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C–C Cross-Coupling of Primary and Secondary Benzylic Alcohols Using Supported Gold-Based Bimetallic Catalysts

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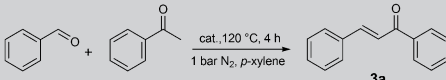
The formation of C–C bonds,^[1] a vital approach to increase the molecular complexity of a simple organic substrate, is one of the central themes in modern synthetic chemistry. Although a plethora of methods have been developed, the search for new, mild, efficient, and straightforward routes that minimize waste generation continues to be an active and challenging subject.^[2] An elegant method such as the Guerbet reaction for C–C bond construction is the transition-metal-catalyzed direct cross-coupling of alcohols^[3–7] by a borrowed hydrogen atom (BH, also known as hydrogen autotransfer).^[8] In such a process, readily available, green alcohols undergo sequential dehydrogenation/aldol condensation/transfer hydrogenation to afford higher alcohols or ketones with only water and/or H₂ as by-products. To date, relevant studies have largely focused on various Ru- or Ir-based homogeneous systems.^[3–5] However, the inherent problems of nonreusability and the necessity of special handling precautions for air-sensitive metal complexes have restricted the utility of these procedures. These limitations reinforce the need for a ligand-free, reusable catalyst system for this type of transformation. In the only two related precedents to this work, Pd/C and Ag/Al₂O₃ were used as efficient catalysts for direct C–C cross-coupling of secondary and primary alcohols.^[9] However, either a sacrificial hydrogen acceptor and/or a considerable amount of inorganic base was required to achieve a high selectivity. From a green and economic viewpoint, there is a great incentive to develop new simple and efficient catalytic protocols that can facilitate direct alcohol cross-coupling under mild, additive-free conditions.

Over the last decade, supported Au nanoparticles (NPs) have emerged as promising new catalytic materials for green organic transformations.^[10] Au was originally considered to be chemically inert and hence a poor catalyst. However, if small Au particles or clusters are dispersed on a suitable support, Au becomes a highly active and selective catalyst capable of facilitating a broad range of synthetic reactions, which include selective oxidation,^[11] chemoselective reduction,^[12] and one-pot multistep reactions.^[13, 14a, b, 15] Very recently, from our continuing studies on Au catalysis,^[14] we discovered an excellent hetero-

geneous Au-catalyzed BH strategy that allows rapid and highly selective C–N bond construction by the direct coupling of alcohols with amines under mild, clean conditions.^[15] Herein, we demonstrate that bimetallic Au–Pd NPs in combination with a basic layered clay of hydrotalcite (HT)^[16] can work as a robust and efficient multitask catalyst for the direct C–C cross-coupling of equimolar amounts of primary and secondary alcohols under additive-free conditions. To the best of our knowledge, this new one-pot, Au-based bimetallic catalytic protocol constitutes the first base-free, recyclable solid catalytic system for clean and efficient C–C bond construction through alcohol cross-coupling.

In a preliminary experiment, a model aldol condensation reaction between benzaldehyde and acetophenone, the key step to form the desired C–C bond, was performed over various noble-metal-free solid materials, and the results are summarized in Table 1. Mg–Al/HT, TiO₂, and MgO showed high activi-

Table 1. Aldol condensation of benzaldehyde and acetophenone.^[a]

			
Entry	Catalyst	t [h]	Yield [%] ^[b]
1	HT	4	97
2	TiO ₂	4	96
3	MgO	4	92
4	CeO ₂	4	87
5	ZrO ₂	6	34
6	Al ₂ O ₃	6	45
7	SiO ₂	6	n.r.
8	La ₂ O ₃	6	n.r.

