Biaryls

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Extrusion of CO from Aryl Ketones: Rhodium(I)-Catalyzed C–C Bond Cleavage Directed by a Pyridine Group**

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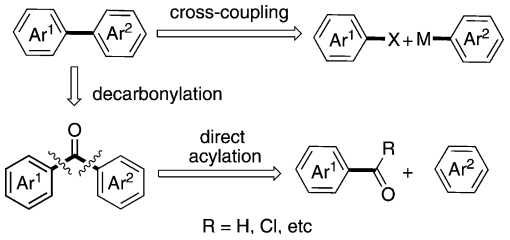
Carbon–carbon bond cleavage is a significant strategy for organic group transfer, and is conceptually different from conventional organic synthesis because the existing molecular skeletons can be reorganized through this method to build the desired structural units. It is also a challenging field because of the inherent stability of the carbon–carbon linkages (for example, steric hindrance).[1] Recently, many efforts have been made to approach this goal through transition-metal catalysis.[2] For instance, the ring-opening of strained molecules, such as three- and four-membered rings, has been well studied.[3] Other than these studies, the cleavage of the carbon–nitrile (C–CN) bond of nitriles[4] and various unique substrates by forming the stable organometallic intermediates (for example, π-allyl species) and releasing the small molecules have been well investigated.[5] Another significant contribution to the C–C bond-cleavage approach using a group-directing strategy has been made by Suggs et al., Jun et al., and others.[6]

Biaryls are useful scaffolds in natural products, synthetic drugs, and organic materials.[7] Transition-metal-catalyzed cross-coupling reactions have been developed as one of the most powerful tools for constructing such motifs.[8] Additionally, transition-metal-catalyzed decarbonylation of aldehydes and decarboxylation of acids and their derivatives, for example anhydride and acyl chlorides, were carried out under many different reaction conditions.[9] Although the photolytic decarbonylation with the bridged ring substrates[10] and transition-metal-catalyzed decarbonylation of strained ring system have been well developed,[11] direct decarbonylation of stable, linear ketones to construct C–C bonds by metal-based catalysis has been rarely reported. To date only one example has been reported by Daugulis and Brookhart, who were the first to discover the rhodium-catalyzed decarbonylation of diaryl ketones albeit at a high catalyst loading, relatively low conversion, and limited substrate scope.[12] Herein we report the efficient extrusion of CO from both biaryl ketones and alkyl/alkenyl aryl ketones to construct biaryls and alkenyl/alkyl arenes, respectively by rhodium(I) catalysis directed by a pyridinyl group. The reported protocol involves a simple and easy-to-handle catalyst system and has a broad substrate scope for accessing biaryls as well as alkenyl and alkyl benzenes from aryl ketones, which can easily be produced through direct acylation (Scheme 1).[13] The use of directing groups aids the decarbonylation although it complicates the overall synthesis and limits the scope of the accessible products to those that can be made by the direct arylation of pyridyl arenes.[14]



Scheme 1. Reaction design.

Starting from this point, we searched for efficient catalytic systems to carry out the designed decarbonylation. We first tested the idea using phenyl(2-(pyridin-2-yl)phenyl) methanone (**1a**) under various reaction conditions (Table 1). Actually, this substrate is extremely stable under thermal conditions (entry 1). To our delight, in the presence of 5.0 mol% of $[(CO)_2Rh(acac)]$, the extrusion of CO was observed at 150 °C at a high efficiency with PhCl as the solvent. After 7 hours, the decarbonylation was complete and **2a** was isolated in 91% yield (entry 2). Wilkinson's catalyst does not show any catalytic ability regardless of the presence $AgSbF_6$ (entries 3 and 4). The $[\{(CO)_2RhCl\}_2]$ dimer showed comparable reactivity as $[(CO)_2Rh(acac)]$ while the corresponding cationic complex did not enhance the yield (entries 5 and 6).[15] $[\{Rh(C_2H_4)_2Cl\}_2]$ also showed good reactivity (entry 7). Other Rh^I and Rh^{III} salts showed much lower efficacies (entries 8–10). Metal catalysts other than rhodium completely failed to react and the starting material remained unreacted (entries 11–14).

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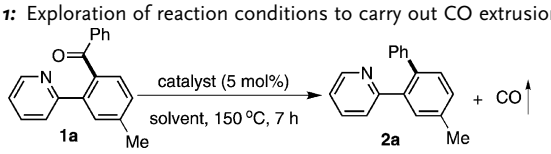
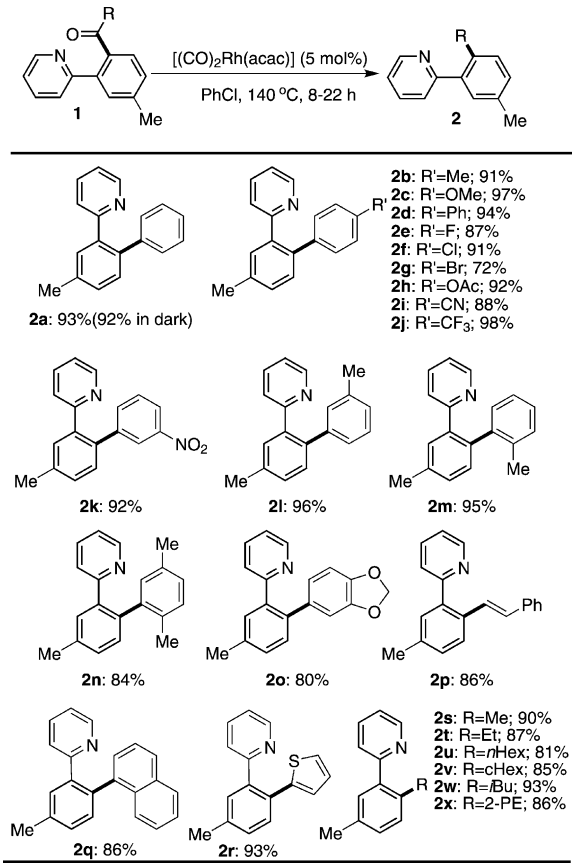
Table 1: Exploration of reaction conditions to carry out CO extrusion.



