DOI: 10.1002/chem.201103061

Gold-Catalysed Oxyarylation of Styrenes and Mono- and *gem*-Disubstituted Olefins Facilitated by an Iodine(III) Oxidant

Liam T. Ball, Guy C. Lloyd-Jones,* and Christopher A. Russell*[a]

Abstract: 1-Hydroxy-1,2-benziodoxol-3(1*H*)-one (IBA) is an efficient terminal oxidant for gold-catalysed, three-component oxyarylation reactions. The use of this iodine(III) reagent expands the scope of oxyarylation to include styrenes and *gem*-disubstituted olefins, substrates that are incompatible with the previously reported Selectfluor-based methodology. Diverse arylsilane coupling partners can be employed, and in benzotrifluoride, homocoupling is substantially reduced. In addition, the IBA-derived co-products can be recovered and recycled.

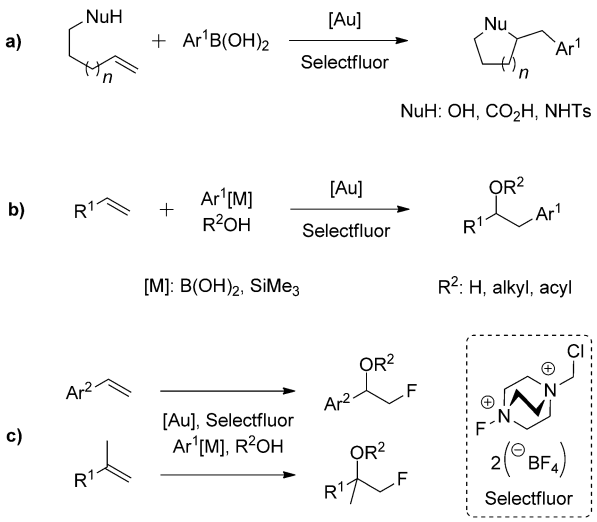
Keywords: arylation · gold · homogeneous catalysis · hypervalent iodine · styrenes

Introduction

The past decade has seen homogeneous gold catalysis transformed from a chemical curiosity into an intensely active field of research.[1] The methodology developed to date, which has found application in several target-oriented syntheses,[2] is unified by a mechanistic theme in which the metal, most commonly cationic Au^I, functions as a carbophilic Lewis acid, mediating nucleophilic addition to an unsaturated substrate. Importantly, the metal remains redox neutral throughout the transformation, which stands in stark contrast to the facile two-electron redox cycles typically exhibited by other late transition metals.[3]

Recently, however, access to higher oxidation states from Au^I precatalysts during the catalytic cycle has been realised by addition of a stoichiometric oxidant, thereby increasing the diversity of gold-promoted transformations.[4] In this regard, the Selectfluor[5]-mediated two-component heteroarylation of olefins with arylboronic acids[6] (Scheme 1 a) constitutes a particularly significant development, as it served to illustrate the feasibility of oxidative $C(sp^3)$–$C(sp^2)$ bond formation in an intermolecular (i.e., cross-coupling) fashion.[7] The concept has subsequently been extended to three-component oxyarylation (Scheme 1 b),[8] and the suitability of arylsilanes as the aryl source has been reported both by ourselves[9] and by Toste.[10] Importantly, replacement of the arylboronic acid by an arylsilane was found to reduce the formation of biaryl side products.

Previous studies[6,8a,9,10] indicated that the choice of oxidant is critical for successful heteroarylation. Whilst several



Scheme 1. a) Two-[6] and b) three-component[8–10] heteroarylation of monosubstituted olefins, employing Selectfluor as both terminal oxidant and fluoride source. c) Envisaged electrophilic fluorination of more-nucleophilic substrates.

reagent combinations were reported to promote the transformation, all were outperformed by Selectfluor in the dual role of oxidant and nucleophilic activator,[11] further illustrating the unique utility of the fluoronium reagent within gold-mediated oxidative catalysis.[12] However, in addition to acting as an oxidant in both organic[13] and organometallic[14] chemistry, Selectfluor is widely employed as a potent electrophilic fluorinating agent.[15] We recognised that direct fluorination may be competitive for more-nucleophilic substrates (Scheme 1 c), and therefore envisaged that an alternative oxidant needed to be identified before the scope of gold-catalysed oxyarylation could be extended further. Indeed, whilst the existing oxyarylation methodology has been demonstrated to allow transfer of electronically and sterically diverse aryl moieties, and to tolerate a range of *O*-

[a] L. T. Ball, Prof. Dr. G. C. Lloyd-Jones, Dr. C. A. Russell
School of Chemistry, University of Bristol
Cantock's Close, Bristol, BS8 1TS (UK)
Fax: (+44) 117-9251295
E-mail: guy.lloyd-jones@bris.ac.uk
chris.russell@bris.ac.uk

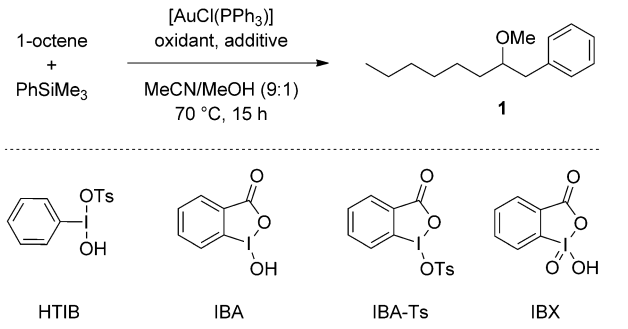
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201103061.

nucleophiles, the olefin scope has been entirely restricted to substrates bearing a single alkyl substituent.[16] Herein, we report the gold-catalysed, three-component methoxyarylation of both styrenes and *gem*-disubstituted olefins in the presence of an iodine(III) oxidant.

