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Oxidative 1,2-Difunctionalization of Ethylene via Gold-Catalyzed Oxyarylation

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S Supporting Information

ABSTRACT: Under the conditions of oxidative gold catalysis, exposure of ethylene to aryl silanes and alcohols generates products of 1,2-oxyarylation. This provides a rare example of a process that allows catalytic differential 1,2-difunctionalization of this feedstock chemical.

Ethylene is available on vast scale, with the majority of the annual global production of 155 million tons used in the synthesis of commodity chemicals (e.g., polyethylene, ethylene oxide, acetaldehyde).¹ Despite underpinning a wide range of industrial processes, the direct conversion of ethylene into fine chemical products is uncommon, such that this abundant feedstock is rarely exploited as a reactant in organic synthesis (Scheme 1A).^{2,3} Although unusual, examples of catalytic

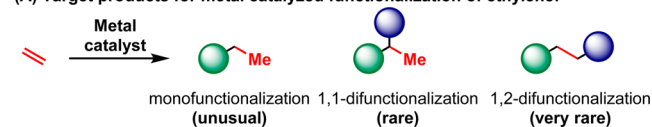
difunctionalization of ethylene.⁶ Existing (noncatalytic) methods require harsh reaction conditions.⁷

We considered whether Au-catalyzed oxidative 1,2-heteroarylation might provide a platform to difunctionalize ethylene. First reported by Zhang and co-workers,^{8a} this process enables the 1,2-addition of arylmetal(loid) reagents and N- or O-based nucleophiles to olefins, with the heteroatom component exhibiting Markovnikov selectivity (Scheme 1B).^{8a–g} For each class of alkene, careful selection of the aryl nucleophile and oxidant is required to promote the desired process and suppress nonproductive oxidation of the reactants. However, extending the reaction to ethylene raised a number of thought-provoking questions: (i) As gaseous ethylene might be present in low concentrations compared with other reaction partners, would competing oxidation pathways predominate? (ii) Would Au(III) provide sufficient π -activation of ethylene⁹ to allow addition of the heteroatom nucleophile?¹⁰ (iii) Are the stabilizing substituents on the alkene that have been employed in previous 1,2-oxyarylations needed to enhance the rate of C–X bond formation? Here we report an Au-catalyzed oxidative process that enables efficient 1,2-addition of diverse alcohols and aryl silanes to ethylene, providing a modular approach to homobenzylic ethers (Scheme 1C).¹¹ The new process is critically dependent on the use of IBA-OTf, an iodine(III) oxidant not previously used in Au catalysis. In broader synthetic terms, this study also establishes ethylene as an effective and atom-economical biselectrophilic two-carbon building block.¹²

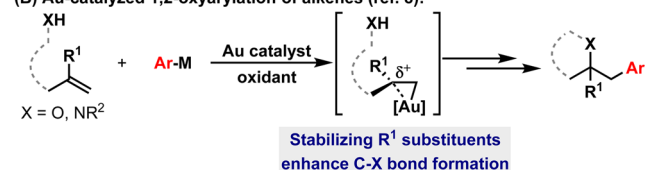
Initial studies evaluated a wide range of conditions for conversion of ethylene (1 atm) to homobenzylic ether **2a**. After extensive investigation, we found that **2a** could be generated in 21% yield using the combination of PhSiMe₃ (**1a**) as the nucleophile, 5 mol % Ph₃PAuCl as the precatalyst, and Selectfluor^{8a–d} as the oxidant in MeCN/MeOH (Table 1, entry 3). Under analogous conditions, other oxidants that have been employed in Au-catalyzed 1,2-oxyarylation, such as PhI(OAc)₂ and 1-hydroxy-3-oxobenziodoxole (IBA),^{8f} were completely ineffective (entries 1 and 2).¹³ Although the result in entry 3 was promising, further optimization studies using Selectfluor did not provide substantial efficiency gains. Accordingly, we re-evaluated the use of IBA in the presence of TsOH, an additive that has previously been shown to enhance the activity of this oxidant.^{8f} This modification generated **2a** in 35% yield (entry 4); similar results were achieved using other gold precatalysts, including the phosphine-free system tHtAuCl

