[9] An arylative version of a related rearrangement of propargyl acetates with arylboronic acids was disclosed in a seminal report by Zhang and co-workers in 2009 using Selectfluor® as an external oxidant. However, in this study, the competing formation of enones, enone dimers, and fluoroenones, resulting from conventional hydrofunctionalization, homocoupling, and fluorination, respectively, was observed.[9c] Taking the conditions from our previous studies,[7a] substrate **1a** was reacted with benzenediazonium tetrafluoroborate (**2a**) in the presence of the photoredox catalyst [Ru(bpy)$_3$](PF$_6$)$_2$ (2.5 mol%; bpy = 2,2′-bipyridine) and the Au^I complex [Ph$_3$PAu]NTf$_2$ (10 mol%; Tf = trifluoromethanesulfonyl) under visible-light irradiation in MeOH for 4 h (Table 1, entry 1). As predicted, no formation of the desired α-arylenone product **3aa** was observed using this Au^I complex catalyst and enone **4a**, resulting from the conventional Meyer–Schuster rearrangement, was instead obtained in 20% NMR yield. The weakly coordinating $^-$NTf$_2$ counterion in [Ph$_3$PAu]NTf$_2$ is thought to dissociate in solution and release catalytically active cationic Au^I,

Table 1. Reaction optimization.[a]



Entry	Au^I Complex	Photocatalyst	Yield [%] (E/Z)[b]
1[c]	[Ph$_3$PAu]NTf$_2$	[Ru(bpy)$_3$](PF$_6$)$_2$	**3aa**: 0; **4a**: 20
2[c]	[Ph$_3$PAuCl]	[Ru(bpy)$_3$](PF$_6$)$_2$	78 (88:12)
3	[Ph$_3$PAuCl]	[Ru(bpy)$_3$](PF$_6$)$_2$	78 (**71**) (>95:5)
4	[((4-MeO)C$_6$H$_4$)$_3$PAuCl]	[Ru(bpy)$_3$](PF$_6$)$_2$	56 (>95:5)
5	[Cy$_3$PAuCl]	[Ru(bpy)$_3$](PF$_6$)$_2$	79 (>95:5)
6	[IPrAuCl]	[Ru(bpy)$_3$](PF$_6$)$_2$	–
7[d]	[Ph$_3$PAuCl]	eosin Y	72 (>95:5)
8[e]	[Ph$_3$PAuCl]	fluorescein	68 (>95:5)
9[f]	[Ph$_3$PAuCl]	[Ru(bpy)$_3$](PF$_6$)$_2$	78 (>95:5)
10[g]	[Ph$_3$PAuCl]	[Ru(bpy)$_3$](PF$_6$)$_2$	71 (84:16)

[a] General conditions: **1a** (0.10 mmol), **2a** (0.40 mmol), photocatalyst (2.5 mol%), gold complex (10 mol%), and MeOH (1.0 mL) under argon. [b] NMR yields using CH$_2$Br$_2$ as internal standard; isolated yield in bold; unless otherwise stated, enone **4a** was not observed in any case. [c] No base. [d] Eosin Y (5 mol%), 12 h. [e] Fluorescein (5 mol%), 12 h. [f] 5 W Blue LEDs or 23 W CFL, 4 h. [g] Sunlight, 3 h. See the Supporting Information for details. IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene.