Results and Discussion

Oxidant development and reaction optimisation: The presence of basic/nucleophilic additives (e.g., Cs_2CO_3, TBAF = tetrabutylammonium fluoride) was shown to have a detrimental effect on the Selectfluor-mediated oxyarylation of monosubstituted olefins.[10] In addition, the combination of nucleophilic promoters (e.g., TBAF, TBAT = tetrabutylammonium triphenyldifluorosilicate) and alternative oxidants (e.g., $PhI(OAc)_2$) afforded only traces of the desired oxyarylation products.[9] The evident inhibitory effect of basic additives on the transformation prompted us to assay the oxyarylation of 1-octene under Brønsted acidic conditions (Table 1). Thus, whilst employing $PhI(OAc)_2$ in place of Selectfluor (under previously optimised conditions) proved unsuccessful (entry 1), the addition of two equivalents of *p*-toluenesulfonic acid monohydrate (*p*-TSA) afforded the desired product **1** in a promising yield of 20% (entry 2). The facile nature of ligand exchange at iodine(III)[17] suggested that the active oxidant was likely based on [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent)[18] rather than $PhI(OAc)_2$; this supposition was supported by the very similar yields obtained with either freshly prepared[19] or commercially sourced HTIB (entry 3).[20]

Table 1. Oxidant screen.[a]



Entry	Oxidant	Additive	Yield [%][b]
1	$PhI(OAc)_2$	–	<1
2	$PhI(OAc)_2$	*p*-TSA	20
3	HTIB	–	23
4	HTIB	–	48[c]
5	IBA	–	0
6	IBA-Ts	–	55
7	IBA	*p*-TSA	83[d]
8	IBA	MsOH	65
9	IBA	TfOH	15
10	IBA	TFA	4
11	IBA	*p*-TSA	3[e]
12	IBA	*p*-TSA	0[f]
13	IBA	*p*-TSA	0[g]
14	IBX	–	44
15	IBX	*p*-TSA	37

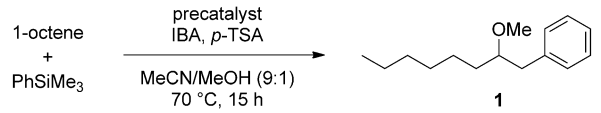
[a] Conditions: $[AuCl(PPh_3)]$ (5 mol%), 1-octene (0.1 mmol), $PhSiMe_3$ (0.2 mmol), oxidant (0.2 mmol), additive (0.2 mmol), MeCN/MeOH (9:1, 1 mL), 70 °C, 15 h. Ms = methanesulfonyl; Tf = trifluoromethanesulfonyl; TFA = trifluoroacetic acid. [b] Yields are an average of at least 2 repetitions and were determined by GC-FID (FID = flame ionisation detector) against an internal standard. [c] HTIB was added in six equal portions over 100 min. [d] **1** was not formed in the absence of $[AuCl(PPh_3)]$.[25] [e] $PhB(OH)_2$ was used in place of $PhSiMe_3$. [f] $PhSi(OMe)_3$ was used in place of $PhSiMe_3$. [g] $PhSiMe_2OH$ was used in place of $PhSiMe_3$.

The yield of **1** was doubled by portionwise addition of HTIB (entry 4), but, despite significant efforts, could not be improved further. Subsequent investigation of iodine(III) reagents derived from 2-iodobenzoic acid[21] revealed that the use of the tosyloxy analogue IBA-Ts (entry 6) was preferable to either the parent benziodoxolone IBA (1-hydroxy-1,2-benziodoxol-3(1*H*)-one; entry 5) or its acyclic relative HTIB. The yield of **1** was increased to 83% by employing a combination of IBA and two equivalents of *p*-TSA (entry 7) in place of preformed IBA-Ts; this result could not be improved by varying the acid additive (entries 8–10)[23] or the aryl source (entries 11–13). IBX (2-iodoxybenzoic acid) proved an unsuitable oxidant (entries 14 and 15), presumably owing to the competing reaction between the iodine(V) reagent and the alcohol.[24] Importantly, control reactions[25] indicated the need for both the acid and the oxidant, as well as a gold precatalyst; the failure of palladium, and various other late transition metals, to catalyse the transformation provided evidence against low-level impurities being responsible for the catalytic activity ascribed to gold.[26]

Subsequent reaction optimisation[25] revealed that both Au^I and Au^{III} species—as well-defined complexes, simple salts or in combination with Ag^I salts—were able to act as precatalysts for the IBA/*p*-TSA-mediated oxyarylation (Table 2, entries 1–12). As with our previously reported methodology,[9] the reaction was sensitive to the steric and electronic environment about the gold centre: $[AuCl(PPh_3)]$ proved a more efficient precatalyst than complexes of bulky and/or strong donor ligands (entry 1 vs. entries 6–10). Interestingly, the reactivity of $[AuCl(PPh_3)]$ was also unsurpassed by the digold complexes $[(AuX)_2(dppm)]$ (entries 11 and 12; dppm = bis(diphenylphosphino)methane; X = Cl, Br).[27] Whilst a significant halide effect was observed for the Selectfluor system at approximately 50 °C, this was found to diminish at higher temperatures,[6b,8a,10] as is reflected in our own results (compare entry 11, X = Cl with entry 12, X = Br).