Scheme 1. Introduction

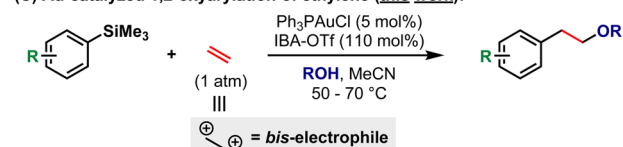
(A) Target products for metal catalyzed functionalization of ethylene:



(B) Au-catalyzed 1,2-oxyarylation of alkenes (ref. 8):



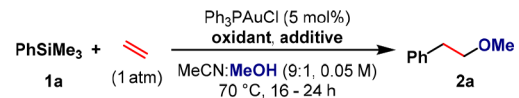
(C) Au-catalyzed 1,2-oxyarylation of ethylene (this work):



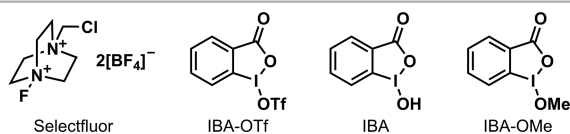
processes that effect monofunctionalization of ethylene include Heck-like reactions,^{4a} Rh-catalyzed hydroacylations,^{4b} alkene hydrovinylations,^{4c} and processes where ethylene functions as a vinylmetal surrogate.^{4d,e} Catalytic protocols that enable the differential difunctionalization of ethylene are even rarer. Indeed, only recently have Sigman and co-workers reported methods to achieve 1,1-diarylation and -arylvinylation of ethylene.⁵ Very few catalytic methodologies currently exist for differential 1,2-

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Table 1. Optimization of the 1,2-Oxyarylation Process^a


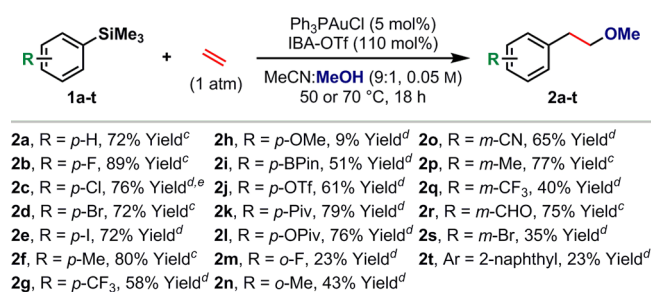
Entry	Oxidant (mol%)	Additive (mol%)	Yield / % ^b
1	PhI(OAc) ₂ (200)	-	0
2	IBA (200)	-	0
3	Selectfluor (100)	-	21
4	IBA (100)	TsOH (100)	35
5 ^c	IBA (100)	TsOH (100)	35
6	IBA (100)	TsOH (200)	68
7	IBA (100)	TfOH (200)	81
8 ^d	IBA (110)	TfOH (150)	92
9 ^d	IBA-OTf (110)	-	98 (72) ^e



^a0.25 mmol scale. ^bDetermined by GC analysis using dodecane as an internal standard. ^ctAuCl (5 mol %) was used in place of Ph₃PAuCl. ^dThe reaction was run at 50 °C. ^eIsolated yield in parentheses (losses are due to the volatility of 2a).

(see entry 5 and the Supporting Information (SI)). When the loading of TsOH was increased to 200 mol %, 2a was generated in 68% yield (entry 6), suggesting that stronger acid additives might offer further benefits. Indeed, substitution of TsOH with TfOH resulted in significant improvement, giving an 81% yield of 2a (entry 7). Further refinement saw an increase to 92% yield when 110 mol % IBA and 150 mol % TfOH were used at a lower reaction temperature of 50 °C (entry 8). We reasoned that under these conditions IBA-OTf likely forms in situ,¹⁴ suggesting that addition of this oxidant at the outset might circumvent the use of strongly acidic TfOH. Gratifyingly, this proved to be the case, and 2a was formed in 98% yield using 110 mol % IBA-OTf (entry 9). The protocol is operationally simple and can be conducted with conventional experimental apparatus using either a balloon of ethylene or a sealed reaction flask blanketed with the gas at 1 atm. To the best of our knowledge, the conditions outlined in entry 9 are the first to use IBA-OTf as an oxidant in Au catalysis.