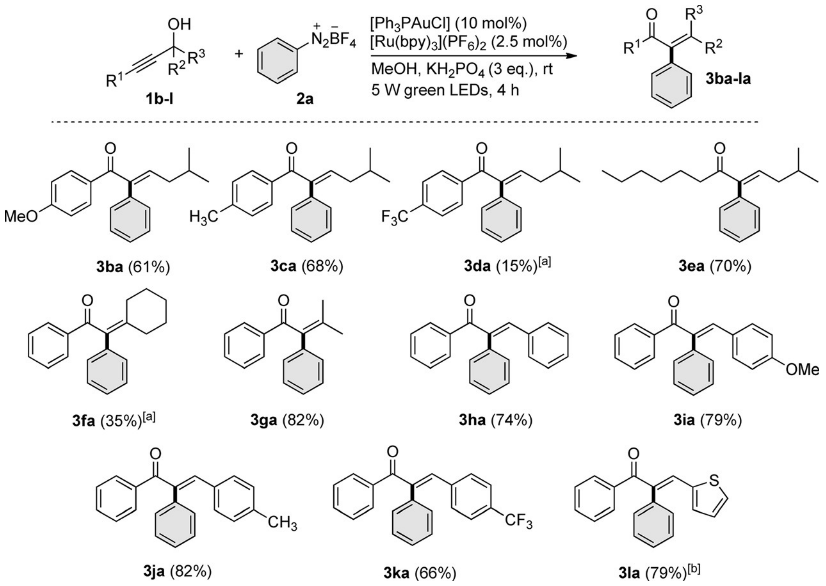
which is capable of reacting directly with **1a** without first engaging with the aryl coupling partner. Switching to the coordinatively saturated Au^I complex [Ph_3PAuCl], which can only react with the alkyne after having first undergone activation to form an arylgold(III) species (**B**; Scheme 1), led to much more satisfactory results. Using 10 mol% of the precatalyst [Ph_3PAuCl] under the same conditions, the cross-coupled product **3aa** was delivered in 78% NMR yield in a respectable *E/Z* ratio of 88:12 with formation of **4a** being completely suppressed (entry 2).

At this stage, an optimization study was carried out aimed at maximizing both the yield and *E/Z* selectivity of **3aa** (see the Supporting Information for full details). As shown in Table 1, the basic additive KH_2PO_4 (3 equiv) was found to greatly improve the diastereoselectivity of the process with the *E*-isomer being exclusively delivered with the same overall yield (78% NMR, 71% isolated yield; Table 1, entry 3). The preference for the *E*-isomer is consistent with the previously reported gold-catalyzed rearrangement reactions with propargyl alcohols.[9] Various coordinatively saturated gold(I) chloride precatalysts could be successfully employed in this process, albeit with efficiency not exceeding that of [Ph_3PAuCl] (entries 4–6). A selection of photoredox catalysts, including the inexpensive organic dyes eosin Y and fluorescein, was also suitable, although these latter species required longer reaction times (entries 7 and 8). Finally, the tolerance of the reaction to different sources of visible light was evaluated. 5 W Blue LEDs (λ_{max} = 465 nm) or a 23 W CFL gave the same performance to that obtained under 5 W green LED (λ_{max} = 525 nm) irradiation (entry 9). Interestingly, even sunlight was suitable for this transformation, giving **3aa** in 71% NMR yield in good selectivity towards the *E*-isomer (entry 10).[10]

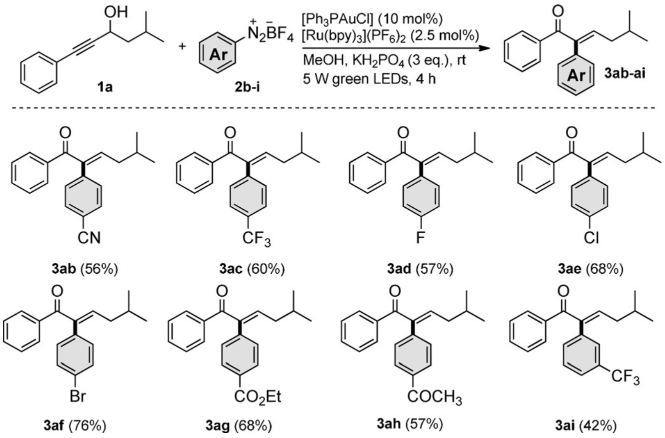
Having the optimized conditions in hand, the substrate scope of the transformation was assessed using a range of propargyl alcohols **1b–l** (Scheme 2). Electron-rich aromatic groups and alkyl chains at the acetylenic position (R^1) were found to be well tolerated in this transformation, giving access to the corresponding α-arylenones **3ba**, **3ca** and **3ea** in good isolated yields and perfect selectivity for the *E*-isomer. On the other hand, poor reactivity was observed when electron-withdrawing groups were installed at this position. We then turned our attention to the propargylic moiety. Electron-poor and -rich aromatic groups performed well for this transformation affording good yields of the chalcone derivatives **3ha–ka** up to 82%, again exclusively as the *E*-isomers. 2-Thiophene groups and tertiary alkyl propargyl alcohols were also suitable, giving moderate to good yields of the enones **3fa**, **3ga** and **3la**, although the latter thiophene-substituted compound was obtained as a 3:1 diastereoisomeric mixture.