[a] Reaction conditions: benzaldehyde (1 mmol), acetophenone (1 mmol), *p*-xylene (3 mL), catalyst (400 mg), 120 °C, 1 bar N₂; n.r. = no reaction.
[b] Conversion and yield based on benzaldehyde consumption determined by GC using *n*-dodecane as the internal standard.

ties for the desired aldol condensation, and the yields of the target product 1,3-diphenyl-2-propen-1-one (**3a**) were 92–97% (Table 1, entries 1–3). CeO₂ catalyzed the aldol condensation moderately to give **3a** in 87% yield (Table 1, entry 4). Other inorganic solid materials, such as Al₂O₃, ZrO₂, SiO₂, and La₂O₃, had far inferior activities toward **3a** (Table 1, entries 5–8). To rationalize these results, the surface acidity and basicity of the catalysts were measured by CO₂ and NH₃ temperature-programmed desorption (CO₂/NH₃-TPD, Figure S1 a–b and Table S1). In general, the solids that feature prominent surface

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basicity (HT, MgO, CeO₂) can effectively promote the aldol reactions. Interestingly, surface-neutral TiO₂ also exhibits excellent activity for this reaction. However, most importantly and relevantly, after loading with Au, Pt, or Pd, only the highly basic HT is the most appropriate material that can catalyze the desired aldol condensation (Figure S1c and Tables S1 and S2).^[17]

Based on these results, we focused on combining the capability of HT-supported metals to facilitate the dehydrogenation of alcohols as well as the subsequent autotransfer reduction of the C=C bond involved in the titled reaction. To this end, two equivalents of benzyl alcohol (**1a**) was employed to promote the reduction of the C=C bond of **3a** in the presence of a series of HT-supported metal catalysts (see the Supporting Information) under N₂. As can be seen in Table 2, Au/HT has

Table 2. Transfer reduction of **3a** by **1a**.^[a]

Entry	Catalyst	Conversion [%] ^[b]	Yield [%] 4a ^[c]	5a ^[b]	6a ^[b]
1	Au/HT ^[d]	97	83	97	n.d.
2 ^[e]	Pd/HT	96	74	77	19
3	Ag/HT	75	62	75	n.d.
4	Ru/HT	70	55	69	1
5	Rh/HT	36	28	29	7
6	Pt/HT	24	16	23	1

[a] Reaction conditions: **1a** (2 mmol), **3a** (1 mmol), *p*-xylene (3 mL), catalyst (metal: 1 mol%, based on **3a**), 120 °C, 1 bar N₂, 4 h; n.d. = not detected. [b] Conversion and yield based on consumption of **1a** determined by GC using *n*-dodecane as the internal standard. [c] The yield of **4a** is based on the consumption of **3a**. [d] Au loading = 0.50 wt% (based on ICP analysis). [e] 3 h.

a distinct advantage over other supported noble metals. Notably, Au/HT can effectively catalyze the chemoselective transfer hydrogenation of **3a** to give an 83% yield of the desired product 1,3-diphenylpropan-1-one (**4a**; Table 2, entry 1). Ag/HT and Ru/HT also converted **3a**, but their activities for this transfer reduction transformation were much lower than that of Au/HT (Table 2, entries 3 and 4). In the presence of Rh/HT or Pt/HT, the yields of **4a** were very low (Table 2, entries 5 and 6). A high conversion of **1a** was observed with Pd/HT as the catalyst (Table 2, entry 2), however, only a moderate yield of **3a** was obtained because a substantial amount of toluene (**6a**) was produced through the undesired hydrogenolysis of **1a**.^[18]

Having established suitable conditions for each step of the sequential reaction, we were interested in the use of Au/HT to promote the direct coupling of primary and secondary alcohols to afford the corresponding higher ketones. For this purpose, the reaction between 1-phenylethanol (**2a**) and **1a** was performed in *p*-xylene under N₂. Gratifyingly, Au supported on HT, which possesses beneficial surface redox and basic properties,

Table 3. Reaction of **1a** with **2a** with various catalysts.^[a]

Entry	Catalyst ^[b]	Conversion [%] ^[c]	Yield [%] ^[c] 3a	4a	5a	6a
1	Au/HT ^[d]	100	12	85	2	< 1
2	Pd/HT	100	0	79	1	20
3	Au-Pd(13:1)/HT	100	1	97	1	1
4 ^[e]	Au-Pd(13:1)/HT	100	1	96	2	1
5 ^[f]	Au-Pd(13:1)/HT	97	5	90	1	1
6	Au-Pd(8:1)/HT	100	2	94	2	2
7	Au-Pd(4:1)/HT	100	1	93	0	6
8	Au-Pd(5:2)/HT	100	1	87	2	10
9	HT	n.r.	n.d.	n.d.	n.d.	n.d.

