Synthetic Methods

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Reductive Cleavage of the C_{sp^2}–C_{sp^3} Bond of Secondary Benzyl Alcohols: Rhodium Catalysis Directed by N-Containing Groups**

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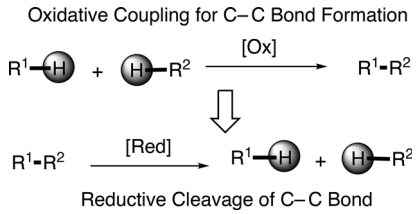
Oxidative coupling of two nucleophiles to construct a C–C bond (Scheme 1) is gradually becoming a prestigious and powerful method relative to the traditional cross-coupling reactions.[1] Specifically, recent developments in cross-dehydrogenative coupling/arylation made such a transformation more popular and "greener" and produces valuable compounds by avoiding the preactivation of easily available and inexpensive chemicals.[2] In contrast, less attention has been paid to its reverse reaction, that is the reductive cleavage of a C–C bond (Scheme 1). Such a reductive cleavage is challenging, but important for a number of reasons. First of all, such investigations are of theoretical importance for understanding the reactivity of C–C bonds, which are abundant in nature and the synthetic world. Secondly, this method offers the potential to make valuable chemicals from easily available starting materials and even from chemical waste. Finally, such a method also offers a new and useful tool for cleaving and degrading synthetic polymers[3] and biomass[4] to produce platform chemicals, as well as provide a solution to diminish the "white pollution" from synthetic polymers.



Scheme 1. Oxidative coupling versus reductive cleavage.

Unfortunately, this field has been neglected by chemists and only limited examples have been reported. Alkylaluminum was often used as the reductant in transition-metal-catalyzed deallylation reactions.[5] It was also applied to the reductive cleavage of cycloalkanes in the presence of rare-earth-metal catalysts.[6] Other reductants, such as active metals,[7] metal hydrides,[8] and hydrosilanes[9] were also reported to realize the goal of the reductive cleavage of C–C bonds. Compared with the above reductants, H_2 is a superior choice for reductive cleavage. H_2 as a source is extremely abundant, and more importantly, no extra waste is introduced into the reaction system. Early efforts to utilize H_2 as the reductant mainly focused on relatively active strained molecules.[10] However, for unstrained C–C bonds, harsh reaction conditions using heterogeneous catalytic systems[11] or the assistance of a specially designed pincer ligand[12] were required. To date, only a few examples on the cleavage of activated C–C bonds adjacent to a carbonyl group or aromatic ring under mild reaction conditions have been reported.[13] In our previous studies we observed that N-containing heterocycles were successful directing groups for transition-metal-catalyzed C–C bond cleavage.[14] On this basis, we demonstrate the first successful example of the reductive C–C bond cleavage of benzyl alcohols with H_2 through rhodium catalysis.[15]

To prove our concept of reductive cleavage, we chose the substrate **1a** as a model to investigate the hydrogenative cleavage of C–C bonds (Table 1). First of all, we tried some commonly used hydrogenation catalysts such as Pd/C, Rh^I, and Ir^I complexes in our system. Unfortunately, none of them worked for this transformation (Table 1, entries 1–4). The Rh^{III} catalyst [{Cp*$RhCl_2$}$_2$], which was successfully applied in our previous studies,[14a] also failed to deliver the desired product. To our delight, the cationic Rh^{III} catalyst [Cp*Rh-$(CH_3CN)_3$][SbF_6]$_2$ exhibited excellent catalytic activity (entries 5 and 6). Further screening of solvents indicated that EtOH and DCE gave the best results for this transformation (entries 6–10). We choose EtOH for additional studies because it is environmentally friendly. Further studies unveiled that the reactivity was highly dependent upon the reaction temperature. Systematic studies indicated that the highest yield of **3a** was obtained at 80 °C (entries 6, 11, and 12). Increasing the scale to 0.3 mmol led to a slight decrease of the yield of benzyl alcohol as well as the appearance of a small amount of benzaldehyde in the crude reaction mixture. This

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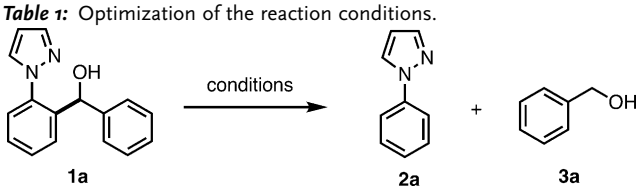
Table 1: Optimization of the reaction conditions.