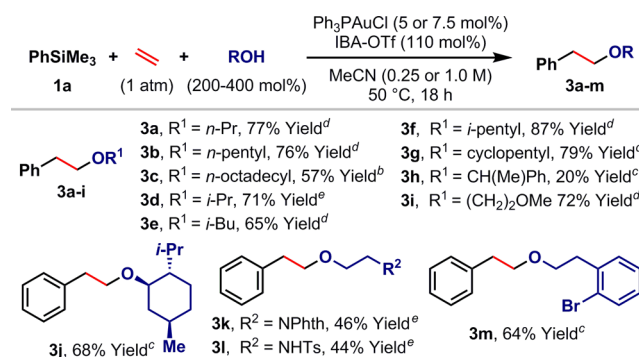
With the optimized conditions in hand, aryl silanes 1a–t bearing a variety of different functionalities were examined for 1,2-methoxyarylation of ethylene (Table 2).¹⁵ Aryl silanes bearing substitution at the para position were well-tolerated, with the exception of electron-rich methoxy variant 1h, for which competing protodesilylation was problematic. Of particular note is the ability to synthesize systems 2c, 2d, 2e, 2i, and 2j, which contain either nucleophilic or electrophilic units that can be exploited in subsequent Pd-catalyzed cross-couplings; these results highlight the orthogonal reactivity of Au versus Pd. The ability to access oxidatively sensitive pinacolboron system 2i and aldehyde 2r highlights the mild nature of the oxidative process. Ketones (1k), esters (1l), and nitriles (1o) were also found to be compatible with the reaction conditions. Sterically demanding ortho-substituted aryl silanes are more challenging, such that 2n was generated in only 43% yield. Electron-withdrawing ortho substituents (e.g., 1m) provide electronic deactivation of the silane, leading to decreased efficiency. This

Table 2. Scope of the Aryl Silane Component^{a,b}

^a0.30 - 0.40 mmol scale. ^bTrace amounts (approx. < 1-5% by GCMS) of biphenyl byproducts were also observed, but were not isolated or quantified. ^cThe reaction was run at 50 °C. ^dThe reaction was run at 70 °C. ^eThe reaction time was 42 h.

effect is also evident in the lower yields observed for meta-substituted products 2q and 2s.

The 1,2-difunctionalization processes in Table 2 use MeOH cosolvent as the nucleophile. We were aware that extension of the process to higher-value alcohols required the identification of conditions that could tolerate lower amounts of this component; existing intermolecular Au-catalyzed alkene oxyarylations invariably require a large excess of the alcohol.^{8b-d,f} Ultimately, we found that with an increase in the reaction concentration, efficient 1,2-oxyarylation could be achieved using only a 2–4-fold excess of alcohol (Table 3). Under these conditions, diverse

Table 3. Scope of the Alcohol Component^d

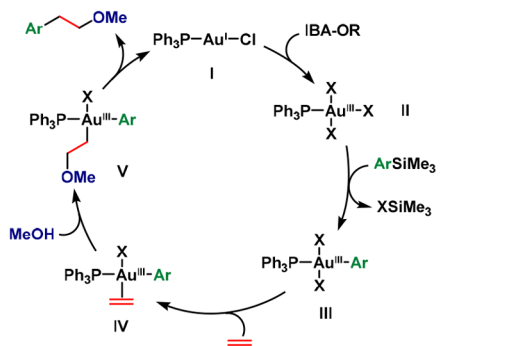
^a0.30 - 0.40 mmol scale. ^b200 mol% ROH, 7.5 mol% Ph₃PAuCl, 1.0 M. ^c300 mol% ROH, 5 mol% Ph₃PAuCl, 1.0 M. ^d400 mol% ROH, 7.5 mol% Ph₃PAuCl, 0.25 M. ^e400 mol% ROH, 5 mol% Ph₃PAuCl, 0.25 M.

primary and secondary alcohols engage in ethylene oxyarylation to provide 3a–m in moderate to excellent yields. Of the secondary alcohols examined, benzylic systems proved most challenging, with 3h formed in only 20% yield.^{16a} Structurally complex alcohols (3j) and those containing protected heteroatoms (3i, 3k, 3l) participated smoothly to generate the targets in moderate to very good yields.^{16b} The formation of 3l demonstrates that oxyarylation is more facile than potential aminoarylation via the NH-sulfonamide moiety.