Notably, upon changing the reaction solvent[25] to benzotrifluoride ($PhCF_3$) and diluting from 0.1 M (entry 13) to 0.05 M (entry 14), the yield of **1** was significantly improved and the formation of biaryl side products was largely suppressed (<3%).[28] However, no additional benefits resulted from further dilution. Subsequent investigations indicated that, whilst the amounts of arylsilane, IBA and *p*-TSA could be reduced, two molar equivalents of each reagent were required for consistently high yields, particularly when employing more challenging substrates.[29] In addition, the reaction proceeded most efficiently at 70 °C; hence, optimised

Table 2. Reaction optimisation.[a]



Entry	Precatalyst	Yield [%][b]
1	[AuCl(PPh$_3$)]	83
2	[AuCl(PPh$_3$)]/AgBF$_4$	38
3	AuCl	59
4	HAuCl$_4$·3H$_2$O	29
5	[AuCl$_2$(pyca)]	6
6	[AuCl(PCy$_3$)]	33
7	[AuCl{P(*o*-tol)$_3$}Cl]	21
8	[AuCl(JohnPhos)]	1
9	[AuCl{P(*t*Bu)$_3$}]	1
10	[AuCl(IPr)]	0
11	[(AuCl)$_2$(dppm)]	38[c]
12	[(AuBr)$_2$(dppm)]	40[c]
13	[AuCl(PPh$_3$)]	43[d]
14	[AuCl(PPh$_3$)]	93[e,f]

[a] Conditions: Precatalyst (5 mol%), 1-octene (0.1 mmol), PhSiMe$_3$ (0.2 mmol), IBA (0.2 mmol), *p*-TSA (0.2 mmol), MeCN/MeOH (9:1, 1 mL), 70°C, 15 h. [b] Yields are an average of at least 2 repetitions and were determined by GC-FID against an internal standard. Pyca = 2-pyridinecarboxylato; JohnPhos = 2-(di-*tert*-butylphosphino)biphenyl; IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene. [c] Precatalyst (2.5 mol%) was used. [d] Solvent system: PhCF$_3$/MeOH (9:1, 1 mL). [e] Solvent system: PhCF$_3$/MeOH (9:1, 2 mL). [f] **1** was not formed in the absence of [AuCl(PPh$_3$)].

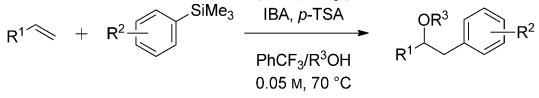
conditions were assessed to be those shown in Table 2, entry 14.

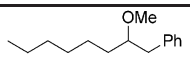
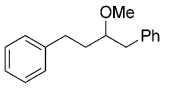
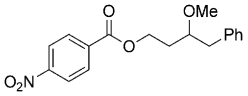
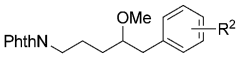
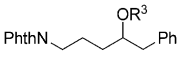
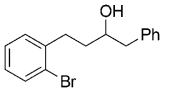
Scope—monosubstituted olefins: The generality of the newly developed oxyarylation conditions was probed initially for monosubstituted olefins (Table 3). A range of methyl ethers was prepared in good yield from the reaction of PhSiMe$_3$ with both simple and functionalised substrates (entries 1–4). The potentially sensitive functionality of nitrobenzoate **3** (entry 3) was well tolerated and no transesterification side products were observed.[30] In addition, both moderately electron-rich and electron-poor aryl moieties could be transferred (entries 4–6), including the sterically demanding *o*-tolyl moiety, which had proved challenging with Selectfluor as the oxidant.[9] For *O*-nucleophiles other than MeOH, MeCN was required as the solvent: water and a range of alcohols could then be employed, giving the expected products in moderate yields (entries 8–13).[31] Carboxylic acids performed poorly in the role of *O*-nucleophile (entry 12), and, as observed previously, very electron-rich arylsilanes (entry 7) and tertiary alcohols (entry 11) were unsuited to the reaction.

Intramolecular coupling of an olefin and a tethered arylsilane occurred in a 6-*endo*-trig fashion to give tetrahydronaphthalene **14** in a yield similar to that obtained with Selectfluor as the oxidant[10] (Scheme 2, top). By contrast, the two-component heteroarylation of olefins bearing tethered *O*- or *N*-nucleophiles did not proceed to afford the expected tetrahydrofurans or pyrrolidines: in the case of 4-penten-1-ol, a complex mixture of products was obtained, whilst *N*-(4-pentenyl)tosylamide furnished a 9:1 mixture of piperidine **15** and pyrrolidine **16** (Scheme 2, bottom). Although the essential role of gold in related aminooxygenations has been demonstrated under basic conditions,[32] we found that, as expected under acidic conditions,[33] the formation of **15** and **16** proceeded equally efficiently in the absence of gold.[25]