The scope of the arylative Meyer–Schuster rearrangement with respect to different aryldiazonium salts **2b–i** was then assessed. As shown in Scheme 3, a selection of derivatives bearing electron-withdrawing or -neutral groups were successfully coupled with **1a**, delivering the corresponding arylenones **3ab–ai** in moderate to good yields (up to 76%). As with previously reported gold-catalyzed coupling reactions, halogen substituents were well tolerated and products **3ae** and **3af** could be further functionalized using standard cross-coupling methodologies. In all cases, no enone products, resulting from conventional hydrofunctionalization, or homocoupled enone derivatives were observed in the reaction mixtures, highlighting the selectivity of the method.

As the next stage of our study, we sought to investigate whether dual gold/photoredox catalysis could be applied to one of the simplest gold-catalyzed transformations of alkynes in an arylative hydration reaction.[11] This process would deliver α-arylketone derivatives, which are useful as building blocks in organic synthesis. Applying the set of optimized reaction con-

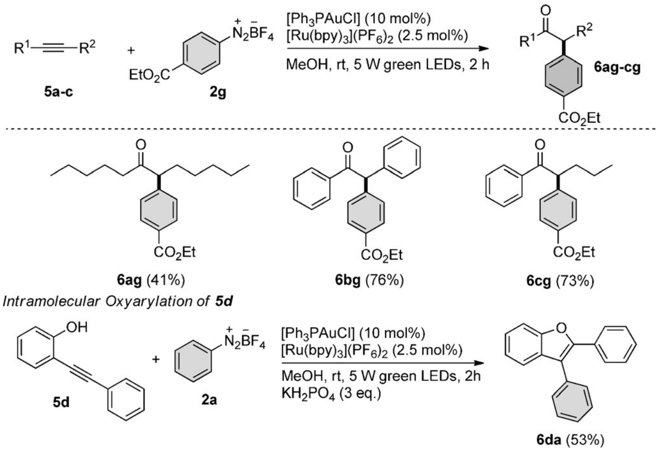


Scheme 2. Scope of propargyl alcohols **1b–l** in the dual gold/photoredox-catalyzed arylative Meyer–Schuster rearrangement. General conditions: propargyl alcohol (**1b–l**, 0.30 mmol), **2a** (1.2 mmol), [$Ru(bpy)_3$](PF_6)$_2$ (2.5 mol%), [Ph_3PAuCl] (10 mol%), and KH_2PO_4 (0.90 mmol) under argon. [a] **2a** (1.8 mmol) for 16 h. [b] 3:1 *E/Z* ratio. Isolated yields.



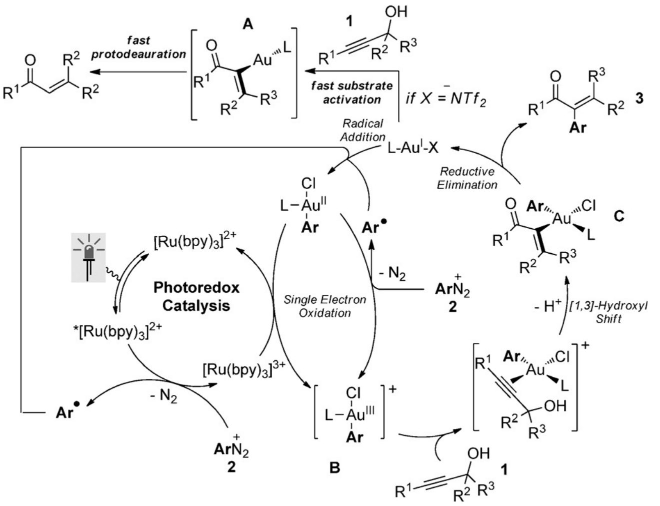
Scheme 3. Scope of aryldiazonium salts **2b–i** in the dual gold/photoredox-catalyzed arylative Meyer–Schuster rearrangement. General conditions: **1a** (0.30 mmol), **2b–2i** (1.2 mmol), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), $[Ph_3PAuCl]$ (10 mol%), and KH_2PO_4 (0.90 mmol) under argon. Isolated yields.

