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Mechanistic Studies of Gold and Palladium Cooperative Dual-Catalytic Cross-Coupling Systems

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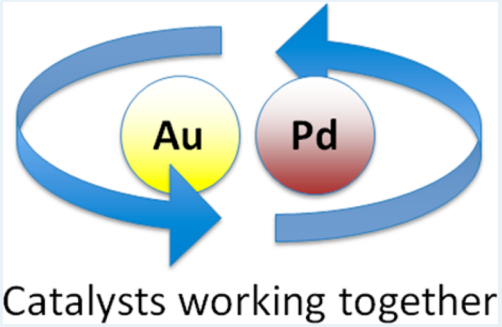
Supporting Information

ABSTRACT: Double-label crossover, modified substrate, and catalyst comparison experiments in the gold and palladium dual-catalytic rearrangement/cross-coupling of allenoates were performed in order to probe the mechanism of this reaction. The results are consistent with a cooperative catalysis mechanism whereby (1) gold activates the substrate prior to oxidative addition by palladium, (2) gold acts as a carbophilic rather than oxophilic Lewis acid, (3) competing olefin isomerization is avoided, (4) gold participates beyond the first turnover and therefore does not serve simply to generate the active palladium catalyst, and (5) single-electron transfer is not involved. These experiments further demonstrate that the cooperativity of both gold and palladium in the reaction is essential because significantly lower to zero conversion is achieved with either metal alone in comparison studies that examined multiple potential gold, palladium, and silver catalysts and precatalysts. Notably, employment of the optimized cocatalysts, PPh_3AuOTf and Pd_2dba_3, separately (i.e., only Au or only Pd) results in zero conversion to product at all monitored time points compared to quantitative conversion to product when both are present in cocatalytic reactions.



KEYWORDS: *gold, palladium, cooperative catalysis, dual catalysis, cross-coupling, crossover, mechanism, intermediates*

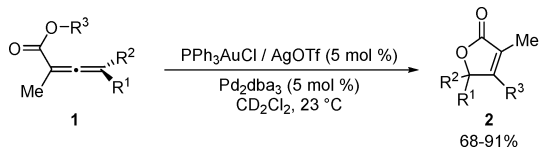
INTRODUCTION

High-yielding reactions that maximize the number of bond-forming processes per pot are attractive because they avoid the isolation of intermediates,[1] which is often the most time- and cost-intensive part of a synthesis.[2] One approach toward these efficient multiple-bond-forming reactions is through dual catalysis.[3−16] For example, dual-catalytic cross-coupling reactions with gold and palladium access novel reactivity unavailable to single-metal systems, use substoichiometric amounts of each catalyst, avoid the stochiometric transmetalation byproducts common to cross-coupling reactions (except the Sonogashira reaction), and do not require the isolation and purification of reaction intermediates.[3−16] Less is known, however, about the mechanisms available to dual-metal-catalyzed systems as compared to their single-metal counterparts; this dearth of mechanistic understanding hinders the design of additional dual-catalytic systems despite their advantages.

We herein report mechanistic studies in the gold-and-palladium cooperative catalytic cyclization/cross-coupling reaction. These experiments include double-label crossover studies and modified substrate studies that "isolate" individual steps in the reaction. Experiments are consistent with a "gold cyclization first" mechanism whereby gold catalyzes (i.e., lowers the barrier for) a subsequent palladium-catalyzed oxidative addition and further confirms[5b] the involvement of both of the Au and Pd cocatalysts in the conversion to product. This fundamental information provides insight into the reactions available to gold and palladium together and thus contributes to the broader understanding needed to design future dual-metal systems.

RESULTS AND DISCUSSION

We turned our attention to probing the mechanism of catalysis in order to better understand and predict future chemo- and regioselectivities and reactivity in Au/Pd and related dual-catalytic systems. Our group had previously proposed a consistent catalytic cycle for the Au/Pd dual-catalyzed synthesis of butenolides. Optimized conditions are shown in eq 1. We



1 → 2, 68-91% (1)

proposed a mechanism in which a carbophilic[17] gold Lewis acid first activated the C−C π system prior to involvement by palladium (Scheme 1).[5b] Recent work by our group and others suggests that oxophilic[18] and azaphilic[17a,19−21] activation by gold and SET[10b] mechanisms may also be possible. In this series of mechanistic studies, we investigated the precise order of steps and the possibility of these alternative activation pathways which will be called "palladium first", "oxophilic",

