Article

Gold Catalyzed Decarboxylative Cross-Coupling of Iodoarenes

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ABSTRACT: This report details a decarboxylative cross-coupling of (hetero)aryl carboxylates with iodoarenes in the presence of a gold catalyst (>25 examples, up to 96% yield). This reaction is site specific, which overcomes prior limitations associated with gold catalyzed oxidative coupling reactions. The reactivity of the (hetero)aryl carboxylate correlates qualitatively to the field effect parameter (F_{ortho}). Reactions with isolated gold complexes and DFT calculations support a mechanism proceeding through oxidative addition at a gold(I) cation with decarboxylation being viable at either a gold(I) or a silver(I) species.

- simple starting materials ● no external oxidant ● >25 examples
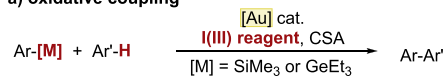- decarboxylation as Ar-M source
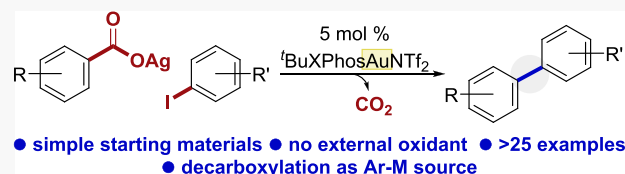
INTRODUCTION

Gold was once thought to have few uses in fine chemical synthesis.[1] Advances in homogeneous gold catalysis demonstrated that gold(I) complexes can promote a wide variety of synthetically relevant transformations.[2−12] Most employ a gold(I) catalyst as a Lewis acid or π−activator, where gold is thought to formally remain at the +1 oxidation state. The apparent redox stability of gold(I) complexes[13−15] contrasts with prominent two electron redox events known for palladium, rhodium, platinum, and iridium complexes. The redox stability of gold(I) complexes has limited development of complementary methods utilizing redox gold catalysts.[16−18] This work describes a gold catalyzed decarboxylative cross-coupling reaction, where the redox events are proposed to occur from a gold(I) complex. Pioneering studies demonstrated that gold(I) complexes can participate in oxidative addition with methyl iodide,[19,20] trifluoromethyl iodide,[21,22] aryl diazonium salts,[23−29] iodine(III) reagents,[30−41] and other strong oxidants.[16,42,43] Initially Lloyd-Jones and co-workers demonstrated a catalytic oxidative coupling of aryl-silanes in the presence of a strong acid and a stoichiometric iodine(III) oxidant (Scheme 1a).[31,34] A limiting feature of this and subsequent work[35−40,44,45] is that the site selectivity of C−H bond activation is governed by an apparent electrophilic aromatic substitution (EAS) mechanism. Patil and co-workers demonstrated a dual gold/photoredox catalyzed cross-coupling with aryl silanes[27] or aryl stannanes, which is thought to occur via a radical mechanism (Scheme 1b).[28]

The direct oxidative addition with more typical and less hazardous aryl halide electrophiles (e.g., Ar−I), which are standard for palladium(0) complexes, are relatively rare with gold(I) complexes.[13,14,44−52] The barrier for the oxidative addition of gold(I) complexes into aryl halides can be decreased through the use of bidentate ligands with a hemilabile site.[13,47,51] Amgoune and co-workers recently disclosed a gold catalyzed arylation of electron rich indoles
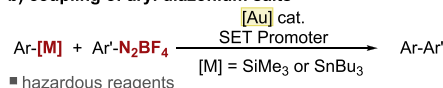
Scheme 1. Gold Catalyzed Biaryl Formations

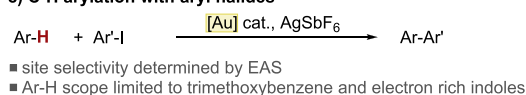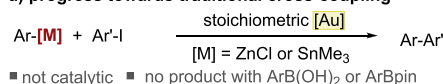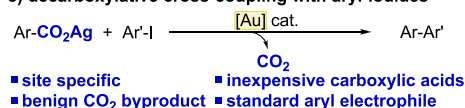and trimethoxybenzene with aryl halides (Scheme 1c).[44,45] This was recently expanded to other transformations.[52−55] Attempts at expanding this reactivity to more common

