Gold-Catalyzed Heck Reaction

Vivek W. Bhoyare, Chetan C. Chintawar, and Nitin T. Patil*

 Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhauri, Bhopal 462 066, India
Email: npatil@iiserb.ac.in

ABSTRACT: Herein, we report a gold-catalyzed Heck reaction facilitated by the ligand-enabled Au(I)/Au(III) redox catalysis. The elementary organometallic steps such as migratory insertion and β-hydride elimination have been realized in the catalytic fashion for the first time in gold chemistry. The present methodology not only overcomes the limitations of previously known transition metal-catalyzed Heck reactions such as the requirement of specialized substrates and formation of a mixture of regioisomeric products as a result of the undesirable chain-walking process but also offers complementary regioselectivity as compared to other transition metal catalysis.

Since its discovery, the transition metal-catalyzed Heck reaction has emerged as one of the indispensable tools for state-of-the-art organic synthesis.[1] However, this reaction suffers from certain limitations; the most restrictive limitation is the requirement of electronically biased olefins, such as styrenes, vinyl ethers, or α, β-unsaturated carbonyl compounds, in order to obtain a single regioisomeric Heck product.[2] The use of long-chain aliphatic alkenes often leads to the inseparable mixture of regioisomers (Scheme 1a). It is mainly due to the incompetence of the metal center to distinguish between H^a and H^b when undergoing β-hydride elimination which results in the mixture of styrenyl and allylic products. Further, these products are highly susceptible to undergo chain-walking process in which the reinsertion of the metal-hydride species followed by iterative β-hydride elimination/migratory insertion cascade leads to the mixture of regioisomers.[3] Over the past two decades, several efforts have been devoted to control the undesired chain-walking process. In particular, the palladium-catalyzed oxidative Heck reactions independently developed by Sigman,[4] White,[5] Engle,[6] and Zhao[7] emerged as an attractive strategy to access a single regioisomeric Heck product in good yield and regioselectivity (Scheme 1b). However, the requirement of stoichiometric external oxidant and preinstalled directing/chelating group on alkene substrate hinders the broad applicability of this approach.

Over the past 15 years, Au(I)/Au(III) redox catalysis has emerged as one of the most dynamic areas of research.[8] Number of gold-catalyzed cross-coupling and 1,2-difunctionalization reactions have been developed by utilizing external oxidants,[8g,l,m] photocatalysts,[8e,f,l,m] EBX reagents,[8h,l,m] electrochemical,[9] or ligand-enabled approach.[8l,m,10] Even, very recently, our group[11] and Shi's group[12] reported the first example of enantioselective Au(I)/Au(III) redox catalysis.[13] In spite of such significant advancements, the gold-catalyzed Heck reaction which is also supposed to operate *via* Au(I)/Au(III) redox catalysis has not been realized yet. This could be attributed to the reluctance of gold complexes to undergo migratory insertion and β-hydride elimination processes which are the key steps in Heck reaction.[14] The combined experimental and theoretical studies carried out by Köppel/Hashmi group clearly indicated the non-feasibility of β-hydride elimination in IPrAu(I)-ethyl complex even at higher temperature.[15] However, the theoretical studies conducted by Cremer/Faza group suggested that the β-hydride elimination could be facilitated at Au(III)-ethyl dichloride complex.[16] Recently, in a stoichiometric study, Toste,[17] Bourissou[18] and Nevado[19] group showcased the feasibility of β-hydride elimination in Au(III)- difluoroalkyl, Au(III)-alkyl, and Au(III)-formate complexes, respectively. Similarly, the feasibility of (formal) migratory insertion in Au(I) and Au(III) complexes is shown by the research group of Bochmann,[20] Bourissou/Amgoune,[21] and Tilset.[22] Despite these stoichiometric studies, until now there is no report