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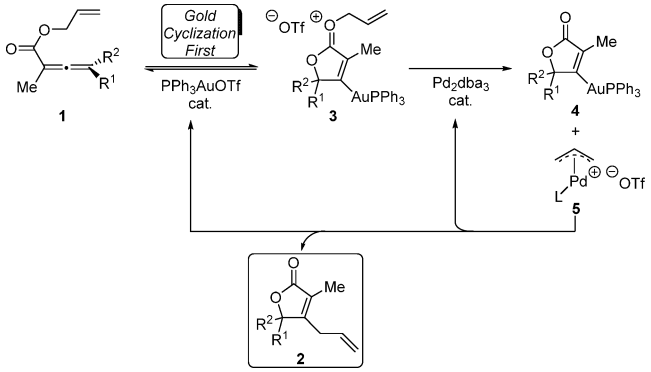
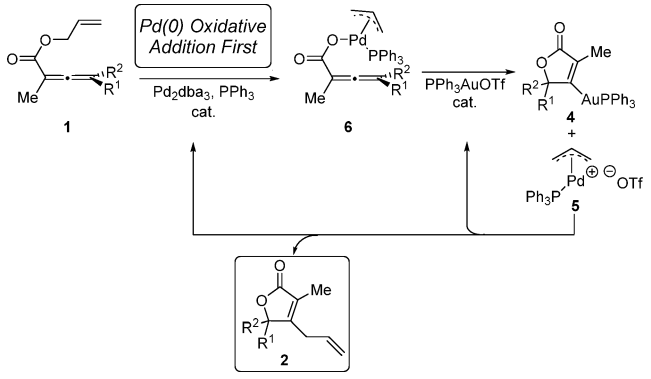
Scheme 1. Original Proposed Gold Cyclization First Mechanism for Au/Pd Dual-Catalytic Synthesis of Butenolides



Scheme 2. Alternative Palladium First Possible Mechanism for Au/Pd Dual-Catalytic Cyclizaiton/Cross-Coupling



"palladium π-allyl cation catalyzed", and "SET" for clarity. Our data are consistent with the originally proposed "gold cyclization first" catalytic cycle wherein gold acts as a carbophilic[17] Lewis acid and generates an organogold cross-coupling partner in situ.

Summary of Previous Experiments. *Kinetics.* In our initial communication,[5b] we reported the first-order kinetic dependence of product formation on palladium concentration. Product decomposition at higher loadings of gold (>5 mol %) complicated measurement of the kinetic dependence on gold. Over the examined loadings of gold and palladium, the reaction exhibited substrate saturation kinetics, consistent with a resting state with the substrate bound to the gold, palladium, or both.

Characterization of Potential Intermediate. Proposed intermediate **5**, with L = dba and L = $((PPh_3)_2)$, was present in the catalytic reaction mixture prior to reaction completion, as characterized by HRMS. This "build up" of a substrate-bound organometallic species is consistent with the observed substrate saturation kinetics.

Equilibria. A trapping experiment established that **1** and **3** were in rapid equilibrium in the presence of stoichiometric gold. This result indicates a low barrier for the initial cyclization step compared to subsequent steps. Thus, gold-mediated/catalyzed cyclization is not rate-determining if it is indeed on the reaction path.

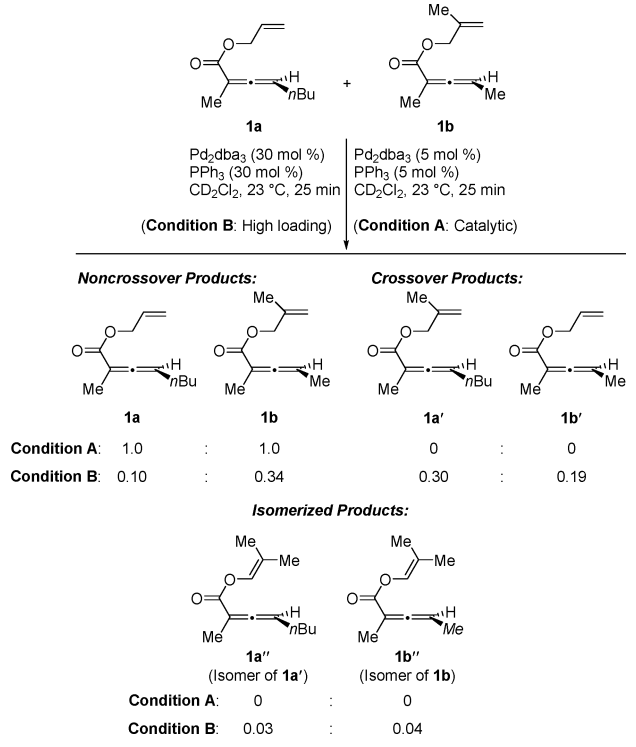
Motivation for Additional Data. As mentioned in the Introduction, at least five plausible mechanistic pathways match the previous data; these mechanistic pathways are considered plausible in part due to studies by our group[5f] and others[10b] on dual-metal systems after our original publication. Determination of the precise order and nature of steps informs on the activation chemistry uniquely available to dual-metal systems, as will now be described.

Experiments Inconsistent with a "Palladium First" Mechanism. We first considered an alternative mechanism in which the order of reactivity of Au and Pd is reversed from our initial proposal: Pd(0) may first undergo oxidative addition into the allyl group of **1**, followed by a Au-catalyzed cyclization (Scheme 2). The catalyst Pd_2dba_3 generally requires addition of a phosphine ligand to promote allyl acetate oxidative addition.[22] Thus, PPh_3 dissociated from the PPh_3AuOTf could bind to Pd to promote the oxidative addition; this ligand exchange has been characterized previously in our system by HRMS.[5b] For these reasons, the palladium first mechanism is depicted in Scheme 2 as containing "PPh_3" in the oxidative addition step. In the last step, a cross-coupling reaction between the organogold complex **4** and π-allyl Pd complex **5** would afford the observed butenolide product **2**.