Table 1. Optimization for Decarboxylation

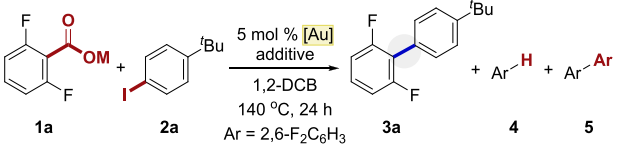| entry[a]	[Au]	1a:2a	M	additive, mol %	3a[b] (%)	4[b] (%)	5[b] (%)
1	MeDalphosAuCl	1:10	Na	NaOTf, 110	n.d.	n.d.	trace
2	MeDalphosAuCl	1:10	Na	AgOTf, 110	51	27	trace
3	MeDalphosAuCl	1:10	Ag	AgOTf, 110	61	32	n.d.
4	MeDalphosAuCl	1:10	Ag	AgOTf, 5	91	9	n.d.
5	MeDalphosAuCl	5:1	Ag	AgOTf, 5	25	N/A	N/A
6[c]	MeDalphosAuCl	1:10	Ag	AgOTf, 5	66	11	14
7[c]	IPrAuCl	1:10	Ag	AgOTf, 5	33	27	24
8[c]	CyJohnphosAuCl	1:10	Ag	AgOTf, 5	74	trace	16
9[c]	^{t}BuJohnphosAuCl	1:10	Ag	AgOTf, 5	>95	trace	n.d.
10[c]	CyXPhosAuCl	1:10	Ag	AgOTf, 5	68	14	18
11[c]	^{t}BuXPhosAuCl	1:10	Ag	AgOTf, 5	95	9	n.d.
12[c,d]	^{t}BuJohnphosAuCl	1:5	Ag	AgOTf, 5	73	n.d.	19
13[c,d]	^{t}BuXPhosAuCl	1:5	Ag	AgOTf, 5	94	n.d.	n.d.
14[c,d]	^{t}BuXPhosAuCl	1:5	Ag	none	35	8	44
15[c,d]	^{t}BuXPhosAuI	1:5	Ag	none	61	7	31
16[c,d]	^{t}BuXPhosAuSbF$_6$[e]	1:5	Ag	none	60	11	18
17[c,d]	**^{t}BuXPhosAuNTf$_2$**	**1:5**	**Ag**	**none**	**91**	**7**	**n.d.**
18[d]	^{t}BuXPhosAuNTf$_2$	1:3	Ag	none	82	10	8
19[c,d,f]	^{t}BuXPhosAuNTf$_2$	1:5	Ag	none	85	9	trace
20[c,d,f,g]	5 mol % L No [Au]	1:5	Ag	none	6	30	trace

[a]Reactions conducted with benzoate **1a** (0.1 mmol), iodoarene **2a** (0.3−1.0 mmol), in 1,2-dichlorobenzene (0.5 M, DCB), with 5 mol % [Au]. [b]Yield determined by ^{19}F NMR analysis. All yields reflect the average of duplicate trials. [c]Reactions conducted neat in iodoarene **2a**. [d]Reactions conducted with 0.15 mmol of benzoate **1a**. [e]CH$_3$CN adduct. [f]Reaction conducted with a new stir bar. [g]Used 5 mol % ^{t}BuXPhos no [Au]. Trace = less than 5% detected, n.d. = not detected. N/A = not applicable. ^{t}BuXPhos = 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl. See the SI.

organometallic reagents have been problematic. In an elegant study, Bower and co-workers demonstrated that all three elementary steps in a putative gold(I/III) cross-coupling are viable (Scheme 1b).[13,46] However, this reactivity was not incorporated into a catalytic method. Additionally, aryl boron reagents were found to be suboptimal coupling partners, which may be due to a challenging and potentially endothermic transmetalation.[56,57] An alternative approach is metal catalyzed aryl decarboxylation.

Our lab has focused on developing decarboxylative cross-coupling reactions.[58,59] Decarboxylative functionalization reactions are recognized as promising alternatives to traditional cross-couplings because expensive or unstable organometallic reagents can be replaced by readily available benzoic acids.[60−64] Inspired by two reports describing stoichiometric gold(I) mediated decarboxylation,[65,66] we surmised that this elementary step could offer an alternate pathway to gold-aryl complexes.[13,56,57] Alternatively, a dual catalytic cycle using a second metal, also capable of decarboxylation, could enable access to less frequently used transmetalation partners. Presented herein is a gold catalyzed decarboxylative cross-coupling reaction between iodoarenes and (hetero)aryl carboxylates (Scheme 1e). This work represents the first site-specific gold catalyzed cross-coupling with standard coupling partners.
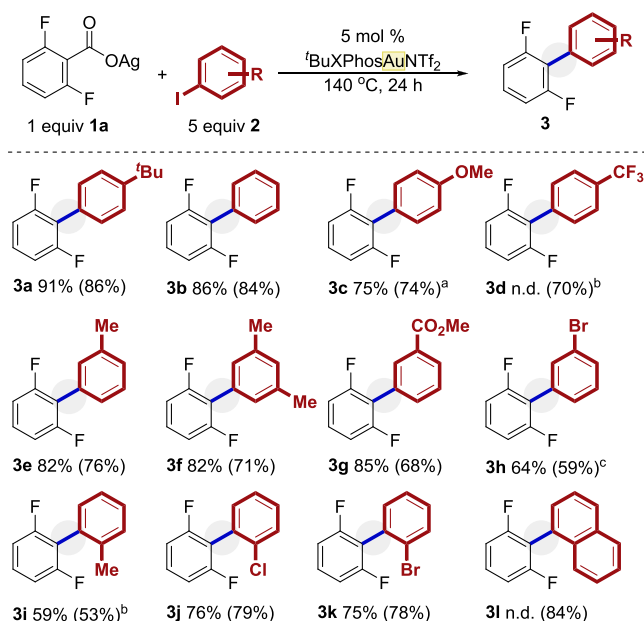
■ RESULTS AND DISCUSSION