1a 2a 3a

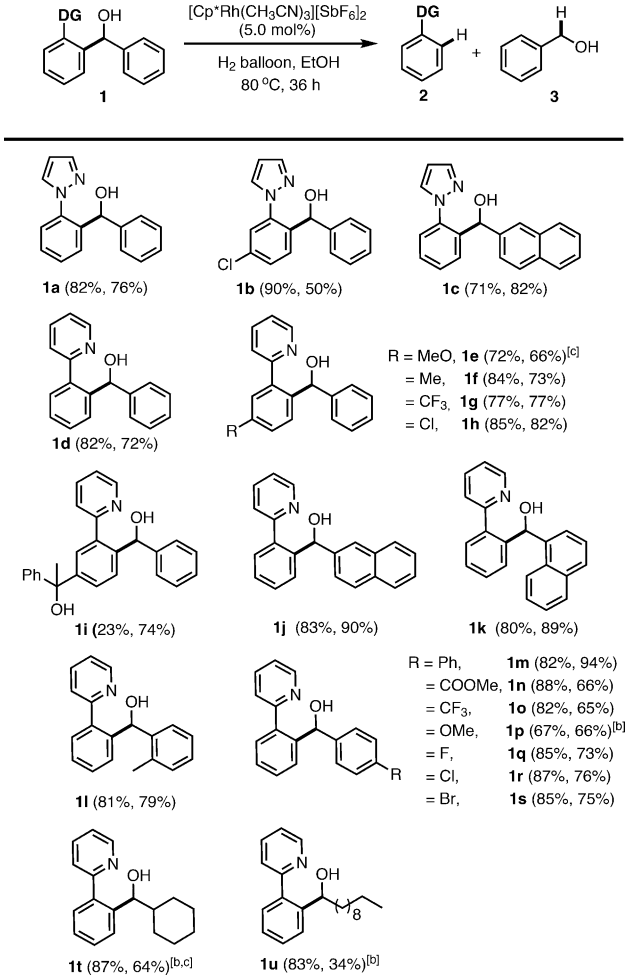
Entry[a]	Catalyst	Solvent	*T* [°C]	Yield[b]
1	Pd/C	EtOH	80	n.d.
2	$[\{Ir(cod)Cl\}_2]$	EtOH	80	n.d.
3	$Rh(cod)_2BF_4$	EtOH	80	n.d.
4	$Rh(PPh_3)_3Cl$	EtOH	80	n.d.
5	$[\{Cp^*RhCl_2\}_2]$	EtOH	80	n.d.
6	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	EtOH	80	96%
7	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	MeOH	80	20%
8	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	*t*BuOH	80	70%
9	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	DCE	80	99%
10	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	toluene	80	88%
11	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	EtOH	70	52%
12	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	EtOH	90	92%
13	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	EtOH	80	91%
14	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	EtOH	80	93%
15	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	EtOH	80	96%

[a] 0.1 mmol sacle in 1.0 mL solvent for 24 h unless otherwise noted. [b] Yield of **3a** as determined by ^{1}H NMR spectroscopy using benzyl methyl ether as the internal standard. [c] 0.3 mmol scale, 3.0 mL EtOH, 24 h. [d] 0.3 mmol scale, 2.0 mL EtOH, 24 h. [e] 0.3 mmol scale, 2.0 mL EtOH, 36 h. cod = 1,5-cyclooctadiene, Cp* = C_5Me_5, DCE = 1,2-dichloroethane.

problem could be addressed by simply increasing the concentration of the substrate and increasing the reaction time.

With the best reaction conditions in hand, we set out to test the reactivity of other substrates. To extend the potential application of the reaction, different directing groups were tested (Scheme 2). We found that the substrates bearing a removable pyrazolyl group (**1a–c**) could undergo reductive cleavage of the C–C bond smoothly, thus giving moderate to good yields of the corresponding products. The pyridinyl group also proved to be an efficient directing group. Substituents, having various electronic properties, on the ring bearing the directing group (**1d–g**) were compatible in this catalyst system. To our delight, Cl (**1h**) was tolerated under these reductive conditions, and thus provides opportunities for additional functionalization.[16] The substrate bearing a tertiary alcohol substituent (**1i**) led to a low yield of the corresponding arylpyridine derivatives. Importantly, the low yield of the desired product was not a result of the cleavage of the C–C bond at the tertiary alcohol moiety, but to the nucleophilic substitution of the tertiary hydroxy group by an ethoxy group.[17] This result indicated that the directing group played a key role in controlling the regioselectivity of the C–C bond cleavage.