We probed the potential of the Pd(0) oxidative addition with our allenoate substrates through a series of double-label crossover experiments.[23] In the first experiment, allyl allenoates **1a** and **1b** (in a 1:1 mixture) were treated with catalytic and high loading of palladium only, specifically, Pd_2dba_3 and PPh_3 in CD_2Cl_2 (Scheme 3). These results were later compared to a second crossover experiment under dual-catalytic conditions with *both* gold and palladium (Scheme 4).[5b]

The reaction with palladium alone was monitored for the presence of the crossover products from palladium-catalyzed deallylation.[24] If this deallylation occurs, the resulting intermediates could recombine in an intermolecular fashion to give crossover products. However, it must be noted that after deallylation the resulting π-allyl palladium complex and

Scheme 3. Crossover Experiment with Allenoate Substrates 1a and 1b with Only Palladium Demonstrates Crossover Is Slower in the Absence of Gold



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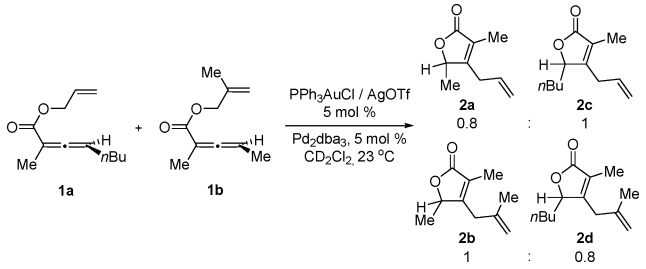
Scheme 4. Crossover Experiment with Allenoate Substrates 1a and 1b under Optimized Dual-Catalytic Conditions with Both Gold and Palladium



carboxylate might not be solvent separated[25] but rather covalently attached in dichloromethane, a relatively nonpolar solvent. Inaccessibility of the solvent-separated ion pairs may retard crossover product formation, and this caveat should be taken into account during data interpretation. The presence of the crossover products with the optimized low loading of catalytic palladium would indicate that the Pd(0) oxidative addition step is feasible under the catalytic reaction conditions, without the need for Au-catalyzed carbophilic[17] activation of the substrate first. The absence of crossover products, or a slower rate of crossover product formation, with catalytic palladium alone when compared to dual-catalytic conditions would establish that gold is required for the observed rate of crossover.

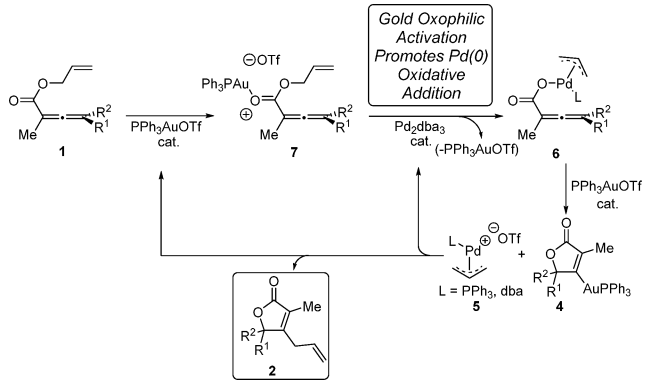
Accordingly, the crossover study was carried out for allyl allenoates **1a** and **1b** in the presence of Pd_2dba_3 (5 mol %) and PPh_3 (5 mol %) in CD_2Cl_2 (Scheme 3, condition A). After 25 min, no other peaks except the starting allenoates were observed by GCMS; thus 5.0 mol % of palladium—identical to reaction conditions—generates no conversion to either crossover product in the absence of gold.

To test if crossover could occur at presumably higher concentrations of metal-bound intermediates, the same crossover experiment was performed with significantly higher palladium loading, with 6 times the amount of Pd_2dba_3 (30 mol %) and PPh_3 (30 mol %). Under these highly concentrated substoichiometric conditions, the crossover products **1a′** and **1b′** were obtained along with competing internal olefin isomerization, **1a″** and **1b″** (Scheme 3, condition B). The time point 25 min was chosen for analysis because under cocatalytic conditions with both 5 mol % of gold and 5 mol % of palladium conversion to product is significant (69%). Thus crossover does not occur with palladium alone under the conditions or time scale of the optimized butenolide-forming reaction but can be induced at significantly higher loadings.

Since oxidative addition into the allyl group (leading to deallyation/solvent separation/recombination and crossover to form products **1a′** and **1b′**) does not occur with 5 mol % of palladium (the optimized reaction conditions) in the absence of gold, gold appears required to activate the substrate toward oxidative addition. These data are most consistent with a "gold first" mechanism operating under the optimized dual-catalytic conditions because the presence of both gold and palladium affects crossover (Scheme 4),[5b] whereas at identical concentration of only palladium, no crossover occurs (Scheme 3).