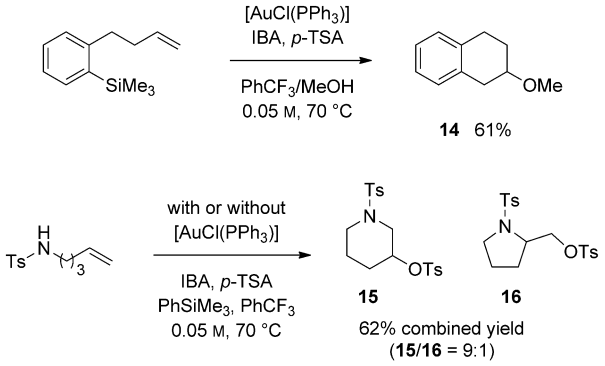
In all cases, the oxyarylation products were accompanied by alkyl 2-iodobenzoates, formed in situ from the IBA-de-

Table 3. Oxyarylation of monosubstituted olefins.[a]



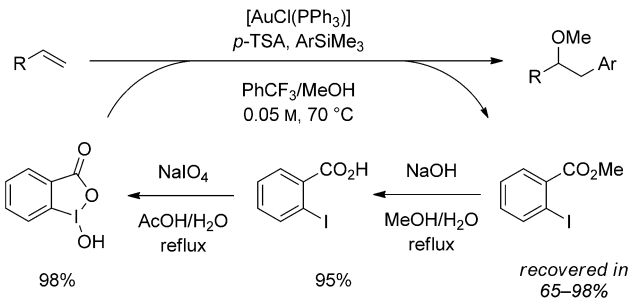
Entry	Product		Yield [%][b]
1		**1**	69[c]
2		**2**	68
3		**3**	71
4		**4** R^2: H	87
5		**5** R^2: 4-Br	65
6		**6** R^2: 2-Me	62
7		**7** R^2: 4-OMe	8[d]
8		**8** R^3: Et	58[e]
9		**9** R^3: (CH$_2$)$_2$OMe	44[e]
10		**10** R^3: *i*Pr	49[e]
11		**11** R^3: *t*Bu	0[d,e]
12		**12** R^3: Ac	2[e]
13		**13**	46[e]

[a] Conditions: [AuCl(PPh$_3$)] (5 mol%), olefin (0.5 mmol), arylsilane (1.0 mmol), IBA (1.0 mmol), *p*-TSA (1.0 mmol), PhCF$_3$/MeOH (9:1, 10 mL), 70°C. PhthN = phthalimido. [b] Isolated yield. [c] Isolated yield is lower than chemical yield (Table 2, entry 14) owing to difficulties in purification. [d] Yield determined by ^{1}H NMR spectroscopy using nitrobenzene as internal standard. [e] MeCN/R^{3}OH was used in place of PhCF$_3$/MeOH.



Scheme 2. Reaction of olefins bearing a tethered arylsilane (top) and a tethered nucleophile (bottom) under oxyarylation conditions.

rived 2-iodobenzoic acid. Typically isolated in 65–98% yield, the ester side products could be hydrolysed and subsequently oxidised[34] to IBA in near-quantitative yield (Scheme 3), allowing for the efficient and scalable recycling of the organoiodine moiety.



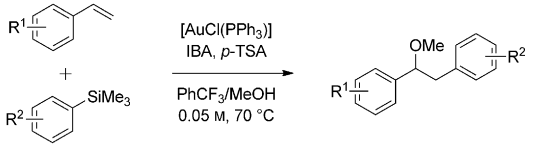
Scheme 3. Hydrolysis and subsequent oxidation of recovered methyl 2-iodobenzoate.

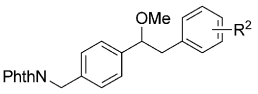
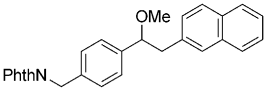
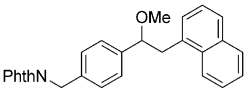
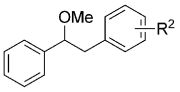
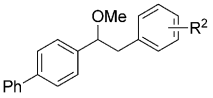
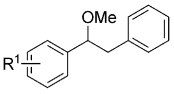
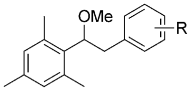
Having established the scope and limitations of the new conditions with respect to monosubstituted olefins, we considered substrate classes incompatible with the existing methodology: gratifyingly, both styrenes and *gem*-disubstituted olefins[35] were found to undergo oxyarylation (see below).

Scope—styrenes: The high reactivity of styrenes towards electrophiles, and their propensity to polymerise in the presence of Brønsted or Lewis acids, including gold,[36] renders them a particularly challenging class of substrates for oxyarylation. Indeed, attempting to employ styrenes under conditions optimised previously with Selectfluor[9] afforded only a trace of the desired product, and significant amounts of fluorinated compounds.[25] In contrast, oxyarylation proceeded smoothly in the presence of IBA and *p*-TSA (Table 4), although the scope of the *O*-nucleophile was limited to MeOH.[31] Whilst the electronic nature of the arylsilane coupling partner was more pronounced than for monosubstituted olefins, oxyarylation proved less sensitive to the electronic nature of the substrate (entry 18 vs. 20).[37] The expected bibenzyls were obtained in good to excellent yields for electron-neutral and moderately electron-rich arylsilanes (entries 1–6, 9–11 and 15–21), including a synthetically useful[38] aryl mesylate (entry 5). In comparison, coupling with electron-deficient arylsilanes proved more challenging (entries 7, 8 and 12–14): presumably the slower reaction of the deactivated arylsilanes allowed for consumption of the styrene by competing side reactions. Additionally, both sterically demanding arylsilanes (entry 2) and styrenes (entry 20) were well tolerated, and even the very congested product **37** (entry 21) was isolated in reasonable yield.