**Scheme 1.** Heck Reaction: General Overview and Present Work
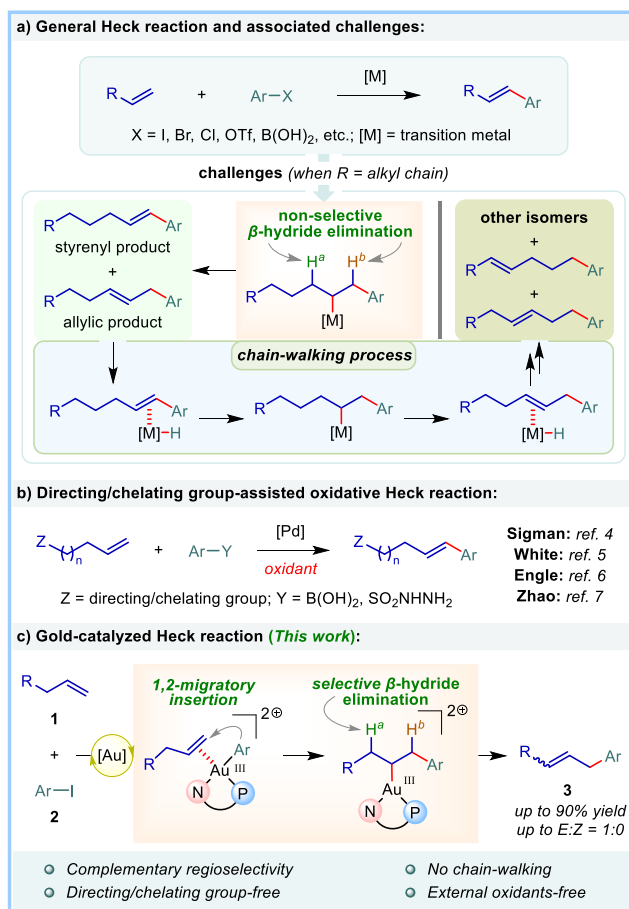
available on the gold-mediated migratory insertion and β-hydride elimination steps in catalytic fashion.

Herein, we disclose the first example of gold-catalyzed Heck reaction where the catalytic cycle involves the key migratory insertion and β-hydride elimination steps (Scheme 1c). The reaction utilizes long-chain aliphatic alkenes without the need of a preinstalled directing/chelating group. Interestingly, gold catalysts offered a complementary regioselectivity as compared to other transition metal catalysts. For instance, the Au(III)-alkyl intermediate generated *in situ* after migratory insertion could selectively undergo β-hydride elimination with H^a over H^b to favor the formation of allylic products over styrenyl products. To the best of our knowledge such reversal of regioselectivity for electronically unbiased alkenes has never been reported. Apart from this, the so-formed allylic Heck products did not undergo

the chain-walking process, yielding the desired products as a single regioisomer.

Initial explorations on the gold-catalyzed Heck reaction were began by using 1-hexene **1a** and 4-iodoanisole **2a** as coupling partners in presence of MeDalPhosAuCl (10 mol%), AgOTf (1.1 equiv) and K$_3$PO$_4$ (0.7 equiv) in DCE (0.1 M) at 80 °C (Table 1). To our delight, the desired Heck products **3a** and **4a** were obtained in 57% combined yield with 8.7:1 regioisomeric ratio (entry 1). With this encouraging outcome, we turned our attention towards improving the yield and regioselectivity of the reaction. The screening of several bases revealed that the organic bases such as DTBP, 2,6-lutidine, and pyridine are more suitable for this reaction (entries 3–5). The desired product **3a** was isolated in the

Table 1. Optimization of Reaction Conditions[a]
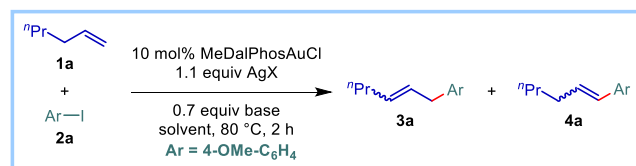
Entry	AgX	Base	Solvent	Yield (%)[b]	3a:4a[c]
1[d]	AgOTf	K$_2$PO$_4$	DCE	57	8.7:1
2[d]	AgOTf	Na$_2$CO$_3$	DCE	76	8.7:1
3[e]	AgOTf	DTBP	DCE	75	1:0
4[e]	AgOTf	2,6-lutidine	DCE	76	1:0
5[e]	**AgOTf**	**pyridine**	**DCE**	**80**	**1:0**
6[e,f]	AgOTf	pyridine	DCE	67	1:0
7[e,g]	AgOTf	pyridine	DCE	68	8.3:1
8	AgSbF$_6$	pyridine	DCE	NR	--
9[e]	AgNTf$_2$	pyridine	DCE	50	1:0
10[e]	AgBF$_4$	pyridine	DCE	47	18:1
11[d]	AgOTf	pyridine	DCB	78	35:1
12[e]	AgOTf	pyridine	chloroform	30	8.3:1
13[d]	AgOTf	pyridine	1,4-dioxane	08	4.2:1
14[e,h]	AgOTf	pyridine	DCE	73	1:0
15[e,i]	AgOTf	pyridine	DCE	68	1:0
16[e,j]	AgOTf	pyridine	DCE	51	17:1