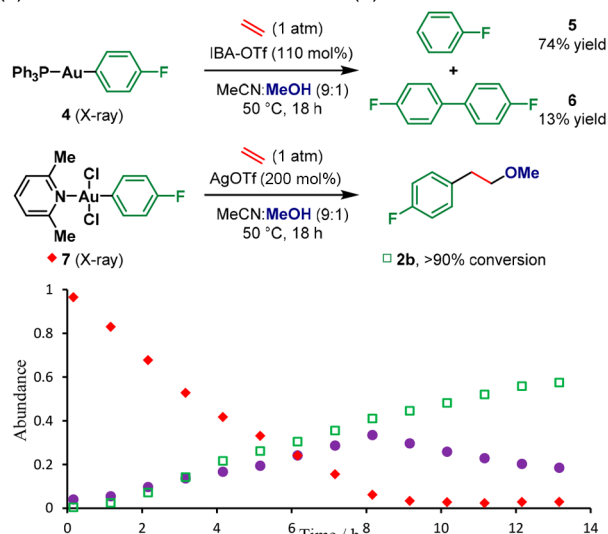
The proposed mechanisms for established 1,2-oxyarylation processes vary depending on the nature of the arylmetaloid reagent, oxidant, and alcohol.⁸ Our working mechanistic hypothesis for the processes described here is outlined in Scheme 2A. Commencing with Au(I) complex I, oxidation by IBA-OTf (or a related species; vide infra) affords Au(III) intermediate II, which undergoes transmetalation with the aryl silane¹⁷ to afford aryl-Au(III) species III. Coordination of ethylene is followed by attack of the alcohol to generate

Scheme 2

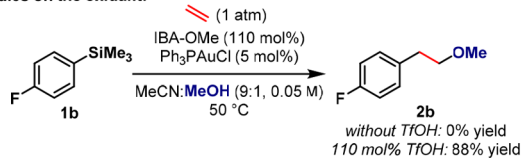
(A) Working mechanistic hypothesis:



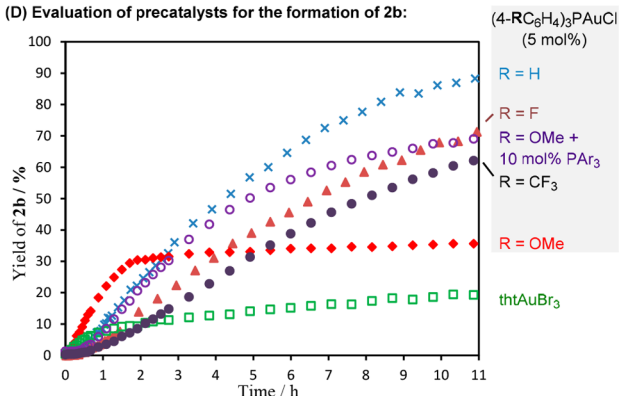
(B) Evidence for initial transmetalation onto Au(III):



(C) Studies on the oxidant:



(D) Evaluation of precatalysts for the formation of 2b:



intermediate V.^{10b-e} C–C reductive elimination then releases the product to close the catalytic cycle. Although detailed mechanistic support for each step has so far proven elusive,¹⁸ studies using model Au–aryl complexes have provided circumstantial evidence for the ordering of the first two steps (Scheme 2B). Exposure of PPh₃-ligated Au(I)–aryl complex 4^{17b,19} to the optimized reaction conditions (in the absence of aryl silane) did

not afford 1,2-oxyarylation product 2b; instead, proto-deauration product 5 and oxidative coupling product 6 were formed in an 85:15 ratio. This result indicates that oxidation of Au(I) to Au(III) occurs prior to transmetalation rather than after. In support of this, exposure of lutidine-ligated Au(III)–aryl complex 7 to the optimized conditions in the presence of AgOTf resulted in the clean formation of 2b (>90% yield).²⁰ Monitoring this process by ¹⁹F NMR spectroscopy revealed an intermediate (purple circles, graph in Scheme 2B) that exhibited ¹H NMR signals in CD₃CN/CD₃OH (9:1) at 3.42 ppm (t, *J* = 6.5 Hz) and 2.31 ppm (br m) in a 1:1 ratio; these data are broadly consistent^{10c} with the methoxyethyl ligand of a species akin to intermediate V.²⁰ The implication that transmetalation occurs prior to alkene activation contrasts with mechanisms proposed for several previous alkene 1,2-heteroarylation protocols.^{8b,c,e,g}