Oxyarylation of α-methylstyrene afforded methyl ether **38** (Figure 1) in 8% yield (determined by ^{1}H NMR spectroscopy[39]), whilst reaction of (*E*)-β-methylstyrene proved more successful: ether **39** was formed as a single regio- and diastereoisomer in 22% yield (determined by ^{1}H NMR spectroscopy[40]). Despite the low yield, this latter result is particularly significant, as it represents the first example of an internal olefin being successfully subjected to gold-catalysed oxyarylation and demonstrates the stereospecific nature of the transformation.

Table 4. Methoxyarylation of styrenes.[a]



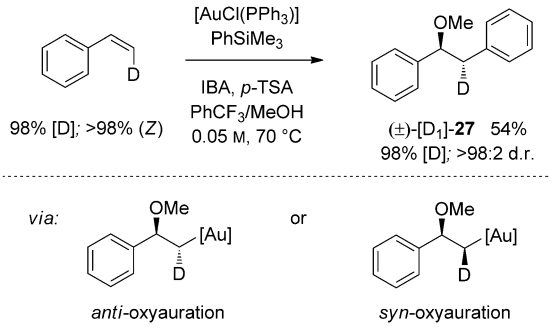
Entry	Product		Yield [%][b]
1		**17** R^2: H	77
2		**18** R^2: 2-Me	54
3		**19** R^2: 3-Me	77
4		**20** R^2: 4-Me	75
5		**21** R^2: 4-OMs	69
6		**22** R^2: 4-NMeTs	78
7		**23** R^2: 4-F	55
8		**24** R^2: 4-Cl	48
9		**25**	77
10		**26**	83
11		**27** R^2: H	71
12		**28** R^2: 4-F	54
13		**29** R^2: 4-Cl	35
14		**30** R^2: 3-CO_2Me	36
15		**31** R^2: 3-Me	51
16		**32** R^2: 4-OMs	29
17		**33** R^1: 4-Cl	72
18		**34** R^1: 3-NO_2	92
19		**35** R^1: 4-Me	37
20		**36** R^2: H	65
21		**37** R^2: 2-Me	31

[a] Conditions: [AuCl(PPh$_3$)] (5 mol%), styrene (0.5 mmol), arylsilane (1.0 mmol), IBA (1.0 mmol), *p*-TSA (1.0 mmol), PhCF$_3$/MeOH (9:1, 10 mL), 70 °C. [b] Isolated yield.

38 8% (±)-**39** 22%

Figure 1. Oxyarylation products from α-methylstyrene (left) and (*E*)-β-methylstyrene.

Subjecting (*Z*)-β-[D$_1$]-styrene to the standard reaction conditions (Scheme 4) afforded bibenzyl (±)-[D$_1$]-**27** as a single diastereoisomer,[41] confirming the stereospecificity observed for methoxyarylation of (*E*)-β-methylstyrene. The net *anti*-addition across the olefin precludes intermediacy of a benzylic carbocation or radical, and is consistent with, but

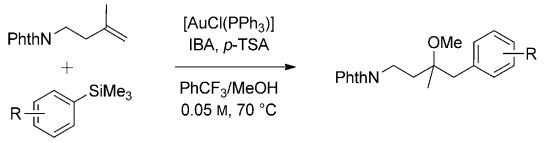


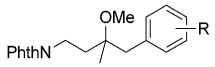
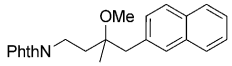
Scheme 4. Stereospecific oxyarylation of (*Z*)-β-[D_1]-styrene.

cannot differentiate between, two possible scenarios: 1) *anti*-oxyauration, followed by arylation with retention of configuration, or 2) *syn*-oxyauration, followed by arylation with inversion.[42]

Scope—*gem*-disubstituted olefins: As for styrenes, attempted oxyarylation of *gem*-disubstituted olefins in the presence of Selectfluor afforded several fluorinated compounds as part of a complex mixture, of which the desired product was only a minor component.[25] Using the combination of IBA and *p*-TSA, however, allowed for methoxyarylation of 2-methyl-2-alkyl olefins with various arylsilanes (Table 5).

Table 5. Methoxyarylation of *gem*-disubstituted olefins.[a]

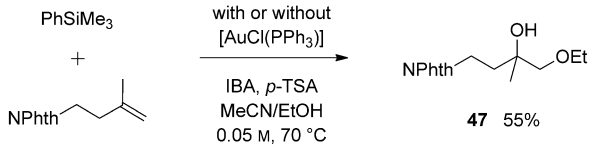


Entry	Product		Yield [%][b]
1		**40** R: H	86
2		**41** R: 2-Me	24
3		**42** R: 4-Me	67
4		**43** R: 4-NMeTs	55
5		**44** R: 4-F	58
6		**45** R: 4-Br	43
7		**46**	62

[a] Conditions: [$AuCl(PPh_3)$] (5 mol%), olefin (0.5 mmol), arylsilane (1.0 mmol), IBA (1.0 mmol), *p*-TSA (1.0 mmol), $PhCF_3$/MeOH (9:1, 10 mL), 70 °C. [b] Isolated yield.

Aryl moieties bearing electron-donating substituents (entries 1–4 and 7) were transferred more readily than those featuring electron-withdrawing substiuents (entries 5 and 6) or *ortho*-substitution (entry 2). The modest yields, relative to monosubstituted olefin and styrene substrates, may be attributed to the difficulty of forming a quaternary centre.