Experiments Inconsistent with the "Oxophilic Activation" Mechanism. We also considered the possibility that Au(I) may first act as an oxophilic[18] Lewis acid and promote the Pd(0) oxidative addition into the allyl group of allenoate **1** (Scheme 5), similar to our recently reported Au(I) azaphilic activation of vinyl aziridines toward Pd(0) oxidative addition.[5b]

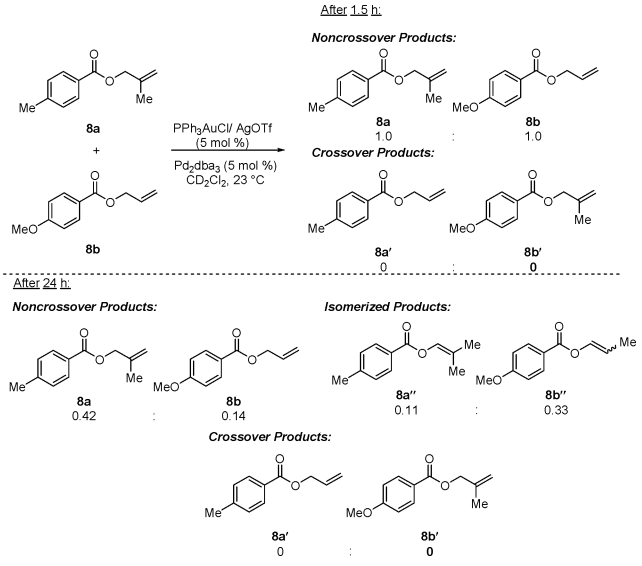
Scheme 5. Alternative Possible Oxophilic Activation Mechanism



In this proposed pathway, gold first coordinates to the carbonyl oxygen, forming activated intermediate **7**. The increased cationic charge on the carbonyl would then lower the barrier (i.e., catalyze) for oxidative addition of palladium to the allyl C−O bond. This pathway provides an alternative mechanism for formation of intermediate **6**, also considered previously in Scheme 2.

To test this hypothesis, a crossover experiment was performed between two substrates that had the possibility for Au(I) oxophilic activation but no opportunity for Au(I)-catalyzed carbophilic cyclization (Scheme 6). These modified

Scheme 6. Crossover Experiment with Substrates 8a and 8b



substrates were therefore employed to "isolate" steps of the cocatalytic reaction for individual study. In Scheme 6, substrates **8a** and **8b** are not capable of cyclization due to the absence of an allene moiety; however, oxidative addition is still possible. Thus these substrates serve to isolate the oxidative addition step of this reaction from other steps.

Substrates **8a** and **8b** were treated with $PPh_3AuCl/AgOTf$ (5 mol %) and Pd_2dba_3 (5 mol %) in CD_2Cl_2. After 1.5 h, no reaction occurred. After 24 h, no crossover products were

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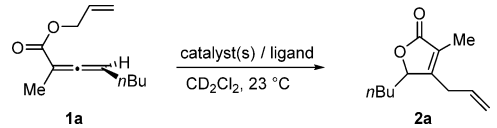
formed; however, partial conversion (45%) of substrates **8a** and **8b** to their respective internal olefin isomerization products, **8a″** and **8b″**, were observed by ^{1}H NMR spectroscopy. The lack of crossover products when no alkyne is present suggests that gold-catalyzed cyclization lowers the barrier for oxidative addition under the normal conditions where crossover does occur. This result, however, does not completely rule out a Pd(0) oxidative addition without gold; the π-allyl palladium complex and carboxylate may not be free ion pairs[25] in dichloromethane, a relatively nonpolar solvent, which may retard crossover product formation.

The data establish that under optimized cocatalytic conditions the presence of both gold and palladium cyclization/cross-coupling to generate butenolide product **5** outcompetes the olefin isomerization that was first detected in the experiments described in Scheme 5. Given the longer time scale for olefin isomerization (24 h) compared to butenolide formation (1.5 h), it is unlikely that olefin isomerization is rapid relative to cyclization to product. Therefore, olefin isomerization does not appear to be fast enough to establish Curtin–Hammett conditions whereby the starting olefin is rapidly isomerizing between the vinyl ester and allyl ester, and only the allyl ester provides a viable oxidative addition pathway that leads to product formation.

Experiments Inconsistent with a "Palladium π-Allyl Cation Catalyzed" Mechanism. We also considered the possibility that π-allyl Pd cation **5**, formed after one turnover in Scheme 1, was the active catalyst for the remainder of the reaction. Specifically, we considered that the role of gold might be only during the first turnover, to generate **5** which then catalyzed the reaction efficiently without gold in subsequent turnovers. To determine whether π-allyl Pd cation could catalyze the reaction alone, allenoate **1a** was treated in the absence of gold under three different conditions: with Pd(allyl)(OTf) in the absence of ligand (Table 1, entry 8), in the presence of dba (Table 1, entry 9), or in the presence of PPh_3 (Table 1, entry 10). The reactions were monitored by ^{1}H NMR spectroscopy at specific time points for comparison. These control reactions displayed a slow, but nonzero, formation of butenolide **2a** (entries 8–10, at 1.5 h: 23% with catalyst death, 13% with catalyst death, and 28% without catalyst death, respectively). In entries 8–10, catalyst death was indicated by a halt in further conversion after early time points. For comparison, the gold-and-palladium dual-catalytic system reached quantitative conversion after 1.5 h (entry 1). An active role for the gold cocatalyst thus was demonstrated.