Reaction Optimization. Initial trials were inspired by Amgoune and Bourissou, who recommended MeDalphos as a ligand.[44,45] The use of sodium carboxylate **1a** (M = Na) with NaOTf did not produce any detectable biaryl (Table 1, entry 1). Excitingly, using AgOTf afforded cross-coupled product **3a** along with protodecarboxylation product **4** (entry 2).[67] Switching from a sodium carboxylate to a silver carboxylate (entry 3) and decreasing the loading of AgOTf dramatically improved the yield (entry 4). Changing the limiting reagent to iodoarene **2a** significantly diminished the yield (entry 5).

A variety of precatalysts were screened and it was discovered that Buchwald style phosphine ligands outperformed other ligands under neat conditions (entries 6−11).[68] The quantity of iodoarene was decreased from 10 equiv to 5 equiv (entries 12−13). The ^{t}BuXPhos ligand outperformed the ^{t}BuJohnphos ligand under these conditions. Next, the counterion on the precatalyst was evaluated (entries 14−16). With LAuCl or LAuI complexes, in the absence of silver trifluoromethanesulfonate, significant homocoupling of benzoate **1a** was observed. The optimal precatalyst was LAuNTf$_2$ (entry 17). A further reduction in iodoarene to 3 equiv was tolerated but decreased the selectivity (entry 18). The reaction was conducted in a new vial with a new stir bar to avoid possible contamination,[69] which did not significantly affect the yield (entry 19). In the absence of gold, small amounts of product were observed along with significant protodecarboxylation (entry 20, see the SI for additional trials and control experiments).[70]

Substrate Scope. The substrate scope of the iodoarene was investigated (Table 2). Biaryl **3a** was isolated in excellent yield (86%). Iodobenzene (**3b**), 4-iodoanisole (**3c**), and 4-iodobenzotrifluoride (**3d**) afforded product, covering the

Table 2. Substrate Scope of Iodoarene[d]

3a 91% (86%)   **3b** 86% (84%)   **3c** 75% (74%)[a]   **3d** n.d. (70%)[b]

3e 82% (76%)   **3f** 82% (71%)   **3g** 85% (68%)   **3h** 64% (59%)[c]

3i 59% (53%)[b]   **3j** 76% (79%)   **3k** 75% (78%)   **3l** n.d. (84%)

[a]120 °C. [b]160 °C. [c]In 1,2-dichlorobenzene. See the SI for details and data. [d]Yield determined by ¹⁹F NMR. Yield in parentheses is the isolated yield. All values are the average of duplicate reactions. Reaction conducted as seen above.