Attempts to extend the methodology to a wider range of *O*-nucleophiles[31] in MeCN resulted in *vic*-dioxygenation of the substrate: products of type **47** (Scheme 5) were formed equally efficiently in the absence of gold.[43]



Scheme 5. Dioxygenation of *gem*-disubstituted olefins under oxyarylation conditions.

Conclusion

In summary, we have demonstrated that the combination of IBA and *p*-TSA acts as an efficient oxidant in the gold-catalysed oxyarylation of olefins. The iodine(III) reagent can be prepared in near-quantitative yield on a multigram scale from 2-iodobenzoic acid; the requirement for superstoichiometric amounts of the oxidant is offset by the recovery and subsequent recycling of the organoiodine moiety. A diverse range of arylsilanes are readily transferred, and in $PhCF_3$, biaryl formation is largely suppressed. Although the scope in terms of the *O*-nucleophile is largely restricted to MeOH, the new conditions allow substrates incompatible with Selectfluor, namely styrenes and *gem*-disubstituted olefins, to be employed, thereby significantly expanding the scope of the existing methodology. Furthermore, successful methoxyarylation of β-methylstyrene hints that further refinement will allow internal, tri- and tetrasubstituted olefins to be employed as substrates. The mechanism of the reaction under our newly developed conditions is under investigation.

Experimental Section

General methoxyarylation procedure: Olefin (0.50 mmol), arylsilane (1.00 mmol) and [$AuCl(PPh_3)$] (12.4 mg, 0.025 mmol, 5 mol%) were added to a 28 mL vial containing a mixture of IBA (264.0 mg, 1.00 mmol) and *p*-TSA (190.2 mg, 1.00 mmol) in $PhCF_3$ (9 mL) and MeOH (1 mL). The vial was sealed and placed in a preheated aluminium heating block. The reaction was stirred at 70 °C until the olefin was consumed (as monitored by TLC), allowed to cool to room temperature and then passed through a silica pad (eluent: CH_2Cl_2). The filtrate was concentrated in vacuo and the crude material was purified by column chromatography.

Acknowledgements

We thank Umicore AG & Co. KG for the generous donation of $HAuCl_4$. L.T.B. thanks the Bristol Chemical Synthesis Doctoral Training Centre, funded by EPSRC (EP/G036764/1), AstraZeneca, GlaxoSmithKline, Novartis, Pfizer, Syngenta and the University of Bristol, for the provision of Ph.D. studentship. G.C.L.J. is a Royal Society Wolfson Research Merit Award holder.

[1] For seminal reports of homogeneous gold catalysis, see: a) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* **2000**, *112*, 2382; *Angew. Chem. Int. Ed.* **2000**, *39*, 2285; b) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553. For dedicated review volumes, see: c) *Chem. Rev.* **2008**, *108*;

d) *Chem. Soc. Rev.* **2008**, *37*; e) *J. Organomet. Chem.* **2009**, *694*; f) *Tetrahedron* **2009**, *65*.

[2] For selected examples, see: a) Q. H. Zhou, X. F. Chen, D. W. Ma, *Angew. Chem.* **2010**, *122*, 3591; *Angew. Chem. Int. Ed.* **2010**, *49*, 3513; b) K. Molawi, N. Delpont, A. M. Echavarren, *Angew. Chem.* **2010**, *122*, 3595; *Angew. Chem. Int. Ed.* **2010**, *49*, 3517; c) Z. S. Liu, A. S. Wasmuth, S. G. Nelson, *J. Am. Chem. Soc.* **2006**, *128*, 10352; d) A. Fürstner, P. Hannen, *Chem. Eur. J.* **2006**, *12*, 3006; e) R. Nakajima, T. Ogino, S. Yokoshima, T. Fukuyama, *J. Am. Chem. Soc.* **2010**, *132*, 1236; f) F. Volz, S. H. Wadman, A. Hoffmann-Roder, N. Krause, *Tetrahedron* **2009**, *65*, 1902; g) Y. Sawama, N. Krause, *Org. Biomol. Chem.* **2008**, *6*, 3573; h) J. A. Kozak, G. R. Dake, *Angew. Chem.* **2008**, *120*, 4289; *Angew. Chem. Int. Ed.* **2008**, *47*, 4221; i) X. Linghu, J. J. Kennedy-Smith, F. D. Toste, *Angew. Chem.* **2007**, *119*, 7815; *Angew. Chem. Int. Ed.* **2007**, *46*, 7671; j) R. M. Zeldin, F. D. Toste, *Chem. Sci.* **2011**, *2*, 1706; for reviews, see: k) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766; l) B. Alcaide, P. Almendros, J. M. Alonso, *Org. Biomol. Chem.* **2011**, *9*, 4405.

[3] *Transition Metals for Organic Synthesis, Vol. 1*, 2nd ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**.

[4] a) M. N. Hopkinson, A. D. Gee, V. Gouverneur, *Chem. Eur. J.* **2011**, *17*, 8248; b) T. de Haro, C. Nevado, *Synthesis* **2011**, 2530; c) H. A. Wegner, M. Auzias, *Angew. Chem. Int. Ed.* **2011**, *50*, 8236; *Angew. Chem.* **2011**, *123*, 8386.

[5] R. E. Banks, S. N. Mohialdin-Khaffaf, G. S. Lal, I. Sharif, R. G. Syvret, *J. Chem. Soc. Chem. Commun.* **1992**, 595.