Experiments Inconsistent with "SET" Mechanism. We examined if PPh_3AuOTf was acting as a single-electron oxidant for Pd(0) to form $(PPh_3)_2Pd(OTf)_2$.[26] Thus, the reaction may proceed through a Pd(II)/Pd(0) mechanism in which the gold does not bind to the substrate. In this mechanism, the gold simply serves to oxidize the palladium precatalyst. To probe this hypothesis, we treated allyl allenoate **1a** with a palladium precatalyst already in the Pd(II) oxidation state. To best mimic catalytic conditions wherein palladium in both +2 and 0 oxidation states might be present, a palladium(0) precatalyst was also added. Specifically, the potentially catalytic mixture of 2.5 mol % of $(PPh_3)_2Pd(OTf)_2$ and 3.75 mol % of Pd_2dba_3 was examined (Table 1, entry 11). The reaction was monitored by ^{1}H NMR spectroscopy. The yield of butenolide product **2a** was low (7–9%) and remained approximately constant between 10 min and 1.5 h, consistent with catalyst death or single turnover and no catalysis. In contrast, the Au/Pd dual-catalytic system reached quantitative conversion at 1.5 h (Table 1, entry 1).

Table 1. Comparison of ^{1}H NMR Yields for Different Precatalysts



1a 2a

		^{1}H NMR yield (%)[a]			
entry	catalyst(s)/ligand (if added)	10 min	25 min	60 min	90 min
1	PPh_3AuCl (5 mol %), AgOTf (5 mol %), Pd_2dba_3 (5 mol %)	24	69	93	100
2	PPh_3AuCl (5 mol %), AgOTf (5 mol %)	0	0	0	0
3	Pd_2dba_3 (5 mol %)	0	0	0	0
4	Pd_2dba_3 (5 mol %), AgOTf (5 mol %)	22	23	24	28
5	PPh_3AuCl (5 mol %), NaBArF (5 mol %), Pd_2dba_3 (5 mol %)	23	28	40	47
6	Pd_2dba_3 (5 mol %), NaBArF (5 mol %)	1	2	5	9
7	NaBArF (5 mol %)	0	0	0	0
8	$Pd_2(allyl)_2Cl_2$ (5 mol %), AgOTf (10 mol %)	7	13	22	23
9	$Pd_2(allyl)_2Cl_2$ (5 mol %), AgOTf (10 mol %), dba (15 mol %)	0	6	12	13
10	$Pd_2(allyl)_2Cl_2$ (5 mol %), AgOTf (10 mol %), PPh_3 (5 mol %)	10	14	17	28
11	$Pd(PPh_3)_2Cl_2$ (2.5 mol %), AgOTf (5 mol %), Pd_2dba_3 (3.75 mol %)	7	8	8	9

[a] ^{1}H NMR yield was determined based on the ratio of product **2a** relative to mesitylene, which was used as an internal standard.

The cyclic voltammograms (CV) of PPh_3AuCl, AgOTf, PPh_3AuCl plus AgOTf, and Pd_2dba_3[27] in dichloromethane also suggest the absence of redox between the precatalysts in the optimized reaction solvent (Figure 1 and also Supporting Information Figures S1–S6). While Pd_2dba_3 shows redox consistent with the studies of Pd-dba complexes by Amatore and Jutand,[27] the gold and gold/silver mixtures did not show distinct redox features. Nevertheless, electron transfer may still be possible between metal-based intermediates generated after reaction initiation.[10b]

Thus, catalyst screening, conversion, and CV studies, when considered together, are most consistent with an absence of SET as a primary catalytic reaction pathway.

Experiments Consistent with Au/Pd Dual-Metal Catalysis Mechanism. As mentioned previously, published kinetics experiments from our group established a kinetic dependence on both gold and palladium in this reaction.[5b] Palladium displayed clean pseudo-first-order kinetics, and gold displayed a clear kinetic dependence (however, the order in gold could not be unambiguously determined due to catalyst decomposition at higher loading).

We next considered whether the single-metal precatalysts could catalyze the reaction when examined over a time range analogous to the optimized cocatalytic conditions. For this comparison, we treated allenoate **1a** under optimized conditions with 5 mol % of PPh_3AuCl and 5 mol % of AgOTf in the presence of 5 mol % of Pd_2dba_3 (Table 1, entry 1). The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed 24, 69, 93, and 100% conversions, respectively. Next, the allenoate **1a** was treated with only Au and only Pd. In these experiments, no

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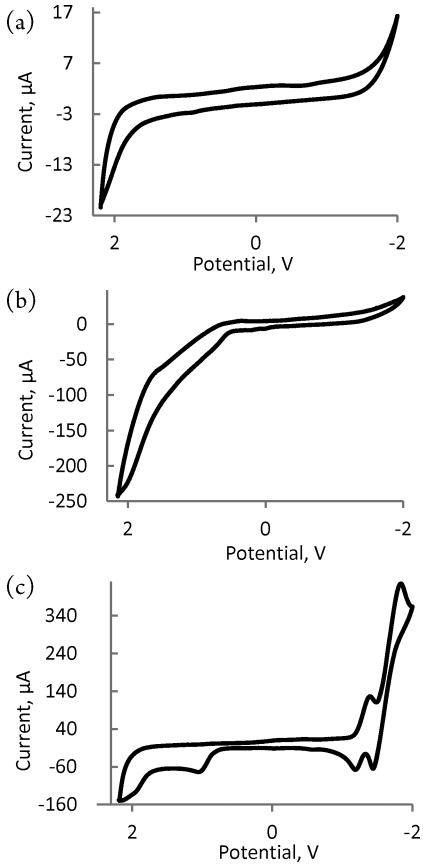