[a]Reaction conditions: 0.3 mmol **1a**, 0.1 mmol **2a**, 0.01 mmol MeDalPhosAuCl, 0.11 mmol AgX, 0.07 mmol base, solvent (0.1 M), 80 °C, 2 h. [b]Isolated combined yields (**3a**+**4a**). [c]Based on ^{1}H NMR. [d]E:Z ratio for **3a** = 3.3:1. [e]E:Z ratio for **3a** = 4:1. [f]0.4 equiv pyridine was used. [g]1 equiv pyridine was used. [h]2 equiv **1a** was used. [i]7.5 mol% MeDalPhosAuCl was used. [j]5 mol% MeDalPhosAuCl was used. NR = no reaction.

highest 80% yield (entry 5), without the formation of other regioisomer (i.e. **4a**), when pyridine (0.7 equiv) was employed as a base. Be noted that the equivalence of base has a significant impact on the yield and regioselectivity of the reaction (entry 6 and 7). Varying the halide scavenger (entries 8–10), solvent (entries 11–13), equivalence of **1a** (entry 14), and catalyst loading (entry 15 and 16) had detrimental effect on the reaction outcome.

Having identified optimal reaction conditions, we set out to explore the scope of alkenes **1** in the gold-catalyzed Heck reac-
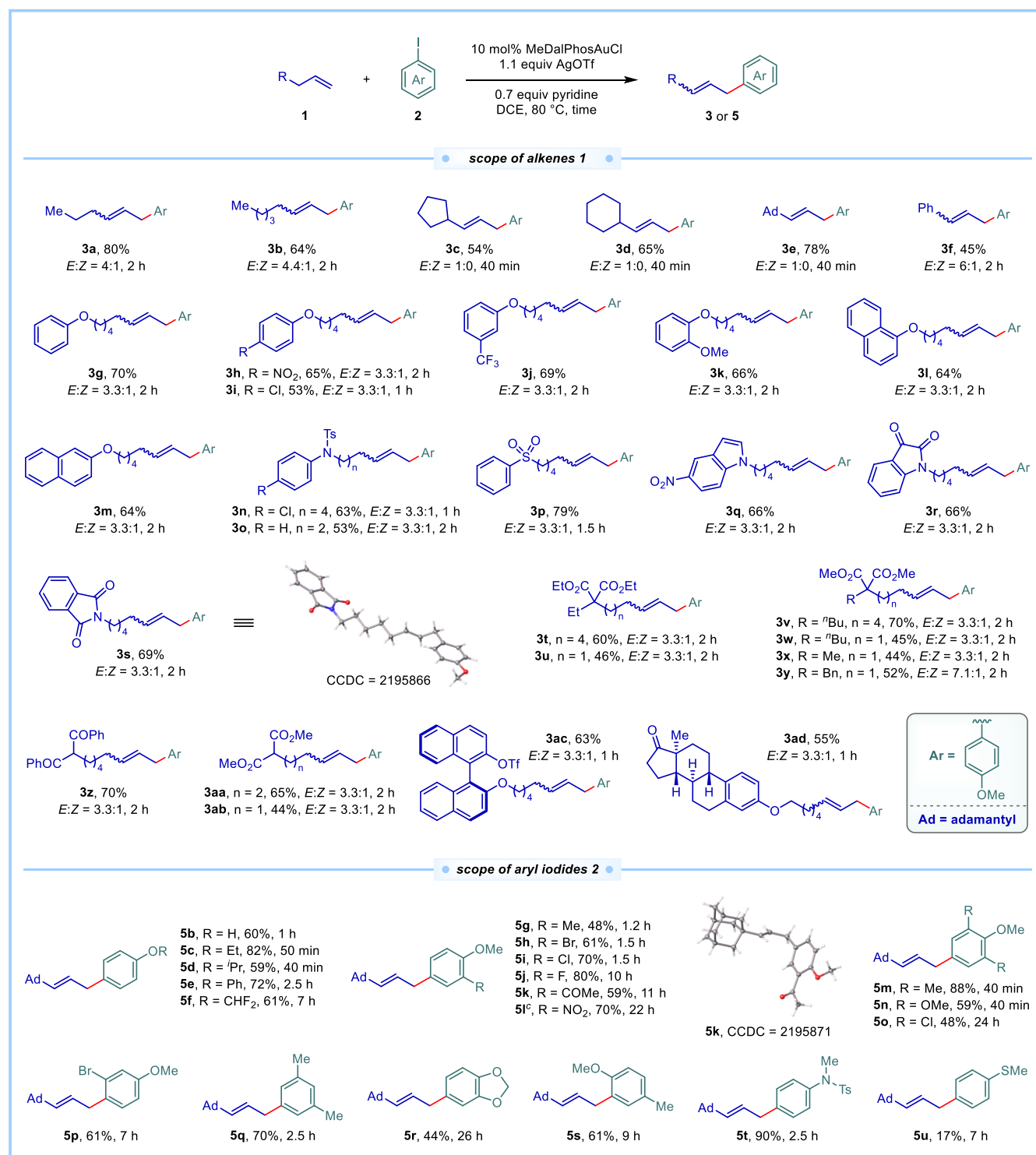
tion by using 4-iodoanisole **2a** as a model substrate (Scheme 2). To our delight, a wide range of alkenes **1** reacted smoothly under the present reaction conditions to afford the corresponding Heck products **3**. For instance, 1-hexene and 1-octene reacted smoothly to furnish corresponding Heck products **3a** and **3b** in 80% (E:Z = 4:1) and 64% (E:Z = 4.4:1) yield, respectively. Notably, exclusive E-isomer of the products **3c-3e** was obtained in 54-78% yields when 1-allylcyclopentane, 1-allylcyclohexane, and 1-allyladamantane were used as alkene source. Allylbenzene also reacted with **2a** to afford the desired product **3f** in 45% yield (E:Z = 6:1). Besides, alkenes tethered with variously substituted phenoxide and naphthoxide groups performed well under the optimized reaction conditions to furnish the desired products **3g-3m** in 53-70% yields (E:Z = 3.3:1). Moreover, the alkenes tethered with protected aniline, sulfone, indole, isatin, and phthalimide derivatives also reacted smoothly with **2a** to deliver the corresponding products **3n-3s** in 53-79% yields (E:Z = 3.3:1). The