traditional Hammett series (4-OMe, $\sigma_p = -0.27$; 4-CF$_3$, $\sigma_p = 0.54$). Iodoanisole gave an improved yield at 120 °C, while iodobenzotrifluoride required heating to 160 °C. This matches prior observations demonstrating that oxidative addition at gold(I) is faster with electron rich substrates (*vide infra*).[45,47] Iodoarenes with meta substituents gave acceptable yields (**3e–3h**). The reaction tolerated ortho groups (**3i–3k**). Chemoselectivity was observed for oxidative addition in the presence of aryl chlorides (**3j**) and aryl bromides (**3h** and **3k**). Iodonaphthalene (**3l**) also worked well.
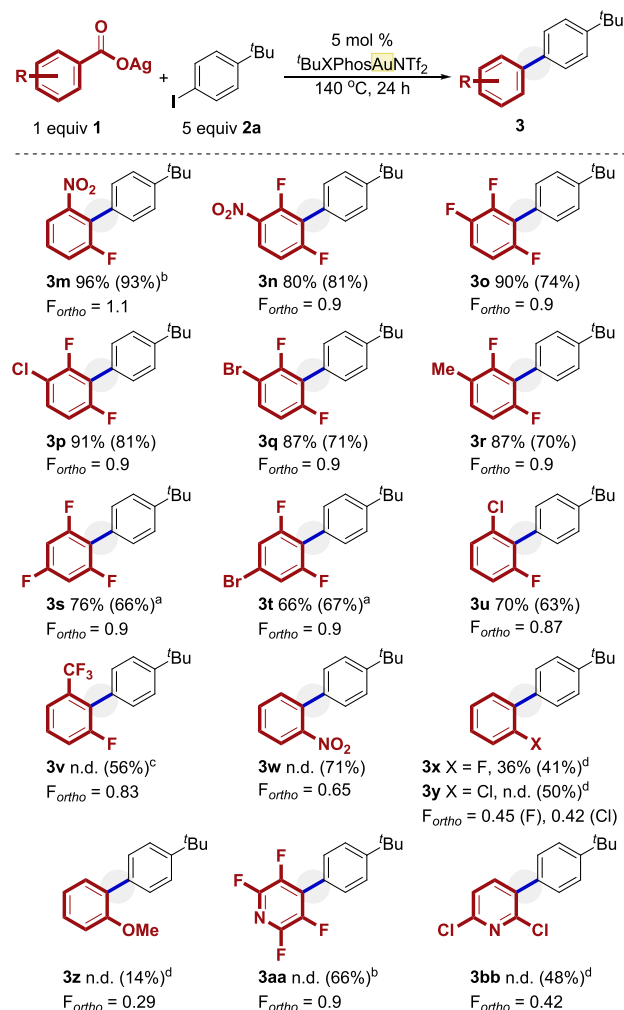
An inversion in iodoarene reactivity, relative to oxidative addition at palladium(0),[71] is a potential hallmark of gold mediated oxidative addition.[42,45,47] In a competition experiment with stoichiometric MeDalphosAuSbF$_6$, the use of 4-iodoanisole (**2c**) and 4-iodobenzotrifluoride (**2d**) afforded gold(III) complexes favoring oxidative addition with 4-iodoanisole in a 6.7:1 ratio.[45] In this system, a competition experiment was conducted (Scheme 2). The reaction afforded biaryl **3c** as the major product with a **3c:3d** ratio of 3.3:1, which is in line with prior gold mediated oxidative additions. These results indicate that the observed cross-coupling

Scheme 2. Competition Experiment of Aryl Iodides
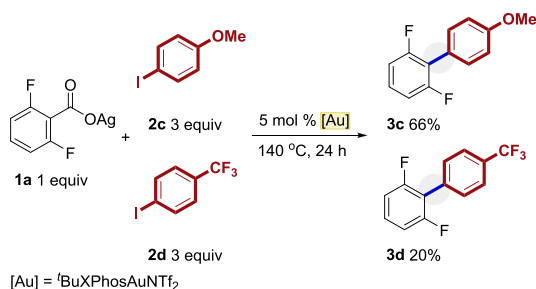
reaction can be attributed to the gold catalyst and not trace palladium contamination.

The substrate scope with respect to the aryl carboxylate was investigated (Table 3). It is well recognized in the area of

Table 3. Substrate Scope of (Hetero)aryl Carboxylates[e]

3m 96% (93%)[b]   **3n** 80% (81%)   **3o** 90% (74%)
F_{ortho} = 1.1 F_{ortho} = 0.9 F_{ortho} = 0.9

3p 91% (81%)   **3q** 87% (71%)   **3r** 87% (70%)
F_{ortho} = 0.9 F_{ortho} = 0.9 F_{ortho} = 0.9

3s 76% (66%)[a]   **3t** 66% (67%)[a]   **3u** 70% (63%)
F_{ortho} = 0.9 F_{ortho} = 0.9 F_{ortho} = 0.87

3v n.d. (56%)[c]   **3w** n.d. (71%)   **3x** X = F, 36% (41%)[d]
F_{ortho} = 0.83 F_{ortho} = 0.65   **3y** X = Cl, n.d. (50%)[d]
                                          F_{ortho} = 0.45 (F), 0.42 (Cl)

3z n.d. (14%)[d]   **3aa** n.d. (66%)[b]   **3bb** n.d. (48%)[d]
F_{ortho} = 0.29 F_{ortho} = 0.9 F_{ortho} = 0.42