[6] a) G. Zhang, L. Cui, Y. Wang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 1474; b) W. E. Brenzovich, D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard, F. D. Toste, *Angew. Chem.* **2010**, *122*, 5651; *Angew. Chem. Int. Ed.* **2010**, *49*, 5519.

[7] For intermolecular $C(sp^2)$–$C(sp^2)$ bond formation, see: a) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem.* **2009**, *121*, 3158; *Angew. Chem. Int. Ed.* **2009**, *48*, 3112; see also: b) W. Wang, J. Jasinski, G. B. Hammond, B. Xu, *Angew. Chem.* **2010**, *122*, 7405; *Angew. Chem. Int. Ed.* **2010**, *49*, 7247.

[8] a) A. D. Melhado, W. E. Brenzovich, A. D. Lackner, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 8885; b) N. P. Mankad, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 12859; c) E. Tkatchouk, N. P. Mankad, D. Benitez, W. A. Goddard, F. D. Toste, *J. Am. Chem. Soc.* **2011**, *133*, 14293.

[9] L. T. Ball, M. Green, G. C. Lloyd-Jones, C. A. Russell, *Org. Lett.* **2010**, *12*, 4724.

[10] W. E. Brenzovich, J.-F. Brazeau, F. D. Toste, *Org. Lett.* **2010**, *12*, 4728.

[11] In situ generated fluoride was proposed to act as a nucleophilic activator for the boronic acid/silane, supported by the observed formation of Me_3SiF; see ref. [9]. In the current investigation, trimethylsilyl methyl ether was observed in the crude reaction mixture (^1H, ^{13}C and ^{29}Si NMR spectroscopy), which indicates that the silyl moiety is ultimately sequestered by MeOH, although it does not necessitate activation of the arylsilane by the *O*-nucleophile.

[12] For the first reported use of Selectfluor in oxidative gold catalysis, see: a) L. Cui, G. Z. Zhang, L. M. Zhang, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3884; for the first use of Selectfluor in non-oxidative gold catalysis, see: b) M. Schuler, F. Silva, C. Bobbio, A. Tessier, V. Gouverneur, *Angew. Chem.* **2008**, *120*, 8045; *Angew. Chem. Int. Ed.* **2008**, *47*, 7927; for Selectfluor-mediated homocoupling of stoichiometric organogold species, see: c) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592; d) A. S. K. Hashmi, T. D. Ramamurthi, M. H. Todd, A. S.-K. Tsang, K. Graf, *Aust. J. Chem.* **2010**, *63*, 1619; whilst less widely employed, iodine(III) reagents have been shown to promote certain gold-catalysed oxidative transformations; for the seminal report, see: e) A. Iglesias, K. Muñiz, *Chem. Eur. J.* **2009**, *15*, 10563.

[13] a) R. E. Banks, N. J. Lawrence, A. L. Popplewell, *Synlett* **1994**, 831; b) R. E. Banks, N. J. Lawrence, M. K. Besheesh, A. L. Popplewell, R. G. Pritchard, *Chem. Commun.* **1996**, 1629.

[14] a) M. N. Hopkinson, A. D. Gee, V. Gouverneur, *Isr. J. Chem.* **2010**, *50*, 675; b) K. M. Engle, T. S. Mei, X. S. Wang, J. Q. Yu, *Angew. Chem. Int. Ed.* **2011**, *50*, 1478; *Angew. Chem.* **2011**, *123*, 1514.

[15] a) G. S. Lal, G. P. Pez, R. G. Syvret, *Chem. Rev.* **1996**, *96*, 1737; b) R. P. Singh, J. M. Shreeve, *Acc. Chem. Res.* **2004**, *37*, 31; c) P. T. Nyffeler, S. G. Duron, M. D. Burkart, S. P. Vincent, C. H. Wong, *Angew. Chem.* **2005**, *117*, 196; *Angew. Chem. Int. Ed.* **2005**, *44*, 192.

[16] For oxyarylation of disubstituted alkynes, see ref. [7b].

[17] G. F. Koser, R. H. Wettach, *J. Org. Chem.* **1980**, *45*, 1542.

[18] HTIB is readily prepared from $PhI(OAc)_2$ and *p*-TSA in MeCN at room temperature (G. F. Koser, R. H. Wettach, J. M. Troup, B. A. Frenz, *J. Org. Chem.* **1976**, *41*, 3609). Further ligand exchange with MeOH was discounted, as the resulting [methoxy(tosyloxy)iodo]benzene is known to be very prone to hydrolysis (G. F. Koser, R. H. Wettach, *J. Org. Chem.* **1980**, *45*, 4988).

[19] M. S. Yusubov, T. Wirth, *Org. Lett.* **2005**, *7*, 519.

[20] The reaction between $PhSiMe_3$ and HTIB is known to form the diaryliodonium salt $[Ph_2I][OTs]$ (G. F. Koser, R. H. Wettach, C. S. Smith, *J. Org. Chem.* **1980**, *45*, 1543), which has been employed extensively in transition-metal chemistry as both an oxidant and an aryl source (E. A. Merritt, B. Olofsson, *Angew. Chem.* **2009**, *121*, 9214; *Angew. Chem. Int. Ed.* **2009**, *48*, 9052). However, control experiments indicated that such species were not involved in gold-catalysed oxyarylation (see the Supporting Information).