structure of product **3s** was unambiguously confirmed by X-ray crystallographic analysis. Next, when alkenes tethered with differently substituted diethyl and dimethyl malonates **1t-1ab** were treated with **2a** under the optimized reaction conditions, the corresponding products **3t-3ab** were obtained in 44-70% yield. Of note, the alkenes with shorter chain length gave slightly lower yields of the products (compare **3t** vs **3u**, **3v** vs **3w**, and **3aa** vs **3ab**). Notably, the current methodology is suitable for the late-stage functionalization as alkenes derived from (S)-BINOL and estrone reacted smoothly affording the corresponding allylic Heck products **3ac** and **3ad** in 63% and 55% yield, respectively.

We next turned to evaluate the scope of aryl iodides **2**, using 1-allyladamantane **1e** as a model substrate. Pleasingly, different derivatives of iodobenzenes **2** reacted efficiently to produce the desired allylic Heck products **5b-5u** as exclusive E-isomer in good to excellent yields. For instance, the products **5b-5f** were obtained in 59-82% yield when different para-substituted aryl iodides **2b-2f** were used as substrates. Further, 4-iodoanisole bearing electron-donating, withdrawing, or halo substituents also reacted well under the optimized reaction conditions furnishing the products **5g-5p** in 48-88% yields. The gold catalyst showed excellent chemoselectivity for the C(sp^2)-I bond as other C(sp^2)-X bonds (X = Br, Cl, F) remained completely unaffected during the reaction (see entries **5h-5j**, **5o**, **5p**), thus offering an opportunity for further functionalization of these products. Other aryl iodides such as 1-iodo-3,5-dimethylbenzene **2q**, 5-iodo-1,3-benzodioxole **2r**, 2-iodo-1-methoxy-4-methylbenzene **2s**, and tosyl-protected 4-iodo-N-methylaniline **2t** also reacted smoothly to afford the corresponding products **5q-5t** in 44-90% yields, respectively. The significant drop in yield of the product **5u** (17% yield) was noticed; which could be accounted for the quenching of the gold catalyst by strong irreversible chelation of sulfur of the 4-iodothioanisole **2u** to the Au(I) or Au(III) intermediate.