[a]Reaction conducted in 1,2-dichlorobenzene at 0.1 M. [b]Reaction conducted in 1,2-dichlorobenzene at 0.17 M. [c]Reaction conducted at 180 °C. [d]Reaction conducted at 180 °C using 10 mol % [Au]. See the SI for details and data. F_{ortho} = field effect parameter. [e]Yield determined by ¹⁹F NMR. Yield in parentheses is the isolated yield. All values are the average of duplicate reactions.
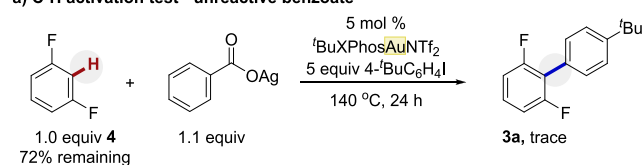
palladium, copper, and silver decarboxylative cross-coupling that substrates with polarizing ortho substituents are particularly reactive.[60–64] Hoover and co-workers correlated the field effect parameter (F_{ortho}) to reactivity for silver mediated protodecarboxylation.[70] Here, products **3m–3v** could be isolated in good to excellent yield and these results qualitatively correlate to the field effect parameter. Less activated substrates required elevated temperatures and/or increased catalyst loading (**3v–3y**). It is particularly exciting that products **3x** and **3y** could be isolated in any yield given the scope limitations of other decarboxylative cross-coupling reactions.[59,64,72] Substrates with an ortho C–H bond did not afford product with palladium catalyzed reactions,[58,59,72] which again disfavors a mechanism based on trace metal contamination. Additionally, a single *ortho*-fluorine (**3x**) or chlorine

(3y) substituent is only mildly polarizing and was sufficient for decarboxylation. A substrate with an *ortho*-methoxy group was not activated enough to provide an appreciable yield (3z, F_{ortho} = 0.29). Activated pyridine carboxylates afforded products 3aa and 3bb. Pyridines are particularly challenging substrates in traditional cross-coupling reactions.[73−75]

Mechanistic Experiments. It is conceivable that the observed cross-coupling reaction could proceed via proto-decarboxylation[67,70] and subsequent C−H bond activation.[76] This concern is valid because product 4 was observed and because metal carboxylates are known to facilitate C−H bond activation.[76] A reaction with 1,3-difluorobenzene (4) and silver benzoate afforded a negligible quantity of product 3a (Scheme 3a). The majority of compound 4 was detected after the

**Scheme 3. Test for C−H Activation Sequence**
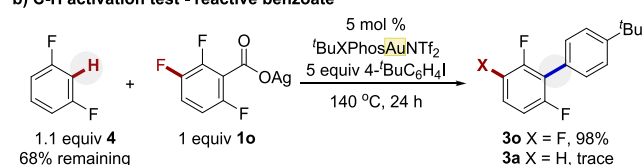
reaction, with the mass loss being attributed to volatility. To confirm that the reaction was still viable under these conditions, 1,3-difluorobenzene (4) and reactive silver benzoate 1o were subjected to the reaction conditions. Only trace quantities of product 3a were observed along with a high yield of product 3o, indicating that product is formed via decarboxylation under these reaction conditions. Using benzoate 1a and 1,2,4-trifluorobenzene provided similar results (see the SI). As such, a protodecarboxylation and C−H bond activation sequence is unlikely.

With evidence disfavoring the C−H activation mechanism, an initial mechanistic proposal was made (Scheme 4). The mechanism could proceed via salt metathesis yielding gold(I) carboxylate complex Au1 (step i). Decarboxylation (step ii) would afford gold(I)-aryl Au2.[65,66] Oxidative addition could proceed from complex Au2 (step iii), followed by silver facilitated reductive elimination (step iv)[19,20,22,42] to complete the catalytic cycle. A series of stoichiometric reactions were
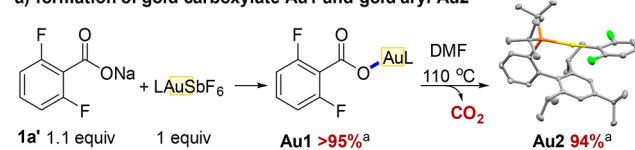
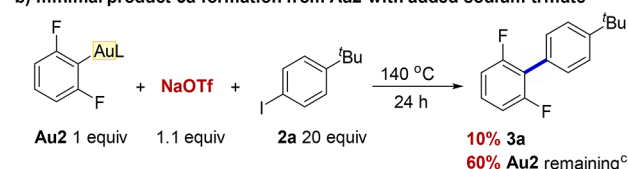**Scheme 4. Mechanistic Proposal with Oxidative Addition from L−Au−Ar Complex**
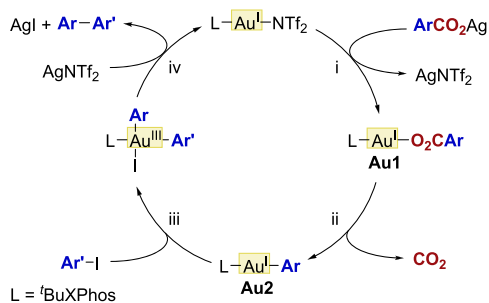
conducted with isolated gold complexes to investigate this sequence (Scheme 5). Gold(I)-aryl complex Au2 could be