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), *p*-xylene (3 mL), catalyst (metal: 1 mol%), 120 °C, 1 bar N₂, 5 h; n.d. = not detected. [b] Data in parentheses represent Au/Pd molar ratios, and the Au and Pd loading are shown in Table S5. [c] Conversion and yield based on the consumption of **1a** determined by GC using *n*-dodecane as the internal standard. [d] Au loading = 0.50 wt% (based on ICP analysis). [e] Third run. [f] Fifth run.

gave an impressive conversion of **1a** and **2a** to achieve **4a** in a high yield of 85% at 120 °C after 5 h (Table 3, entry 1). As metal loading is especially influential for supported metal catalysts, three Au/HT samples with different Au loadings were prepared to explore the optimal catalyst. Interestingly, 0.50 wt% Au/HT gave the highest yield of **4a**, and higher or lower Au loadings both decreased the yield of **4a** (Table S3). These results show that an optimal balance between the Au NPs and the basic sites of the HT surface is essential to promote the desired reaction. Thus, the most active and selective 0.50 wt% Au/HT catalyst was selected for further study. Subsequent experiments focused on the effect of the reaction temperature, which revealed that the reaction rate increased dramatically as the reaction temperature increased from 80 to 110 °C but leveled off at 120–135 °C (Table S4, entries 12 and 13). Among the solvents tested, *p*-xylene was the best, and changing the solvent to mesitylene, *o*-xylene, and dioxane decreased the yield of **4a** to 13, 8, and 2%, respectively.

To explore the reaction performed with Au/HT in detail, the product evolution of the cross-coupling of **2a** and **1a** in *p*-xylene under the conditions of entry 1 in Table 3 was followed by continuous sampling by using GC. As shown in Figure 1A, the desired product **4a** was the main product in the initial stage of the reaction. In addition, 2–11% of **5a** was detected during the whole course of the reaction, and there was still approximately 12% of intermediate **3a** present in the final stage of the reaction. Taken together, these results demonstrate that the present Au/HT-catalyzed cross-coupling may proceed through the sequential reaction pathway depicted in Scheme 1. Furthermore, we have confirmed by a set of kinetic experiments that the initial reaction rates for each step of the overall sequential reaction decreases in the order: $r_a \approx r_b > r_c$

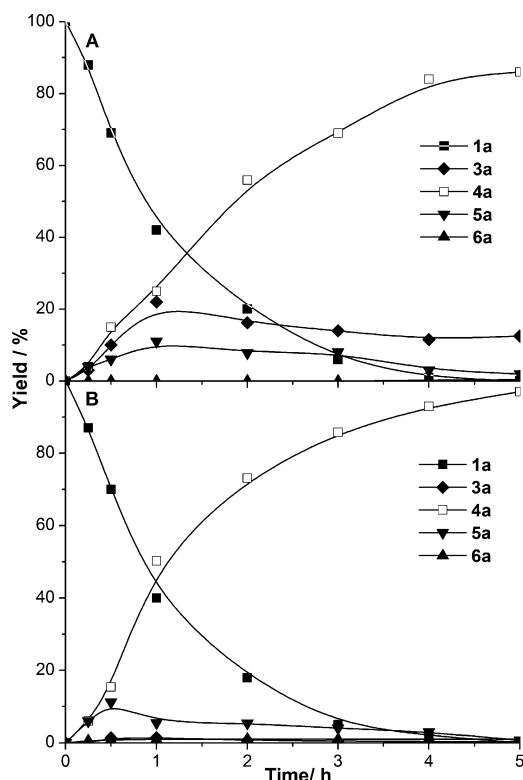
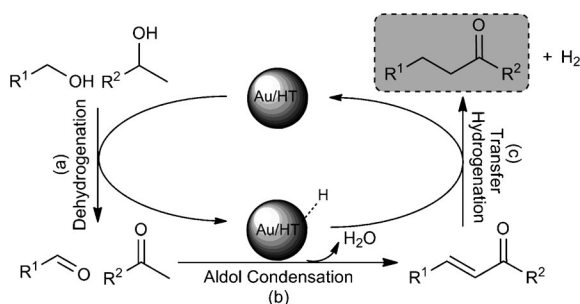


Figure 1. Reaction profiles for the direct cross-coupling of **1a** with **2a** over Au/HT (A) and Au-Pd(13:1)/HT (B). Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), *p*-xylene (3 mL), catalyst (metal: 1 mol %), 120 °C, 5 h under N₂.