Interestingly, the styrenyl Heck product **6** was obtained in 65% yield as exclusive E-isomer when the alkene lacking allylic hydrogen such as 1-vinyladamantane **1ae** was used as a substrate under the standard reaction conditions (Figure 1).

To gain deeper understanding into the reaction mechanism, a few control experiments were performed (Scheme 3). When the in situ generated Au(III) complex **B** derived from MeDalPhosAuCl and 4-iodoanisole was treated with 1-hexene in the presence of AgOTf, the desired product **3a** was obtained in 92% yield along with N-protonated Au(I) complex **I** (Scheme 3a). This clearly indicates that the oxidative addition precedes the migratory

Scheme 2. Scope of the Gold-Catalyzed Heck Reaction[a,b]

R + Ar–I → 10 mol% MeDalPhosAuCl, 1.1 equiv AgOTf, 0.7 equiv pyridine, DCE, 80 °C, time → R—Ar (3 or 5)

scope of alkenes 1

3a, 80%
E:Z = 4:1, 2 h

3b, 64%
E:Z = 4.4:1, 2 h

3c, 54%
E:Z = 1:0, 40 min

3d, 65%
E:Z = 1:0, 40 min

3e, 78%
E:Z = 1:0, 40 min

3f, 45%
E:Z = 6:1, 2 h

3g, 70%
E:Z = 3.3:1, 2 h

3h, R = NO$_2$, 65%, E:Z = 3.3:1, 2 h
3i, R = Cl, 53%, E:Z = 3.3:1, 1 h

3j, 69%
E:Z = 3.3:1, 2 h

3k, 66%
E:Z = 3.3:1, 2 h

3l, 64%
E:Z = 3.3:1, 2 h

3m, 64%
E:Z = 3.3:1, 2 h

3n, R = Cl, n = 4, 63%, E:Z = 3.3:1, 1 h
3o, R = H, n = 2, 53%, E:Z = 3.3:1, 2 h

3p, 79%
E:Z = 3.3:1, 1.5 h

3q, 66%
E:Z = 3.3:1, 2 h

3r, 66%
E:Z = 3.3:1, 2 h

3s, 69%
E:Z = 3.3:1, 2 h

CCDC = 2195866

3t, n = 4, 60%, E:Z = 3.3:1, 2 h
3u, n = 1, 46%, E:Z = 3.3:1, 2 h

3v, R = ^{n}Bu, n = 4, 70%, E:Z = 3.3:1, 2 h
3w, R = ^{n}Bu, n = 1, 45%, E:Z = 3.3:1, 2 h
3x, R = Me, n = 1, 44%, E:Z = 3.3:1, 2 h
3y, R = Bn, n = 1, 52%, E:Z = 7.1:1, 2 h

3z, 70%
E:Z = 3.3:1, 2 h

3aa, n = 2, 65%, E:Z = 3.3:1, 2 h
3ab, n = 1, 44%, E:Z = 3.3:1, 2 h

3ac, 63%
E:Z = 3.3:1, 1 h

3ad, 55%
E:Z = 3.3:1, 1 h

Ar = (4-OMe-phenyl)
Ad = adamantyl

scope of aryl iodides 2

5b, R = H, 60%, 1 h
5c, R = Et, 82%, 50 min
5d, R = ^{i}Pr, 59%, 40 min
5e, R = Ph, 72%, 2.5 h
5f, R = CHF$_2$, 61%, 7 h

5g, R = Me, 48%, 1.2 h
5h, R = Br, 61%, 1.5 h
5i, R = Cl, 70%, 1.5 h
5j, R = F, 80%, 10 h
5k, R = COMe, 59%, 11 h
5l[c], R = NO$_2$, 70%, 22 h

5k, CCDC = 2195871

5m, R = Me, 88%, 40 min
5n, R = OMe, 59%, 40 min
5o, R = Cl, 48%, 24 h

5p, 61%, 7 h

5q, 70%, 2.5 h

5r, 44%, 26 h

5s, 61%, 9 h

5t, 90%, 2.5 h

5u, 17%, 7 h

[a]Reaction conditions: 0.6 mmol **1a**, 0.2 mmol **2a**, 0.02 mmol MeDalPhosAuCl, 0.22 mmol AgOTf, 0.14 mmol pyridine, DCE (0.1 M), 80 °C. [b]Isolated yields. [c]0.9 equiv pyridine was used.