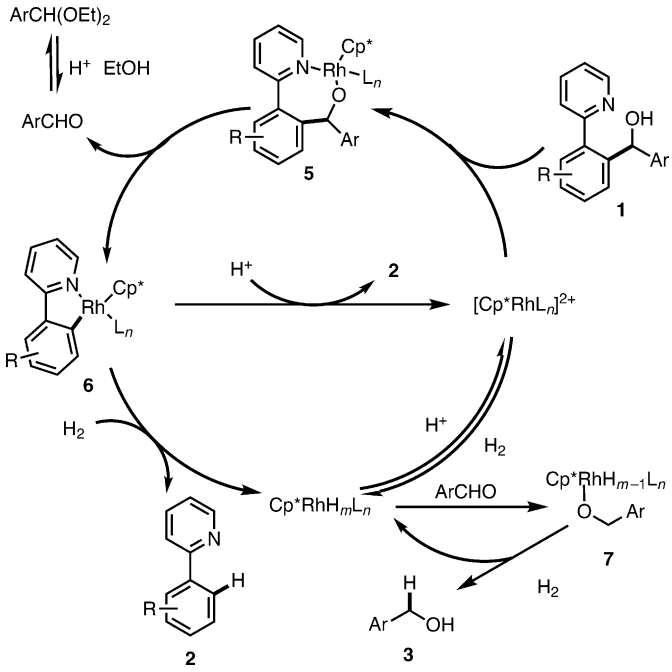
Differently substituted aryl groups on the right-hand side of the substrate alcohols were additionally surveyed (Scheme 2). Substrates with a naphthyl ring or electron-neutral phenyl ring (**1j–m**) exhibited excellent reactivity. Electron-withdrawing substituents, such as ester group or trifluoromethyl group (**1n** and **1o**) led to slightly lower yields



Scheme 2. Substrate scope of 1,1- biarylmethanols for C–C bond reductive cleavage. The yields given in brackets refer to products **2** and **3**, respectively. [a] Alcohol **1** (0.3 mmol), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (0.015 mmol), EtOH (2.0 mL), H_2 balloon, 80°C, 36 h. [b] 48 h. [c] Yield determined by ^{1}H NMR spectroscopy using benzyl methyl ether as the internal standard.

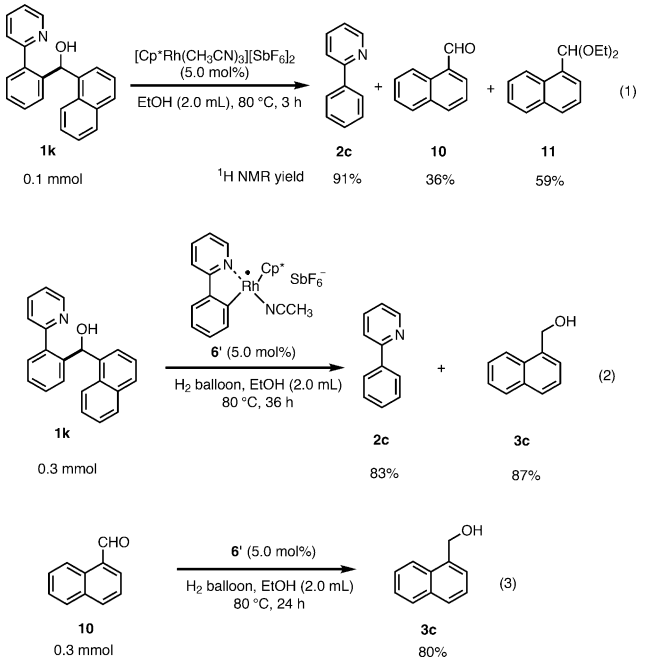
of the alcohol **3**. However, an electron-rich aryl group (**1p**) did not perform well, thus giving moderate yield even after a longer reaction time. Again, halogens (**1q–s**) survived under such reaction conditions. We also tested alkyl-substituted secondary alcohols (**1t** and **1u**), which could undergo the reductive cleavage albeit with lower efficiency.