Scheme 1. Proposed sequence for the direct cross-coupling of primary and secondary alcohols to produce higher ketones.

(Scheme S1), which accounts for the presence of appreciable amounts of benzaldehyde and chalcone intermediates during the alcohol coupling reaction. In contrast to a previous study that used Ag/Al₂O₃,^[9a] in which the rate-determining step of the overall reaction was the initial alcohol dehydrogenation mediated by supported Ag clusters, it seems that the controlling step in the present Au/HT-catalyzed system is the transfer reduction of intermediate **3a** by the gold hydride (Scheme 1, step c).

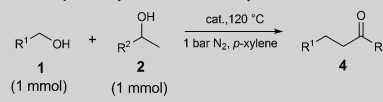
In an effort to further improve the selectivity towards **4a**, we selected metallic Pd as a promoter for the Au/HT catalyst. Pd was chosen because Pd NPs are well known to catalyze a wide range of reductive transformations, which include dehydrogenation and transfer hydrogenation.^[6a,7d,e,g,9b] Given that

monometallic Pd/HT appears to be too active but not selective for the desired transformation, we designed a series of Pd-containing bimetallic Au-Pd/HT catalysts with various Au/Pd atomic ratios (13:1–5:2), which were prepared by following the same procedures used for the monometallic Au/HT catalyst. Notably, the addition of a very small amount of Pd dramatically improves the yield of **4a** from 85 to 97% (Table 3, entry 3). With an increasing Pd/Au atomic ratio from 1:13 to 2:5 (Table 3, entries 3, 6–8), a gradual decrease in the yield of **4a** from 97 to 87% was observed. This may simply be because the undesirable formation of toluene from the disproportionation of **1a** is favored at higher Pd loadings. Thus, a 13:1 mixture of Au/Pd provides the most effective catalyst for the titled reaction, which exhibited both excellent selectivity and activity towards the formation of **4a** (Figure 1B). The advantage of the Au-Pd(13:1)/HT catalyst becomes clear if the reaction profiles obtained with the Au/HT catalyst (Figure 1A) and the Pd catalyst (Figure S2) are compared. The XRD pattern and TEM image of Au-Pd(13:1)/HT are shown in Figures S3 and S4, respectively, which indicate that the metallic particles are finely dispersed on the surface of HT and that most of the particles are 1–4 nm in diameter. The energy-dispersive X-ray (EDX) spectrum (Figure S5) of a single NP shows the presence of both Au and Pd on a single NP. EDX spectroscopy also shows that some of the NPs are monometallic Au. X-ray photoelectron spectroscopy (XPS) confirmed that the small Pd entities affect the electron densities of Au and the binding energy of Au4f_{7/2} for Au-Pd(13:1)/HT shifts to a higher energy than that of Au/HT by 0.1 eV (Figure S6). Although it is difficult to clarify whether a bulk alloy is formed between Au and Pd, the improved performance of the bimetallic Au-Pd catalyst can be ascribed to the beneficial role of a small amount of Pd to promote the transfer hydrogenation of **3a** (Scheme 1, step c).