insertion and β-hydride elimination steps. The N-protonated Au(I) complex **I** was characterized on the basis of ^{1}H, ^{31}P, ^{19}F NMR, and HR-MS analysis.[23] Notably, this complex was found to be catalytically inactive in the absence of base as no product

formation was observed when **1a** and **2a** were treated with 10 mol% **I** in the presence of AgOTf (Scheme 3b). However, when pyridine was added, in otherwise same reaction conditions, the desired Heck product was isolated in 71% yield. This reveals the

importance of base in regenerating the active catalyst during the reaction. Next, when deuterated alkene **1x-D** was subjected to the standard
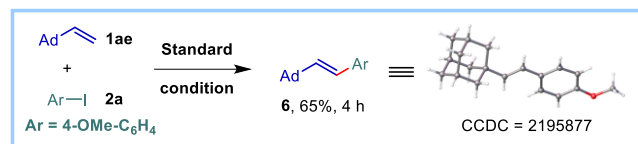
Figure 1. Gold-catalyzed Heck reaction of 4-iodoanisole with 1-vinyladamantane

reaction conditions, the product **3x-D** was obtained in 43% yield with no deuterium scrambling (Scheme 3c). This clearly indicates that the so-formed Heck product doesn't take part in the chain-walking process. The kinetic isotope effect (KIE) studies gave the value of k_H/k_D = ~0.95 for competition experiments (Scheme 3d), suggesting that the β-hydride elimination might not be the rate-limiting step.

Scheme 3. Mechanistic Investigations
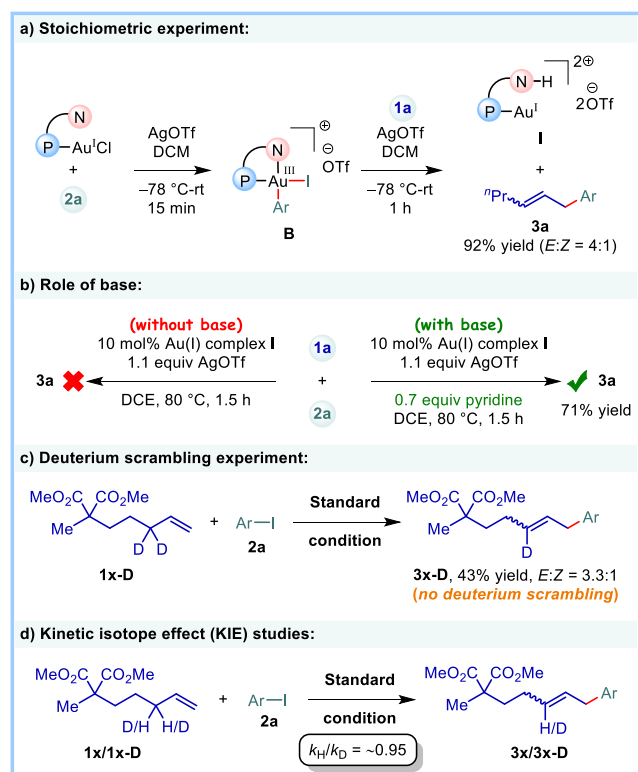
Based on the gathered experimental evidences and literature reports,[10e-i,11,12] we propose a plausible mechanism for the gold-catalyzed Heck reaction (Scheme 4). The cationic Au(I) complex **A**, generated from the reaction of MeDalPhosAuCl with AgOTf, should undergo oxidative addition with Ar-I (**2**) to form the Au(III) intermediate **B**. The subsequent iodide abstraction from this intermediate would lead to the coordinatively unsaturated Au(III) complex capable of intercepting with alkene (*cf*. **C**). The intermediate **C** should then undergo 1,2-migratory insertion furnishing Au(III)-alkyl species **D** stabilized by the π-electron cloud of the

adjacent aryl group.[21c] The subsequent β-hydride elimination with H^a (or H^b) should generate the intermediate **E** (or **F**) which after the release of Au(III)-hydride species affords the allylic (or styrenyl) product **3** (or **4**). Eventually, the reductive elimination from Au(III)-hydride species **G** should generate *N*-protonated Au(I) complex **I** *via* intermediate **H**. The base-mediated deprotonation from **I** would subsequently generate the catalytically active Au(I) complex **A**. While further studies are necessary to shed the light on the observed regioselectivity, we believe that the stabilization of the highly electrophilic Au(III) center by the π-electron cloud of the adjacent aryl group could be crucial in dictating the selectivity in the β-hydride elimination. As this stabilization remains unaffected while undergoing *syn*-specific β-hydride elimination with H^a, the formation of intermediate **E** should be favored over that of **F** (*cf*. **TS-I** *vs* **TS-II**).