A possible mechanism is proposed in Scheme 3. First, the C–C bond of **1** is cleaved with the assistance of Rh^{III} and thus the C–Rh species **6** is generated. The intermediate **6** could then be cleaved by H_2 to generate **2** and the Rh^{III} hydride species,[18] which reduces the aldehyde to the alcohol. Alternatively, **6** could undergo protonation with H^+ to regenerate the cationic Rh^{III} species for the C–C bond cleavage of next catalytic cycle. At this stage, we cannot exclude the conversion of the cationic Rh^{III} precursor into the Rh^{III} hydride species. The Rh^{III} hydride species could then promote both the C–C bond cleavage and reduction of the aldehyde in the same catalytic cycle.



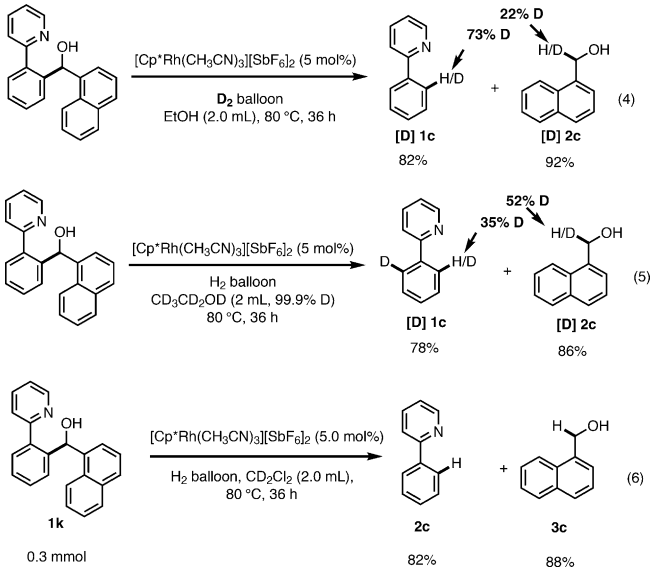
Scheme 3. Proposed mechanisms for the reductive cleavage of the C–C bond.

To understand the catalytic cycle, preliminary studies were conducted. As observed in previous studies, we found that the Rh^{III} precatalyst could indeed catalyze the cleavage of the C–C bond of **1k** in the absence of H_2 [Eq. (1)]. Thus, we



hypothesized that a five-membered rhodacycle intermediate was also involved in the C–C bond cleavage. At this point, we surveyed the reactivity of the Rh^{III} complex **6′**.[19] We found that **6′** could catalyze both the reductive cleavage of **1k** and the reduction of 1-naphthaldehyde (**10**) into **3c** smoothly [Eqs. (2) and (3)]. These results suggested that the five-membered rhodacycle **6′** was a possible intermediate in the catalytic cycle. Importantly, when we subjected **6′** to the reaction conditions in the presence of H_2 but in the absence of **1k**, we observed the formation of phenylpyridine and the signal for Rh–H in the ^{1}H NMR spectrum.[20] Thus, the Rh^{III} hydride species might be generated from the five-membered rhodacycle intermediate **6′** under an H_2 atmosphere.

To explain the sources of the protons on both the alcohol and 2-phenylpyridine, D_2 was used under the same reaction conditions [Eq. (4)]. The results showed that both the C–H



bond at the *ortho* position of the pyridinyl group and α-position of alcohol were partially deuterated. However, when we used [D_6]-EtOH instead of EtOH, more than one *ortho* position of the pyridinyl group was deuterated, and might be attributed to both the direct deuteration of the five-membered rhodacycle intermediate and the reversible C–H bond cleavage of the aromatic ring by the Rh^{III} species. Interestingly, the deuteration ratio at the α-position of the alcohol was even higher than that obtained when the reaction was run under a D_2 atmosphere [Eq. (5)]. The above results indicated that the Rh–H bond was involved in the reduction of the aldehyde and the H/D exchange between the rhodium hydride species and the protic solvent indeed existed. The difference in the deuteration ratio between Equations (4) and (5) may arise from the different concentration of deuterium source in the reaction systems. When we used the nonprotic, deuterated solvent [D_2]-CD_2Cl_2, no H/D exchange took place with either of the two products [Eq. (6)], thus confirming our above conclusion.