ditions from the Meyer–Schuster rearrangement, a fast arylative hydration reaction was observed with 6-dodecyne (**5a**) using 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2g**) as the coupling partner. α-Arylketone **6ag** was obtained in a moderate 41% yield in this reaction while no trace of the simple hydration product was observed (Scheme 4). This latter compound, resulting from standard nucleophilic addition proto-demetalation, was again obtained as the only product using $[Ph_3PAu]NTf_2$ as catalyst. Diphenylacetylene **5b** was found to be a more suitable substrate for the arylative hydration reaction with **6bg** being isolated in 76% yield. A further interesting observation was made with the unsymmetrical alkyne **5c**. Applying the standard dual gold/photoredox catalysis conditions to this compound resulted in the formation of the phenone **6cg** as a single regioisomer. To the best our knowledge, this reaction represents one of the only examples reported to date where perfect selectivity is achieved for internal alkyne hydration-type reactions using gold complexes as catalysts.[12] Finally, intramolecular oxyarylation could be performed using the 2-alkynylphenol derivative **5d**. This reaction delivered the diaryl-substituted benzofuran heterocycle **6da** as the only product in 53% isolated yield.



Scheme 4. Dual gold/photoredox arylative hydration of alkynes **5**. General conditions: **5a–d** (0.30 mmol), **2g**, **2a** (1.2 mmol), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), and $[Ph_3PAuCl]$ (10 mol%) under argon. Isolated yields.

In accordance with previous studies on dual gold/photoredox catalysis,[7,8] we propose a mechanism for the arylative Meyer–Schuster rearrangement of propargyl alcohols analogous to that outlined in Scheme 1. Whereas $[Ph_3PAu]NTf_2$ likely leads to a vinylgold(I) complex of type **A**, and thus is susceptible to fast proto-demetalation, $[Ph_3PAuCl]$ must first undergo oxidative arylation with an aryl radical generated upon oxidative quenching of the visible-light-activated photocatalyst by the aryldiazonium salt **2** (Scheme 5).[13,14] Subsequent single-electron oxidation of the resulting arylgold(II) complex either by the oxidized photocatalyst $[Ru(bpy)_3]^{3+}$ or in a radical chain with another equivalent of **2** would lead to the arylgold(III) species **B**.[15] This coordinatively unsaturated intermediate is now able to activate the alkyne towards the Meyer–Schuster rearrangement and deliver complex **C**, which bears both coupling partners and is set up for reductive elimination, selectively affording the cross-coupled product and regenerating $[Ph_3PAuCl]$.



Scheme 5. Mechanistic proposal.

In conclusion, we have shown that the unique mechanistic features of dual gold/photoredox catalysis can allow for alkynes to be employed as substrates in highly selective tandem nucleophilic addition/cross-coupling reactions, overcoming the conventional hydrofunctionalization and avoiding homocoupling of the alkyne. Using easily prepared propargyl alcohols as substrates, efficient access to useful α-arylenone compounds could be achieved in an arylative version of the Meyer–Schuster rearrangement, whereas simple alkyne hydration could be intercepted with cross-coupling to selectively afford α-arylketones. Both reactions proceed at room temperature under irradiation with visible light from readily available sources or even sunlight. These processes expand the scope of dual gold/photoredox catalysis to the largest class of substrates in gold catalysis and we hope that many new coupling reactions, which exploit the diverse array of alkyne nucleophilic addition reactions, will now be accessible.[16]

Acknowledgements

We thank Dr. A. Gómez-Suárez, Dr. B. Sahoo, and M. Becker (all WWU Münster) for experimental assistance and helpful discussions. Generous financial support by the NRW Graduate School of Chemistry (A.T.A.), the Alexander von Humboldt Foundation (M.N.H.) and the DFG (Leibniz Award) is gratefully acknowledged.

Keywords: alkynes · arylation · diazonium salts · gold · synthetic methods

[1] Selected reviews on homogeneous gold catalysis: a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896; *Angew. Chem.* **2006**, *118*, 8064; b) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395; c) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208; d) N. Krause, C. Winter, *Chem. Rev.* **2011**, *111*, 1994; e) M. Bandini, *Chem. Soc. Rev.* **2011**, *40*, 1358; f) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* **2012**, *41*, 2448; g) R. Dorel, A. M. Echavarren, *Chem. Rev.* **2015**, *115*, 9028.