Figure 1. Cyclic voltammograms of (a) PPh_3AuCl, (b) PPh_3AuCl + AgOTf, and (c) Pd_2dba_3, measured in dry CH_2Cl_2 (0.1 M TBAP) under air-free conditions with a scan rate of 0.1 V s^{-1}.

butenolide product **2a** was observed by ^1H NMR spectroscopy (Table 1, entries 2 and 3). When we treated allenoate **1a** with 5 mol % of Pd_2dba_3 in the presence of 5 mol % of AgOTf (Table 1, entry 4), the yield of butenolide product **2a** was lowered as compared to the Au/Pd dual-catalytic system (Table 1, entry 1). Thus, a kinetic role for the Au/Pd cocatalyst was demonstrated definitely.

A "silver effect" in gold catalysis, where residual silver from the salt metathesis reagent AgOTf is noninnocent, was reported early by our group[5a] and then by others.[28] To probe if silver was noninnocent under the conditions of the dual-catalytic rearrangement, a reaction with a silver-free metathesis reagent was explored. When employing NaBArF (instead of AgOTf), the rate of butenolide product **2a** formation was lowered somewhat (entry 5) compared to the gold/palladium catalytic system (entry 1). This lower yield could be due to the absence of Ag(I) or to the effect of the changing the counterion to BArF instead of OTf.

CONCLUSION

The summary of mechanistic crossover studies and control reactions are consistent with a "gold cyclization first" mechanistic hypothesis. Specifically, (1) gold activates the substrate prior to oxidative addition by palladium, (2) gold acts as a carbophilic rather than oxophilic Lewis acid, (3) competing olefin isomerization is avoided, (4) gold participates beyond the first turnover and therefore does not serve simply to generate the active palladium catalyst, and (5) single-electron transfer is not involved.

In this mechanism, substrate cyclization by gold creates a transmetalation cross-coupling partner in situ for further reactivity with a palladium π-allyl intermediate. Furthermore, the mechanistic data support the cooperative role of both catalysts in that a role of gold is to lower the barrier (i.e., catalyze) for oxidative addition by palladium. In this way, the gold and palladium cocatalysts behave differently from a purely tandem catalyst system where each catalyst acts on the substrate separately; instead the gold and palladium act cooperatively. This understanding of the pathways available in gold and palladium systems is expected to aid in the predictive design of future dual-catalytic reactions.

EXPERIMENTAL SECTION

General. All chemicals were used as received from commercial suppliers unless otherwise noted. Precatalysts PPh_3AuCl and Pd_2dba_3 were purchased from Strem Chemical Co. Dichlorobis(triphenylphosphine)palladium(II) was purchased from Alfa Aesar. Methylene chloride-d_2 was dried over CaH_2, degassed using three freeze, pump, thaw cycles, and vacuum-transferred prior to use. All gold and palladium substrate rearrangement and control reactions were performed in an inert atmosphere (N_2) box unless otherwise noted. Analytical and preparatory TLC was performed on Merck F250 TLC plates. Flash chromatography was performed on Dynamic Absorbents 43-60 μm silica gel. ^1H NMR spectra were acquired on either the GN-500, AV-600, or Bruker CRYO-500 spectrometers. ^{13}C NMR spectra were acquired on the Bruker CRYO-500 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane and referenced to the residual protiated solvent peak (^1H NMR). High-resolution mass spectrometry (HRMS) was performed at the facility operated by the University of California, Irvine.

Synthesis of 1a and 1 b. The two allenoate substrates **1a** and **1b** were prepared according to the previously reported literature[5] and ^1H NMR spectra were consistent with that literature.[5]

Synthesis of Substrate 8a. In the glovebox, *p*-methyl benzoic acid (90 mg, 0.66 mmol) was dissolved in dry DMF (2.0 mL) and $NaHCO_3$ (92.0 mg, 1.10 mmol) was added. The solution was stirred for 2 min, then 1-bromo-2-methyl-1-propene (0.11 mL, 1.1 mmol) was added dropwise and the resulting solution was allowed to stir overnight. Next, the solution was concentrated in vacuo and purified by column chromatography (35:1 hexanes/EtOAc). The resulting oil was put under vacuum (~12 mTorr) overnight, which afforded **8a** (65.0 mg, 51%) as a clear, colorless oil. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.85 (s, 3H), 2.42 (s, 3H), 4.74 (s, 2H), 4.99 (m, 1H), 5.08 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.97 (dd, J = 1.7, 6.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 19.6, 21.7, 68.0, 112.8, 127.5, 129.2, 129.7, 140.2, 143.7, 166.4. HRMS (ESI): $[M + Na]^+$ calcd for $C_{12}H_{15}O_2$, 191.1072; found, 191.1070.