Au-Pd/HT can be easily separated by filtration after the reaction. Inductively coupled plasma (ICP) analysis confirmed that no Au or Pd was present in the filtrate, which indicates that the catalysis is truly heterogeneous in nature. Moreover, Au-Pd/HT can be reused at least three times and still maintains a complete conversion of **1a** to give **4a** in up to 96% yield under the same reaction conditions (Table 3, entry 4), in which the average turnover frequency (TOF) and the turnover number (TON, based on total metal) reached up to 20 h⁻¹ and 300, respectively. These values are one or two orders of magnitude greater than those in catalyst systems reported previously, such as Ag/Al₂O₃ (TOF = 0.5 h⁻¹ and TON = 25 at 115 °C).^[9a] XRD, TEM, EDX, and XPS results showed no change in the dispersion of the Au NPs or the metallic state of Au before and after reuse, which is in good agreement with the excellent retention of activity (Figures S3–S6).^[19]

Building on these results, we extended this direct Au-Pd-mediated C–C coupling protocol to a wider range of primary and secondary alcohols. In these studies, two different strategies were employed to explore the efficiency of the heterogeneous Au-Pd/HT catalytic system for the synthesis of diverse ketones. In the first strategy, various structurally divergent primary alcohols were allowed to react with **2a** for the coupling reaction, and the results are summarized in Table 4. Au/HT

Table 4. Reaction of primary and secondary alcohols.^[a]

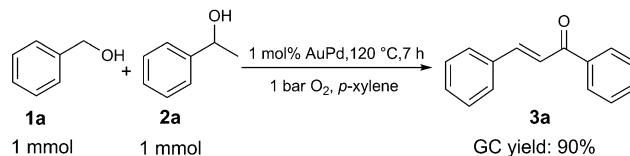
					
Entry	R ¹	R ²	t [h]	Conversion [%] ^[b]	Yield [%] ^[b]
1	Ph	Ph	5	100	97 (95)
2	<i>p</i> -MeC ₆ H ₄	Ph	5	100	93 (90)
3	<i>p</i> -ClC ₆ H ₄	Ph	5	100	90 (85)
4	<i>m</i> -ClC ₆ H ₄	Ph	8	100	87 (84)
5	<i>p</i> -MeOC ₆ H ₄	Ph	8	100	80 (77)
6	<i>o</i> -MeOC ₆ H ₄	Ph	10	100	72 (69)
7	<i>p</i> - <i>i</i> PrC ₆ H ₄	Ph	8	100	89 (85)
8	<i>p</i> -CF ₃ C ₆ H ₄	Ph	8	100	71 (68)
9	PhCH ₂	Ph	36	100	82 (78)
10	2-pyridyl	Ph	20	100	82 (77)
11	<i>n</i> Bu	Ph	24	n.r.	n.d.
12	<i>n</i> -pentyl	Ph	24	n.r.	n.d.
13	Ph	<i>p</i> -MeC ₆ H ₄	8	100	91 (88)
14	Ph	<i>p</i> -MeOC ₆ H ₄	8	100	86 (83)
15	Ph	<i>p</i> -FC ₆ H ₅	8	100	81 (77)
16	Ph	<i>p</i> -ClC ₆ H ₅	8	100	83 (76)

[a] Reaction conditions: primary alcohol (1 mmol), secondary alcohol (1 mmol), *p*-xylene (3 mL), Au–Pd (1 mol%), 120 °C, 1 bar N₂; n.r. = no reaction; n.d. = not detected. [b] Conversion and yield based on alcohol consumption. Numbers in parenthesis refer to yields of isolated products.

gave moderate to good yields (71–97%) with various electron-donating groups, such as CH₃, CH₃O, *i*Pr, and electron-withdrawing groups, such as chloro- or trifluoromethyl-derivatives of benzyl alcohol, and the reaction activity is independent of the electronic character of the substituents (Table 4, entries 1–8). Notably, *m*- or *o*-substituted alcohols had lower reaction rates and yields than *p*-substituted alcohols, which can be explained by steric effects (Table 4, entries 3–6). Chloro-substituted benzyl alcohols were converted to the corresponding ketones without dehalogenation (Table 4, entries 3 and 4), which is often encountered with other catalytic procedures. If 2-phenylethanol was employed as a substrate, a much longer time was needed to complete the reaction (Table 4, entry 9). Interestingly, an N-containing primary alcohol also reacted with **2a** to give a moderate yield of the corresponding N-containing ketone (Table 4, entry 10). Unfortunately, no desired cross-coupling product was detected if aliphatic primary alcohols, such as *n*-butyl and *n*-pentyl alcohols, were employed as substrates even after prolonged reaction times (Table 4, entries 11 and 12). In the second strategy employed for the direct synthesis of ketones, the primary substrate was kept constant (i.e., only **1a** was used) and it was allowed to react with different secondary alcohols such as *p*-substituted 1-phenylethanol, in which the substituents were CH₃, CH₃O, F, and Cl. Again, the corresponding higher ketones were obtained in good to excellent yields (Table 4, entries 13–16).