To gain further insight into the mechanism, we used ^{1}H NMR spectroscopy to monitor the reaction progress (Figure 1). The formation of the alcohol **3c** was observed within 0.5 hours, and the consumption of **1k** was not complete. When all of **1k** was consumed, the yield of **3c** was still increasing with time and the aldehyde **10** also remained in the reaction system. The data indicate that the formation of **2c** is faster than **3c**. According to these results, it is not possible for the Rh^{III} hydride species to catalyze both the C–C bond cleavage and the reduction of the aldehyde in

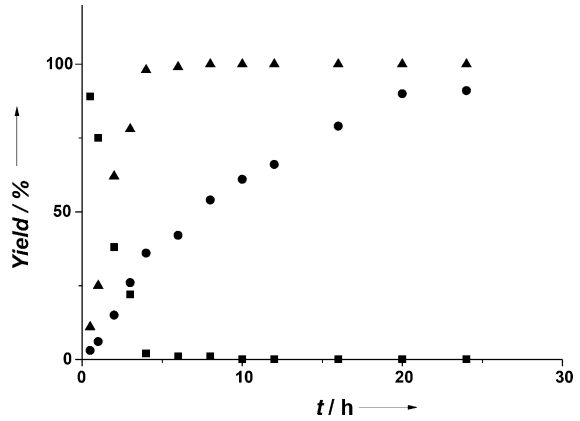


Figure 1. Reductive cleavage of **1k** (■) and the formation of **2c** (▲) and **3c** (●) as monitored by ^{1}H NMR spectroscopy. Reaction conditions: **1k** (0.1 mmol), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (0.005 mmol), EtOH (1.0 mL), H_2 balloon, 80 °C.

the same catalytic cycle, as it would generate **2c** and **3c** at the same rate. With all the above results, we believe the catalytic cycle described in Scheme 3 to be reasonable.

In summary, we have the reported the Rh^{III}-catalyzed reductive cleavage of the C_{sp^2}–C_{sp^3} bond of unstrained 1,1-biaryl methanols in the presence of H_2 as the reducing agent under mild reaction conditions. Various functional groups are tolerated albeit under a reductive atmosphere. Both pyridinyl and pyrazolyl groups can serve as directing groups. Preliminary studies indicate that the Rh^{III} hydride species is generated from a five-membered rhodacycle intermediate. Additional studies into the catalytic pathway and extention of this concept to other systems are underway.

Experimental Section

The secondary alcohol substrate **1** (0.3 mmol) and $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (12.5 mg, 0.015 mmol) were added to the reaction tube. The system was then purged with H_2 (in balloon) three times. Anhydrous EtOH (2.0 mL) was injected into the tube. The mixture was heated at 80 °C in a parallel reactor for 36 h. The solvent was then removed in vacuo and the residue purified by flash chromatography (eluent: petroleum ether/EtOAc 20:1→5:1) to afford compounds **2** and **3**.

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Keywords: C–C activation · cleavage reactions · hydrogenation · reaction mechanisms · rhodium

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[17] 2-(3-(1-ethoxy-1-phenylethyl)phenyl)pyridine (**2h′**) was generated as the major by-product (61 % yield). For characterization see the Supporting Information for details.

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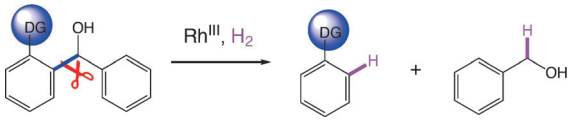
[20] See the Supporting Information for details.

Communications

Synthetic Methods

K. Chen, H. Li, Z.-Q. Lei, Y. Li, W.-H. Ye, Li.-S. Zhang, J. Sun, Z.-J. Shi* _____ ■■■■–■■■■

Reductive Cleavage of the C_{sp^2}–C_{sp^3} Bond of Secondary Benzyl Alcohols: Rhodium Catalysis Directed by N-Containing Groups



Cutting loose: 1,1-Biarylmethanol substrates undergo reductive cleavage of the C–C bond in the presence of a cationic Rh^{III} catalyst and H_2 (see scheme; DG = directing group). Various functional groups are tolerated in the reaction system. Preliminary studies indicate that a five-membered rhodacycle intermediate, which then converts into a Rh^{III} hydride species for the reduction, is involved in the catalytic cycle. DG = directing group.