Synthesis of Substrate 8b. In the glovebox, *p*-methoxy benzoic acid (2.00 g, 1.32 mmol) was dissolved in dry DMF (4.1 mL) and $NaHCO_3$ (332 mg, 3.95 mmol) was added. The solution was stirred for 2 min, then allyl bromide (0.33 mL, 3.9 mmol) was added dropwise and the resulting solution was allowed to stir overnight. Next, the solution was concentrated in vacuo and purified by column chromatography (20:1 hexanes/EtOAc). The resulting oil was put under vacuum (~12 mTorr) overnight, which afforded **8b** (210.0 mg, 84%) as a clear, yellow oil. The ^1H NMR spectrum was consistent with that previously reported in the literature.[29]

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Crossover Experiment between 1a and 1b (Condition A: Catalytic). In a glovebox, Pd_2dba_3 (2.3 mg, 0.0025 mmol), PPh_3 (0.7 mg, 0.003 mmol), **1a** (9.7 mg, 0.049 mmol), and **1b** (8.30 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing **1a**. The solution was transferred to the vial containing **1b**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. Next, dry CD_2Cl_2 (0.1 mL) was added via syringe to the dram vial containing Pd_2dba_3, and this solution was then added to the dram vial containing PPh_3. Next, dry CD_2Cl_2 (0.05 mL) was used as a rinse and added to the Pd_2dba_3/PPh_3 vial. The Pd_2dba_3/PPh_3 solution was added to the dram vial containing the substrates **1a** and **1b**. Again, CD_2Cl_2 (0.05 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.1 mL) was used as a rinse and added to the J. Young tube. The reaction was monitored by GCMS, and after 25 min, peaks of two allenoates **1a** and **1b** were observed by GCMS at RT of 13.83 and 11.31, respectively, and no peaks from crossover products **1a′** and **1b′** were detected by GCMS.

Crossover Experiment between 1a and 1b (Condition B: High Loading). In a glovebox, Pd_2dba_3 (8 mg, 0.009 mmol), PPh_3 (2 mg, 0.009 mmol), **1a** (5.9 mg, 0.030 mmol), and **1b** (5 mg, 0.03 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing **1a**. The solution was transferred to the vial containing **1b**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. Next, dry CD_2Cl_2 (0.1 mL) was added via syringe to the dram vial containing Pd_2dba_3, and this solution was then added to the dram vial containing PPh_3. Next, dry CD_2Cl_2 (0.05 mL) was used as a rinse and added to the Pd_2dba_3/PPh_3 vial. The Pd_2dba_3/PPh_3 solution was added to the dram vial containing the substrates **1a** and **1b**. Again, CD_2Cl_2 (0.05 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.1 mL) was used as a rinse and added to the J. Young tube. The reaction was monitored by GCMS and after 25 min, the peaks of two allenoates **1a** and **1b**, the peaks of their crossover products **1a′** and **1b′**, and peaks of two isomerized products **1a″** (isomer of **1a′**) and **1b″** (isomer of **1b**) were observed by GCMS at RT of 13.66, 11.20, 14.62, 10.05, 17.32, and 14.25 in the ratio of 0.10:0.34:0.30:0.19:0.03:0.04, respectively.

Crossover Experiment between 8a and 8b. In a glovebox, PPh_3AuCl (1.2 mg, 0.0025 mmol), AgOTf (0.6 mg, 0.003 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol), **8a** (4.8 mg, 0.025 mmol), and **8b** (4.8 mg, 0.025 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing **8a**. The solution was transferred to the vial containing **8b**. CD_2Cl_2 (0.05 mL) was used as a rinse. Next, CD_2Cl_2 (0.1 mL) was added via syringe to the dram vial containing PPh_3AuCl, and this solution was then added to the dram vial containing AgOTf. Next, CD_2Cl_2 (0.05 mL) was used as a rinse and added to the PPh_3AuCl/AgOTf vial. The PPh_3AuCl/AgOTf solution was added to the dram vial containing the substrates **8a** and **8b**. Again, CD_2Cl_2 (0.05 mL) was used as a rinse. To the dram vial containing Pd_2dba_3 was added the solution containing substrate and PPh_3AuCl/AgOTf. The vial previously containing Pd was rinsed with CD_2Cl_2 (0.1 mL) and added to the final solution. The final solution was transferred to a J. Young tube. CD_2Cl_2 (0.05 mL) was used as a rinse and added to the J. Young tube. The reaction was monitored by ^{1}H NMR spectroscopy after 1.5 h and after 24 h. After 1.5 h, no reaction had occurred. After 24 h, starting materials **8a** and **8b** were observed, along with olefin isomerization products **8a″** and **8b″** (0.42:0.14:0.11:0.33, respectively). Products were determined based on comparison of the ^{1}H NMR spectrum to known literature compounds.

Control Experiments with 1a (Table 1). *Entry 1. With PPh_3AuCl/AgOTf, Pd_2dba_3.* In a glovebox, AgOTf (0.6 mg, 0.002 mmol), PPh_3AuCl (1.2 mg, 0.0025 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol), and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing PPh_3AuCl. The solution was transferred to the vial containing AgOTf. Dry CD_2Cl_2 (0.05 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The solution was transferred to the vial containing Pd_2dba_3. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.15 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (6 mg, 7 μL, 0.05 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 24, 69, 93, and 100% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 2. With PPh_3AuCl/AgOTf. In a glovebox, AgOTf (0.6 mg, 0.002 mmol), PPh_3AuCl (1.2 mg, 0.0025 mmol), and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing AgOTf. The solution was transferred to the vial containing PPh_3AuCl. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.2 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (6 mg, 7 μL, 0.05 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a zero conversion in each case (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 3. With Pd_2dba_3. In a glovebox, Pd_2dba_3 (2.3 mg, 0.0025 mmol) and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing Pd_2dba_3. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.3 mL) was used as a rinse and added to the J. Young tube. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a zero conversion in each case (determined based on the ratio of butenolide product **2a** to allenoate **1a**).