In conclusion, we have developed the first example of the gold-catalyzed Heck reaction which provides complementary regioselectivity as compared to other transition metal catalysis.[24] The need for specialized alkenes, which are generally required to overcome the formation of a mixture of regioisomers, is not necessary. Preliminary mechanistic studies revealed that the reluctance of the gold(III)-hydride intermediate to reinsert into the so-formed allylic Heck product is the key for avoiding the undesired chain-walking process. Since the migratory insertion and β-hydride elimination processes are central to organometallic chemistry, the realization of these steps in gold catalysis should open up several avenues for accessing novel reactivities and selectivities.

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Scheme 4. Plausible Mechanism
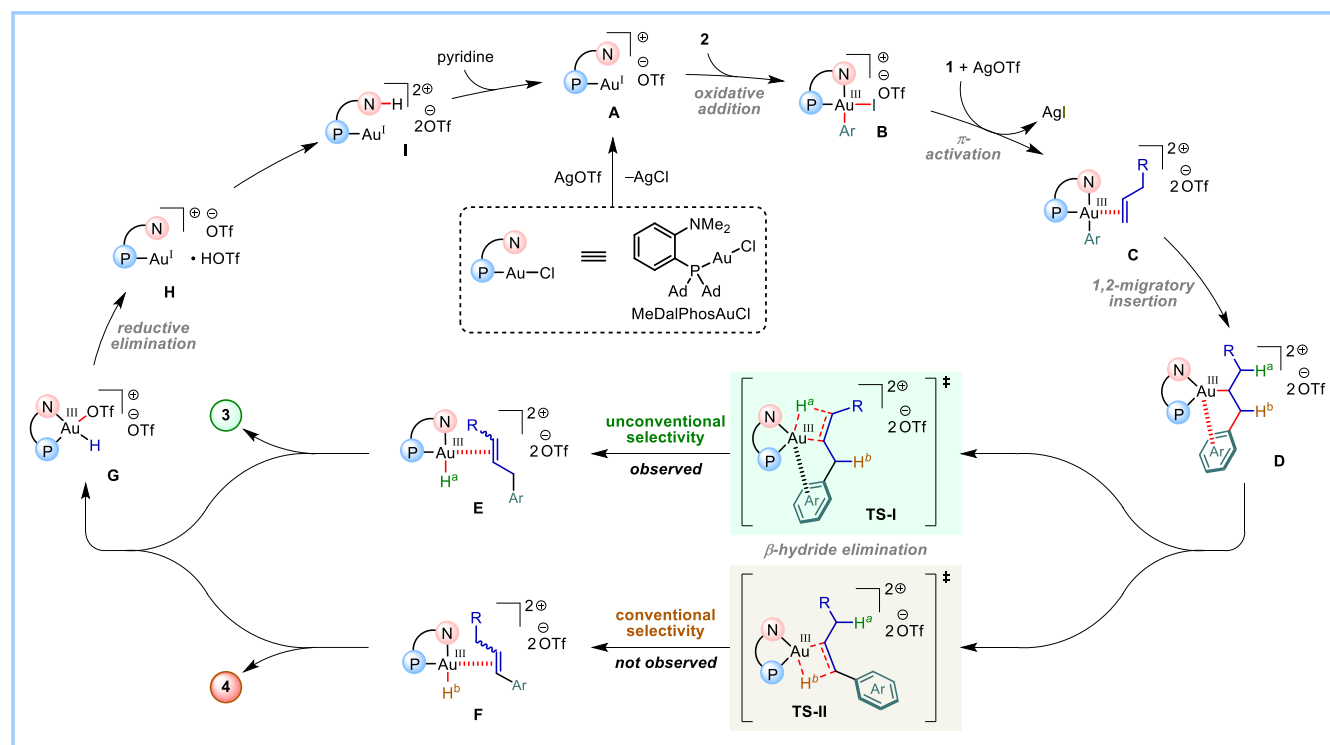
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