[2] For the use of other electrophiles, palladium: a) Y. Shi, S. M. Peterson, W. W. Haberaecker III, S. A. Blum, *J. Am. Chem. Soc.* **2008**, *130*, 2168; b) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi, F. Rominger, *Angew. Chem. Int. Ed.* **2009**, *48*, 8243; *Angew. Chem.* **2009**, *121*, 8392; c) Y. Shi, S. D. Ramgren, S. A. Blum, *Organometallics* **2009**, *28*, 1275; d) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Ackermann, J. D. B. Becker, M. Rudolph, C. Scholz, F. Rominger, *Adv. Synth. Catal.* **2012**, *354*, 133; nickel: e) J. J. Hirner, S. A. Blum, *Organometallics* **2011**, *30*, 1299; rhodium: f) Y. Shi, S. A. Blum, *Organometallics* **2011**, *30*, 1776; iron and ruthenium: g) A. S. K. Hashmi, L. Molinari, *Organometallics* **2011**, *30*, 3457; halogens: h) A. Buzas, F. Gagosz, *Org. Lett.* **2006**, *8*, 515; i) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592; j) B. Gockel, N. Krause, *Eur. J. Org. Chem.* **2010**, 311; k) F. Mo, J. M. Yan, D. Qiu, F. Li, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 2028; *Angew. Chem.* **2010**, *122*, 2072; l) D. Qiu, F. Mo, Z. Zheng, Y. Zhang, J. Wang, *Org. Lett.* **2010**, *12*, 5474; m) M. Schuler, F. Silva, C. Bobbio, A. Tessier, V. Gouverneur, *Angew. Chem. Int. Ed.* **2008**, *47*, 7927; *Angew. Chem.* **2008**, *120*, 8045.

[3] Selected reviews: a) M. N. Hopkinson, A. D. Gee, V. Gouverneur, *Chem. Eur. J.* **2011**, *17*, 8248; b) H. A. Wegner, M. Auzias, *Angew. Chem. Int. Ed.* **2011**, *50*, 8236; *Angew. Chem.* **2011**, *123*, 8386.

[4] S. G. Bratsch, *J. Chem. Phys. Ref. Data* **1989**, *18*, 1.

[5] a) R. L. LaLonde, W. E. Brenzovich Jr., D. Benitez, E. Tkatchouk, K. Kelley, W. A. Goddard III, F. D. Toste, *Chem. Sci.* **2010**, *1*, 226; b) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.* **2008**, *130*, 17642. Reviews: c) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232; *Angew. Chem.* **2010**, *122*, 5360; d) L.-P. Liu, G. B. Hammond, *Chem. Soc. Rev.* **2012**, *41*, 3129.

[6] Selected reviews on visible-light photoredox catalysis: a) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527; b) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102; c) J. Xuan, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828; *Angew. Chem.* **2012**, *124*, 6934; d) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322; e) M. Reckenthäler, A. G. Griesbeck, *Adv. Synth. Catal.* **2013**, *355*, 2727; f) D. M. Schultz, T. P. Yoon, *Science* **2014**, *343*, 1239176; g) D. A. Nicewicz, T. M. Nguyen, *ACS Catal.* **2014**, *4*, 355; h) M. N. Hopkinson, B. Sahoo, J.-L. Li, F. Glorius, *Chem. Eur. J.* **2014**, *20*, 3874; i) E. Meggers, *Chem. Commun.* **2015**, *51*, 3290; j) R. A. Angnes, Z. Li, C. R. D. Correia, G. B. Hammond, *Org. Biomol. Chem.* **2015**, *13*, 9152. Examples of gold complexes as photoredox catalysts: k) G. Revol, T. McCallum, M. Morin, F. Gagosz, L. Barriault, *Angew. Chem. Int. Ed.* **2013**, *52*, 13342; *Angew. Chem.* **2013**, *125*, 13584; l) J. Xie, S. Shi, T. Zhang, N. Mehrkens, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2015**, *54*, 6046; *Angew. Chem.* **2015**, *127*, 6144.