Scheme 5. Reactions with Isolated Gold Complexes

prepared in two steps (Scheme 5a). Salt metathesis between sodium carboxylate 1a′ and the precatalyst afforded gold carboxylate complex Au1. Heating this complex readily afforded the aryl complex Au2, which was fully characterized. Surprisingly, only a minimal quantity of product 3a was observed from complex Au2 even in neat iodoarene 2a after prolonged heating. The same experiment was repeated with NaOTf (in place of NTf_2^- as an additive), which afforded similar results (Scheme 5b). The majority of complex Au2 remained unreacted after 24 h. This contrasts with the catalytic reaction, where only 5 mol % gold affords high yields of product. The observed stability of complex Au2 and the high energy of the transition structure located computationally (*vide infra*) for the proposed oxidative addition (step iii) lead us to disfavor the mechanism outlined in Scheme 4.

With these results in hand, an alternate mechanistic proposal was outlined (Scheme 6). The reaction could be initiated from

Scheme 6. Mechanistic Proposal with Transmetalation
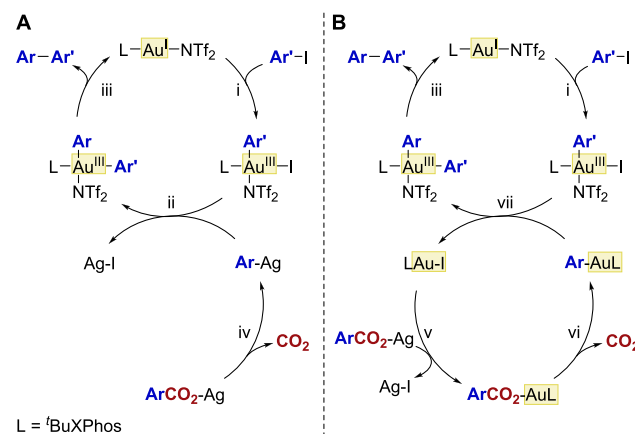
an oxidative addition of the $LAuNTf_2$ complex (step i). This oxidative addition would be more analogous to reported gold(I) oxidative addition reactions with iodoarenes that proceed from a cationic gold complex.[13,44−46] The gold(III) complex could then undergo transmetalation with a metal-aryl species (step ii).[77−79] The metal-aryl species could arise from either silver (mechanism A, step iv)[63,80,81] or gold (mechanism B, step vi)[65,66] mediated decarboxylation. Reductive elimi-
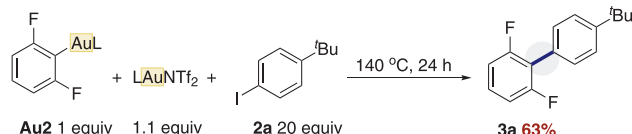
nation (step iii) and a possible salt metathesis (step v) would complete the cycle.
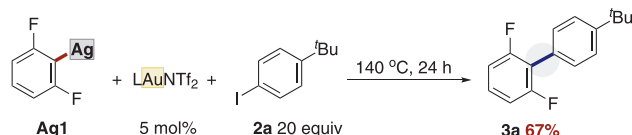
To support this proposal a number of experiments were conducted from isolated intermediates (Scheme 7). While

Scheme 7. Reactions with Metal Aryl Complexes

a) product 3a formation from Au2 in the presence of gold cation

b) product 3a formation from Ag1 in the presence of gold cation

isolated gold aryl complex **Au2** did not provide a high yield of product **3a** in neat iodoarene (Scheme 5b), when complex **Au2** was heated with cationic gold and iodoarene, a reasonable yield of product **3a** was observed (Scheme 7a), supporting step vii (Scheme 6b). Likewise, when isolated silver aryl complex **Ag1** (see the SI for synthesis and characterization) was utilized with catalytic gold, a good yield of product **3a** was observed along with 25% homocoupling of the difluoroaryl (Scheme 7b), supporting step ii (Scheme 6a). The formation of homo-coupled products from the pyrolysis of silver aryl complexes was anticipated based on prior work.[70] Next, an analysis of the presumptive oxidative addition and decarboxylation steps was explored computationally.