The applicability of the heterogeneous Au–Pd/HT-based protocol is highlighted by the one-pot synthesis of **4a** by the direct cross-coupling of **1a** and **2a** under solvent-free conditions. Notably, the in situ C–C bond formation on a 10 mmol scale proceeds smoothly at 130 °C, and **4a** was obtained in an

impressive yield of 89% in the presence of Au–Pd/HT. Compound **4a** (1.74 g) was isolated in high purity after simple manipulation of the reaction mixture (isolated yield of ca. 83%). Furthermore, the bimetallic Au–Pd/HT catalyst can also catalyze the aerobic cross-coupling of **1a** and **2a** to produce the corresponding chalcone **3a**, which is known to have a diverse array of biological properties, such as antimalarial, anti-inflammatory, antileishmanial, and anticancer activities, with a high yield under 1 bar O₂ (ca. 90%; Scheme 2).

**Scheme 2.** Aerobic cross-coupling reaction of **1a** with **2a** under O₂.

In conclusion, we have demonstrated the noteworthy features of solid multifunctional Au–Pd/HT for direct and effective C–C cross-coupling of primary and secondary alcohols through a facile BH pathway. This process has prominent advantages compared with previous alcohol cross-coupling methods: (a) high catalytic activity and selectivity, (b) no external H₂ or other sacrificial agent is necessary, (c) no need to apply a base, and (d) no stabilizing ligands and/or co-catalysts are necessary. The reaction chemistry demonstrated herein will promote the application of the BH strategy in clean and atom-economical chemical processes.

Experimental Section

Preparation of Au/HT catalysts: HT was synthesized according to a literature procedure.^[20] A modified deposition–precipitation (DP) procedure was employed to prepare Au/HT. HT (1.0 g) was dispersed in an aqueous solution of H₂AuCl₄·4H₂O (50 mL, 1.02 × 10^{−3} M) with vigorous stirring. After agitation for 2 h at 25 °C, the mixture was filtered and washed thoroughly with deionized water until no Cl[−] was detected in the filtrate by using AgNO₃. The resulting compound was dried for 12 h under vacuum at rt and reduced by using 5% H₂/Ar at 300 °C for 2 h. Elemental analysis revealed that the Au loading of Au/HT was 0.5 wt %.

Preparation of bimetallic Au–Pd/HT catalysts: Au–Pd/HT catalysts were prepared by using the same procedure as that used to prepare Au/HT. HT (1.0 g) was dispersed in an aqueous solution of H₂AuCl₄ and PdCl₂ with varying Au/Pd atomic ratios (50 mL) with vigorous stirring. The total metal loading was kept at approximately 0.5 wt %. After agitation for 2 h at 25 °C, the mixture was filtered and washed thoroughly with deionized water until no Cl[−] was detected in the filtrate by using AgNO₃. The resulting compound was dried for 12 h under vacuum at rt and reduced by using 5% H₂/Ar at 300 °C for 2 h.

General procedure for the direct cross-coupling of alcohols: A mixture of primary alcohol (1 mmol), secondary alcohol (1 mmol), catalyst (1 mol% metal), *p*-xylene (3 mL), and *n*-dodecane (10 μL) as an internal standard was vigorously stirred at 120 °C under N₂ (1 bar). The product was identified by GC–MS, and the

spectra obtained were compared with those of standards. The conversion and product selectivity were determined by using a GC-17 A equipped with an HP-FFAP column (30 m×0.25 mm) and a flame ionization detector (FID). For isolation, the combined organic components were concentrated under reduced pressure and purified by using silica-gel column chromatography.

Acknowledgements

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Keywords: alcohols • cross-coupling • gold • ketones • palladium

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