[21] J. P. Brand, D. F. Gonzalez, S. Nicolai, J. Waser, *Chem. Commun.* **2011**, *47*, 102.

[22] The involvement of a phenyl benziodoxolone (formed by $Si \rightarrow I^{III}$ transmetallation) as the active oxidant/arene source was discounted by control experiments; see the Supporting Information. For use of alkynyl benziodoxolones in gold-catalysed oxidative alkynylation, see: a) J. P. Brand, J. Charpentier, J. Waser, *Angew. Chem.* **2009**, *121*, 9510; *Angew. Chem. Int. Ed.* **2009**, *48*, 9346; b) J. P. Brand, J. Waser, *Angew. Chem.* **2010**, *122*, 7462; *Angew. Chem. Int. Ed.* **2010**, *49*, 7304.

[23] Whilst the exact role of the acid is unclear, it is reasonable to assume in situ formation of IBA-Ts with a consequent change in both the electrophilicity and solubility of the oxidant.

[24] V. V. Zhdankin, *J. Org. Chem.* **2011**, *76*, 1185.

[25] See the Supporting Information.

[26] The possible role of low-level Pd-impurities in gold catalysis has been disputed; see: a) T. Lauterbach, M. Livendahl, A. Rosellon, P. Espinet, A. M. Echavarren, *Org. Lett.* **2010**, *12*, 3006; b) A. Corma, R. Juarez, M. Boronat, F. Sanchez, M. Iglesias, H. Garcia, *Chem. Commun.* **2011**, *47*, 1446.

[27] Caution must be exercised, when extending the mechanism recently disclosed (ref. [8c]) for Selectfluor-promoted oxyarylation to our present conditions; an in-depth investigation of the reaction mechanism is ongoing.

[28] As in our previous investigation, biaryl species were the sole arylsilane-derived side products; the products of oxidation (i.e., phenols) or protodesilylation (i.e., arenes) were not detected.

[29] An excess of *p*-TSA (relative to IBA) gave no observed increase in the activity of the oxidant (C. W. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Catal.* **2007**, *349*, 2610); see the Supporting Information, Table S3. Attempts to form hypervalent iodine species in situ from 2-iodobenzoic acid and Oxone (M. Uyanik, M. Akakura, K. Ishihara, *J. Am. Chem. Soc.* **2009**, *131*, 251) were unsuccessful; protocols employing *m*-CPBA as the terminal oxidant (E. A. Merritt, V. M. T. Carneiro, L. F. Silva, B. Olofsson, *J. Org. Chem.* **2010**, *75*, 7416) were not pursued owing to the high reactivity of peracids towards olefins.

[30] In a control experiment, treating but-3-enyl 4-nitrobenzoate with *p*-TSA (2 equiv) at 70 °C in $PhCF_3$/MeOH resulted in $< 7\%$ methanolysis after 2 h, and 47% methanolysis after 14 h.

[31] The poor performance of *O*-nucleophiles other than MeOH cannot be explained at present, although oxidation of the alcohol (as a non-productive pathway for consumption of both IBA and *O*-nucleophile) was precluded by control experiments; see the Supporting Information.

[32] T. de Haro, C. Nevado, *Angew. Chem.* **2011**, *123*, 936; *Angew. Chem. Int. Ed.* **2011**, *50*, 906.
[33] a) H. M. Lovick, F. E. Michael, *J. Am. Chem. Soc.* **2010**, *132*, 1249; b) D. J. Wardrop, E. G. Bowen, R. E. Forslund, A. D. Sussman, S. L. Weerasekera, *J. Am. Chem. Soc.* **2010**, *132*, 1188.
[34] L. Kraszkiewicz, L. Skulski, *ARKIVOC* **2003**, *VI*, 120.
[35] Attempts to extend the methodology to internal, tri- and tetrasubstituted olefins were unsuccessful; research towards this goal is ongoing.
[36] J. Urbano, A. J. Hormigo, P. de Fremont, S. P. Nolan, M. M. Diaz-Requejo, P. J. Perez, *Chem. Commun.* **2008**, 759.
[37] A competition reaction between styrene and 4-phenyl-1-butene afforded the expected products in a 1.2:1 (**27**/**2**) ratio (see the Supporting Information); the small difference between the reaction rates for the 2 substrate classes further illustrates the low sensitivity of oxyarylation to the electronic nature of the substrate, although only traces of product were detected (^{1}H NMR spectroscopy) for the very electron-rich 4-methoxystyrene.
[38] C. M. So, F. Y. Kwong, *Chem. Soc. Rev.* **2011**, *40*, 4963.
[39] I. Ho, J. G. Smith, *Tetrahedron* **1970**, *26*, 4277.
[40] A. J. Bloodworth, G. M. Lampman, *J. Org. Chem.* **1988**, *53*, 2668.
[41] Stereochemistry determined by ^{1}H NMR spectroscopy; spectral data for both diastereoisomers have been reported: J. Woning, A. Oudenampsen, W. H. Laarhoven, *J. Chem. Soc. Perkin Trans. 2* **1989**, 2147.
[42] For a discussion of mechanism in homogeneous gold catalysis, see: A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232.
[43] See the Supporting Information. Similar *vic*-dioxygenations have been rigorously established to occur in the absence of a metal under Brønsted acid catalysis, see: Y.-B. Kang, L. H. Gade, *J. Am. Chem. Soc.* **2011**, *133*, 3658.

Received: September 29, 2011
Published online: February 1, 2012