Computational Analysis of Oxidative Addition and Decarboxylation. The direct oxidative addition of gold(I) complexes into iodoarenes has been questioned numerous times in the literature.[14,15] Recently, the seminal works of Amgoune, Bourissou, and co-workers directly showed the viability of this elementary step (Scheme 8a).[44,45] Bower,

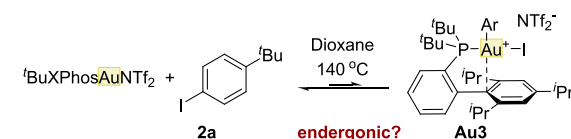**Scheme 8. Oxidative Addition with Gold Cations**

a) oxidative addition with MeDalphosAu complex
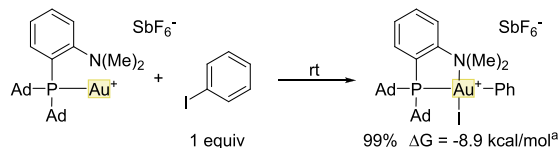
b) oxidative addition with bipyAu complex
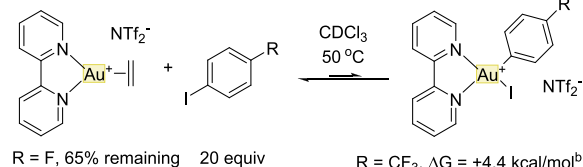
c) oxidative addition with ᵗBuXPhosAu complex

[a]Values and result from ref 44. [b]Values and results from ref 13.

Russell, McGrady, and co-workers elegantly demonstrated that, in some cases, the oxidative addition is endergonic and reversible (Scheme 8b).[13,46] The reaction studied here differs from previous examples of oxidative addition which used bidentate ligands like bipy or a monodentate ligand with a hemilabile amine substituent (MeDalphos). In the decarbox-ylative cross-coupling, the optimal ligand is the monodentate ᵗBuXPhos (Table 1), although the pendant aryl ring on the ligand could conceivably coordinate to gold in a hemilabile manner. This coordination mode is well-known with palladium(II) complexes.[82−85] Notably, MeDalphos is an acceptable ligand for the decarboxylative cross-coupling (Table 1, entry 6, 66% yield); however, the selectivity is superior with ᵗBuXPhos. Consideration of these issues prompted a computational study on the viability of oxidative addition with ᵗBuXPhos (Scheme 8c).

The oxidative addition of iodobenzene with gold(I) complexes relevant to the current reaction was investigated computationally. DFT calculations were performed with Gaussian 16.[86] Geometry optimizations were conducted using the MN15L functional, and energies were further refined with MN15L using a larger basis set and 1,2-dichlorobenzene as an implicit solvent (see the SI).[87] To simplify the calculations, the three iso-propyl groups in ᵗBuXPhos were abbreviated as methyl groups (ligand named here as ModPhos; R = mesityl in Scheme 9). The data obtained here indicate that formation of a ModPhosAu⁺-IPh σ-complex precedes oxidative addition (Scheme 9; 6b−9b).

Scheme 9. Summary of DFT Calculations for Oxidative Addition with Gold Complexes
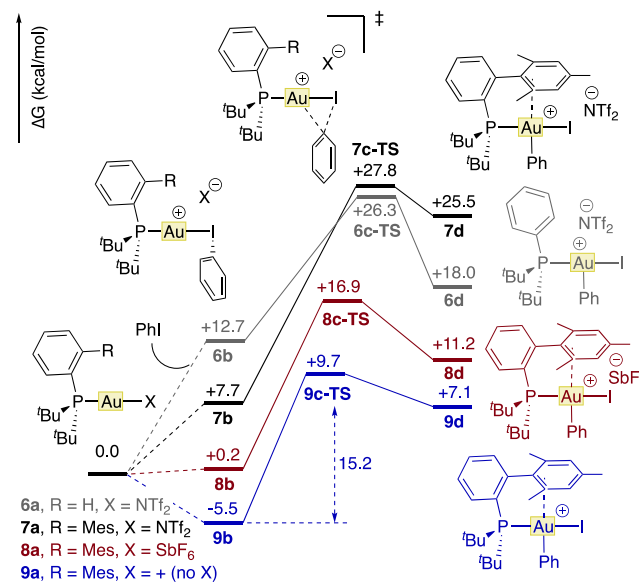
Consistent with previously reported DFT calculations using MeDalphos, the counteranion strongly influences the calcu-lated energy barrier and the highest barrier is predicted using NTf₂⁻ (**7c-TS**, 27.8 kcal/mol).[44] This result is somewhat surprising given the use of ᵗBuXPhosAuNTf₂ in the optimal catalytic system. Excluding the counterion from the calcu-lations leads to more favorable energetics (**9c-TS**, ΔG‡ = 15.2 kcal/mol).[45] As such, the counterion dependence appears to be directly correlated with the energy required to displace the counterion with the iodoarene to form the σ-complex as well as

an energetic penalty for charge separation. Regardless of counterion, oxidative addition with ModPhos is predicted to be much slower than oxidative addition with MeDalphos (see the SI).[44,45] However, the calculated barrier with ModPhosAuNTf$_2$ of 27.8 kcal/mol should be readily surmountable under the experimental conditions (140 °C). The oxidative addition with the bistriflimide ion was calculated to be endergonic by 25.5 kcal/mol, which is in line with the results of Bower, Russell, and McGrady (Scheme 8b).[13]