Entry 4. With Pd_2dba_3/AgOTf. In a glovebox, AgOTf (0.6 mg, 0.002 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol), and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing AgOTf. The solution was transferred to the vial containing Pd_2dba_3. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.2 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (6 mg, 7 μL, 0.05 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 22, 23, 24, and 28% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

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Entry 5. With $PPh_3AuCl/NaBArF$, Pd_2dba_3. In a glovebox, PPh_3AuCl (0.7 mg, 0.002 mmol), NaBArF (1.8 mg, 0.0015 mmol), Pd_2dba_3 (1.8 mg, 0.0015 mmol), and **1a** (6 mg, 0.03 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing PPh_3AuCl. The solution was transferred to the vial containing NaBArF. Dry CD_2Cl_2 (0.05 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The solution was transferred to the vial containing Pd_2dba_3. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.15 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (4 mg, 4 μL, 0.03 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 23, 28, 40, and 47% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 6. With $Pd_2dba_3/NaBArF$. In a glovebox, NaBArF (1.8 mg, 0.0015 mmol), Pd_2dba_3 (1.8 mg, 0.0015 mmol), and **1a** (6 mg, 0.03 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing NaBArF. The solution was transferred to the vial containing Pd_2dba_3. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.2 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (4 mg, 4 μL, 0.03 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 1, 2, 5, and 9% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 7. With NaBArF. In a glovebox, NaBArF (1.8 mg, 0.0015 mmol) and **1a** (6 mg, 0.03 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing NaBArF. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.3 mL) was used as a rinse and added to the J. Young tube. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a zero conversion in each case (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 8. With $Pd_2(allyl)_2Cl_2/AgOTf$. In a glovebox, AgOTf (1.3 mg, 0.0051 mmol), $Pd_2(allyl)_2Cl_2$ (0.9 mg, 0.002 mmol), and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing $Pd_2(allyl)_2Cl_2$. The solution was transferred to the vial containing AgOTf. Dry CD_2Cl_2 (0.05 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.25 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (6 mg, 7 μL, 0.05 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 7, 13, 22, and 23% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 9. With $Pd_2(allyl)_2Cl_2/AgOTf$, dba. In a glovebox, AgOTf (1.3 mg, 0.0051 mmol), $Pd_2(allyl)_2Cl_2$ (0.9 mg, 0.002 mmol), dba (1.8 mg, 0.0075 mmol), and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing $Pd_2(allyl)_2Cl_2$. The solution was transferred to the vial containing AgOTf. Dry CD_2Cl_2 (0.05 mL) was used as a rinse. The solution was transferred to the vial containing dba. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.15 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (6 mg, 7 μL, 0.05 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 0, 6, 12, and 13% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 10. With $Pd_2(allyl)_2Cl_2/AgOTf$, PPh_3. In a glovebox, AgOTf (1.3 mg, 0.0051 mmol), $Pd_2(allyl)_2Cl_2$ (0.9 mg, 0.002 mmol), PPh_3 (0.7 mg, 0.002 mmol), and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing $Pd_2(allyl)_2Cl_2$. The solution was transferred to the vial containing AgOTf. Dry CD_2Cl_2 (0.05 mL) was used as a rinse. The solution was transferred to the vial containing PPh_3. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.15 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (6 mg, 7 μL, 0.05 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 10, 14, 17, and 28% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

Entry 11. With $Pd(PPh_3)_2Cl_2/AgOTf$, Pd_2dba_3. In a glovebox, AgOTf (0.6 mg, 0.002 mmol), $Pd(PPh_3)_2Cl_2$ (0.5 mg, 0.001 mmol), Pd_2dba_3 (1.7 mg, 0.0019 mmol), and **1a** (9.7 mg, 0.049 mmol) were weighed in separate dram vials. Dry CD_2Cl_2 (0.1 mL) was added via syringe to the vial containing $Pd(PPh_3)_2Cl_2$. The solution was transferred to the vial containing AgOTf. Dry CD_2Cl_2 (0.05 mL) was used as a rinse. Next, the solution was transferred to the vial containing **1a**. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The solution was transferred to the vial containing Pd_2dba_3. Dry CD_2Cl_2 (0.1 mL) was used as a rinse. The final solution was transferred to a J. Young tube. Dry CD_2Cl_2 (0.15 mL) was used as a rinse and added to the J. Young tube, and then mesitylene (6 mg, 7 μL, 0.05 mmol) was added as an internal standard. The reaction was monitored by ^{1}H NMR spectroscopy after 10, 25, 60, and 90 min intervals and showed a 7, 8, 8, and 9% conversion, respectively (determined based on the ratio of butenolide product **2a** to mesitylene).

■ ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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