[7] a) B. Sahoo, M. N. Hopkinson, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 5505; b) M. N. Hopkinson, B. Sahoo, F. Glorius, *Adv. Synth. Catal.* **2014**, *356*, 2794; c) X.-Z. Shu, M. Zhang, Y. He, H. Frei, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136*, 5844; d) D. V. Patil, H. Yun, S. Shin, *Adv. Synth. Catal.* **2015**, *357*, 2622.

[8] a) Y. He, H. Wu, F. D. Toste, *Chem. Sci.* **2015**, *6*, 1194; b) A. Tlahuext-Aca, M. N. Hopkinson, B. Sahoo, F. Glorius, *Chem. Sci.* **2016**, *7*, 89; c) S. Kim, J. Rojas-Martin, F. D. Toste, *Chem. Sci.* **2016**, *7*, 85.

[9] Review on the Meyer–Schuster rearrangement: a) D. A. Engel, G. B. Dudley, *Org. Biomol. Chem.* **2009**, *7*, 4149. Selected reports on the gold-catalyzed formation of α-functionalized enones based on the Meyer–Schuster or related rearrangement reactions: b) M. Yu, G. Zhang, L. Zhang, *Org. Lett.* **2007**, *9*, 2147; c) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem. Int. Ed.* **2009**, *48*, 3112; *Angew. Chem.* **2009**, *121*, 3158; d) L. Ye, L. Zhang, *Org. Lett.* **2009**, *11*, 3646; e) M. Yu, G. Zhang, L. Zhang, *Tetrahedron* **2009**, *65*, 1846; f) Y. Peng, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 5062; g) M. N. Hopkinson, G. T. Giuffredi, A. D. Gee, V. Gouverneur, *Synlett* **2010**, 2737; h) D. Wang, X. Ye, X. Shi, *Org. Lett.* **2010**, *12*, 2088; i) T. de Haro, C. Nevado, *Chem. Commun.* **2011**, *47*, 248; j) N. Marion, S. Díez-González, P. de Frémont, A. R. Noble, S. P. Nolan, *Angew. Chem. Int. Ed.* **2006**, *45*, 3647; *Angew. Chem.* **2006**, *118*, 3729; k) Y. Yu, W. Yang, D. Pflästerer, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2014**, *53*, 1144; *Angew. Chem.* **2014**, *126*, 1162.

[10] Control experiments without the Au^{I} catalyst, photocatalyst or visible light gave trace amounts or no product (see the Supporting Information for further details).

[11] Examples of gold-catalyzed functionalized alkyne hydration: a) W. Wang, J. Jasinski, G. B. Hammond, B. Xu, *Angew. Chem. Int. Ed.* **2010**, *49*, 7247; *Angew. Chem.* **2010**, *122*, 7405; b) T. de Haro, C. Nevado, *Adv. Synth. Catal.* **2010**, *352*, 2767; c) B. Xu, W. Wang, G. B. Hammond, *J. Fluorine Chem.* **2011**, *132*, 804.

[12] J. A. Goodwin, A. Aponick, *Chem. Commun.* **2015**, *51*, 8730.

[13] D. P. Hari, B. König, *Angew. Chem. Int. Ed.* **2013**, *52*, 4734; *Angew. Chem.* **2013**, *125*, 4832.

[14] Seminal study on the trapping of carbon-based radicals by gold complexes: a) C. Aprile, M. Boronat, B. Ferrer, A. Corma, H. García, *J. Am. Chem. Soc.* **2006**, *128*, 8388. Recent report on the oxidation of gold(I) by the CF_3 radical: b) M. S. Winston, W. J. Wolf, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136*, 7777. For a recent theoretical study on dual gold/photoredox catalysis, see: c) Q. Zhang, Z.-Q. Zhang, Y. Fu, H.-Z. Yu, *ACS Catal.* **2016**, *6*, 798.

[15] For interesting discussions on the prevalence of radical chain processes in photoredox catalysis see: a) M. Majek, F. Filace, A. J. von Wangelin, *Beilstein J. Org. Chem.* **2014**, *10*, 981; b) M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, *6*, 5426.

[16] During the submission of this manuscript, Shin and co-workers reported a related dual gold/photoredox catalyzed arylative Meyer–Schuster rearrangement, see: J. Um, H. Yun, S. Shin, *Org. Lett.* **2016**, *18*, 484.

Received: February 16, 2016