To examine the role of the pendant aryl of ^{t}BuXPhos, a transition structure was calculated in which the pendant aryl group of ModPhos is rotated away so that it cannot coordinate to gold (see the SI). Reaction through this conformation is prohibitively high-energy ($\Delta G^{\ddagger}$ = 45.0 kcal/mol), indicating that the pendant aryl does interact with gold during oxidative addition (**7c-TS**). However, calculations performed with PPh(^{t}Bu)$_2$, a truncated version of ^{t}BuXPhos lacking the pendant aryl, predict an oxidative addition barrier that is very similar to that using ModPhos (Scheme 9a, **6c-TS**). Overall, the calculations suggest that the pendant aryl of ^{t}BuXPhos does not significantly stabilize the transition state or the resulting Au(III) adduct relative to the starting Au(I) complex. As such, it is likely that the success of ^{t}BuXPhos in the catalytic system is due to its influence on a different step of the reaction mechanism. The possibility for oxidative addition at LAu-Ar (**Au2**, see Scheme 4) was also examined. However, this pathway can be ruled out on the basis of a prohibitively high calculated activation barrier using ModPhosAuAr (Ar = 2,6-difluorophenyl; $\Delta G^{\ddagger}$ = 46.1 kcal/mol; see the SI).

Because both silver(I) and gold(I) carboxylates are reported to undergo decarboxylation, this step was also investigated computationally. The silver mediated decarboxylation is thought to occur in a concerted manner and has been investigated both experimentally[70,88,89] and computationally.[88,90] Here, three sets of calculations were conducted using the free silver carboxylate (Scheme 10, **10a**), ModPhos-ligated silver carboxylate (**11a**), or ModPhos-ligated gold carboxylate (**12a**, analogous to complex **Au1**). In all three cases, the barriers for decarboxylation were similar. As such,

the calculations support the possibility that decarboxylation could proceed from either a gold(I) or silver(I) carboxylate (e.g., both mechanisms in Scheme 6a,b appear viable). The calculated barriers are lower than for the oxidative addition with ModPhosAuNTf$_2$, indicating that decarboxylation may not be turnover limiting. However, DFT can give unreliable comparisons between energies of neutral and ionic species due the challenges associated with accurately modeling solvent effects and ion pairing.[91,92] In light of the counterion dependence noted above, it is possible that another process is turnover limiting.

◼ CONCLUSION

In conclusion, we report the first gold catalyzed decarboxylative cross-coupling. This work expands on recent progress regarding gold(I) oxidative addition with iodoarenes. Decarboxylation overcomes site selectivity limitations associated with prior gold catalyzed oxidative arylation reactions. The substrate scope of the aryl carboxylate correlates qualitatively with the field effect parameter. Preliminary mechanistic studies indicate that the gold(I) oxidative addition is viable and that decarboxylation can proceed from either gold or silver. A more comprehensive mechanistic study will be reported in due course.

◼ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c06244.

Crystallographic information as related to compounds in the text (CIF)

Crystallographic information as related to compounds in the text (TXT)

Experimental procedures, computational data, and spectral data (PDF)

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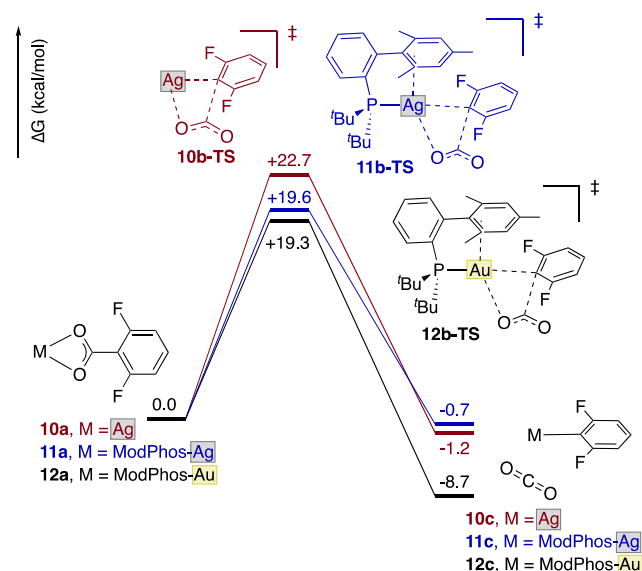
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◼ Notes

The authors declare no competing financial interest.

Scheme 10. Summary of DFT Calculations for Decarboxylation

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