As discussed earlier, the identification of IBA-OTf as an effective oxidant stemmed from the observation that a combination of IBA and a Bronsted acid can also promote the 1,2-oxyarylation process, albeit with decreased efficiency. To gain further insight into the fate of the oxidant under the optimized conditions, IBA-OTf was exposed to MeOH, and this resulted in the quantitative formation (¹H NMR) of IBA-OMe (see the SI). Surprisingly, a bona fide sample of IBA-OMe was found to be inactive as an oxidant for the 1,2-oxyarylation of ethylene with 1b and MeOH (0% yield for 2b); however, addition of 100 mol % TfOH led to an 88% yield of 2b (Scheme 2C). Thus, for efficient 1,2-oxyarylation, it appears that mildly acidic conditions are required to activate IBA-OMe or (for Table 3) related species that are generated by in situ reaction of IBA-OTf with the alcohol.

In certain cases, mechanistic studies of oxidative Au-catalyzed processes using phosphine-ligated precatalysts have highlighted the requirement for initial oxidative removal of the phosphine ligand.^{17b} In contrast, our preliminary mechanistic studies highlight an involved and beneficial role for the phosphine ligand in the processes described here (Scheme 2D). Under the optimized conditions, ¹⁹F NMR analysis of the conversion of 1b to 2b using a series of (4-RC₆H₄)₃PAuCl complexes²¹ revealed that more electron-rich phosphine ligands provide higher initial rates (initial rate order for (4-RC₆H₄)₃P: R = OMe > H > F > CF₃). Notably, the phosphine-free system tAuBr₃ was not an efficient precatalyst, effecting only 20% conversion to 2b after 11 h. For (4-MeOC₆H₄)₃PAuCl, the catalytic activity was attenuated after approximately 2 h (30% conversion); however, higher conversions (approximately 70%) could be achieved by using an additional 10 mol % of P(4-MeOC₆H₄)₃ at the outset of the reaction.³¹ P NMR studies suggest that the observed attenuation of the reactivity for (4-MeOC₆H₄)₃PAuCl may be due to competitive oxidation of the phosphine ligand to [Ar₃POMe]⁺[OTf]⁻.²² This process is expected to be most facile for electron-rich phosphines, such that Ph₃PAuCl offers better overall efficiency even though (4-MeOC₆H₄)₃PAuCl provides the best initial turnover frequency. So far, we have been unable to determine whether the phosphine ligand is ligated to Au during catalysis (as depicted in Scheme 2A) or if its role is to stabilize off-cycle species. Nevertheless, the observations in Scheme 2D highlight the importance of phosphine ligands in oxidative Au catalysis and also emphasize further the requirement of a mild oxidant for the 1,2-oxyarylations described here.

In summary, we have outlined efficient Au-catalyzed oxidative 1,2-oxyarylations of ethylene as the basis of a modular entry to homobenzylic ethers. This study provides a rare example of a catalytic method that enables the differential 1,2-difunctionaliza-

tion of ethylene, establishing this feedstock chemical as an effective two-carbon biselectrophilic building block.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b06668.

Crystallographic data for **7** (CIF)

Experimental details and characterization data (PDF)

Crystallographic data for **4** (CIF)

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Notes

The authors declare no competing financial interest.

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(12) Conventional biselectrophilic reagents, such as 1,2-dibromoethane, suffer from poor reactivity and competing elimination. Other biselectrophilic C₂ reagents offer increased utility at the expense of lower atom economy. For example, see: Yar, M.; McGarrigle, E. M.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3784.

(13) Further optimization studies are given in the SI, including the evaluation of other oxidants.

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(15) For hydrolytically sensitive systems, acid-free conditions were crucial. For example, diminished yields were observed for **2j** (48%) and **2o** (65%) under the conditions in Table 1, entry 8.

(16) (a) Dehydrative dimerization of the alcohol to the corresponding ether was observed. (b) Bulky *t*-BuOH and electron-poor CF₃CH₂OH were tested and did not yield the desired products.

(17) For transmetalation of aryl trimethylsilanes to oxidatively generated Au(III) complexes, see: (a) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Science* **2012**, *337*, 1644. (b) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *J. Am. Chem. Soc.* **2014**, *136*, 254. For a review of elementary organometallic reactions of Au complexes, see: (c) Joost, M.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 15022.

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(21) Under the same conditions. *t*-Bu₃PAuCl was inactive and Cy₃PAuCl showed an activity profile similar to that of (4-CF₃C₆H₄)₃PAuCl (see the SI).

(22) Details are given in the SI.