Entry[a]	Catalyst	Solvent	Yield [%]
1	–	PhCl	0
2	$[(CO)_2Rh(acac)]$	PhCl	91[j]
3	$[(PPh_3)_3RhCl]$	PhCl	< 5
4[b]	$[(PPh_3)_3RhCl]$, $AgSbF_6$	PhCl	< 5
5[c]	$[\{(CO)_2RhCl\}_2]$	PhCl	95
6[b,c]	$[\{(CO)_2RhCl\}_2]$, $AgSbF_6$	PhCl	95
7[d]	$[\{(C_2H_4)_2RhCl\}_2]$	PhCl	91
8[e]	$[\{(cod)_2RhCl\}_2]$	PhCl	< 5
9	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	PhCl	< 5
10[b,f]	$[\{Cp^*RhCl_2\}_2]$, $AgSbF_6$	PhCl	< 5
11	$Pd(OAc)_2$	PhCl	0
12	$[Ru(PPh_3)_2Cl_2]$	PhCl	0
13	$[NiCl_2(dppe)]$	PhCl	0
14	$[\{Ir(cod)Cl\}_2]$	PhCl	0
15	$[(CO)_2Rh(acac)]$	anisole	82[j]
16	$[(CO)_2Rh(acac)]$	mesitylene	43[j]
17	$[(CO)_2Rh(acac)]$	$PhNO_2$	82[j]
18	$[(CO)_2Rh(acac)]$	DMSO	10
19	$[(CO)_2Rh(acac)]$	*trans*-decalin	40[j]
20[g]	$[(CO)_2Rh(acac)]$	PhCl	83[j]
21[h]	$[(CO)_2Rh(acac)]$	PhCl	93[j]
22[i]	$[(CO)_2Rh(acac)]$	PhCl	86[j]

[a] The reactions were carried out in the scale of 0.2 mmol of **1a** in the presence of 5.0 mol% catalyst in 2.0 mL solvent. Yield of isolated product. [b] 5.0 mol% of $AgSbF_6$ was added. [c] 2.5 mol% of $[\{(CO)_2RhCl\}_2]$ was added. [d] 2.5 mol% of $[\{(C_2H_4)_2RhCl\}_2]$ was added. [e] 2.5 mol% of $[\{(cod)_2RhCl\}_2]$ was added. [f] 2.5 mol% of $[\{Cp^*RhCl_2\}_2]$ was added. [g] 160 °C for 6 h. [h] 140 °C for 22 h. [i] 2.5 mol% of $[(CO)_2Rh(acac)]$ was used for 34 h. [j] *ortho*-substituted monoaryl/diaryl > 20:1 as determined by ^1H NMR (400 MHz) analysis of the crude reaction mixture. acac = acetylacetonate, cod = 1,5-cyclooctadiene, $Cp^* = C_5(CH_3)_5$, DMSO = dimethylsulfoxide, dppe = 1,2-bis(diphenylphosphino)ethane.



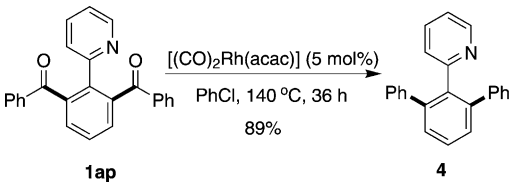
Scheme 2. Extrusion of CO by pyridine-directed rhodium(I)-catalyzed carbon–carbon bond activation. The reactions were carried out using 0.2 mmol of **1** in the presence of 5.0 mol% catalyst in 2.0 mL of PhCl at 140 °C. For experimental details see the Supporting Information. Reported yield is that of the of isolated product. 2-PE = 2-phenylethyl.

Additional studies indicated the great catalytic power of $[(CO)_2Rh(acac)]$. To avoid the confusion on the source of the phenyl group, other solvents were also tested. Anisole and $PhNO_2$ provided credible yields whereas mesitylene showed a moderate efficiency (Table 1, entries 15–17). DMSO and *trans*-decalin were not ideal solvents and only a small amount of product was obtained (entries 18 and 19). Although the slight change of the temperature did not show significant effect on the yields, the high yield was only obtained at 140 °C by lengthening the reaction time (entries 20 and 21). Finally, a full conversion and high yield was also obtained at lower catalyst loadings with a prolonged reaction time (entry 22).

By using the optimized reaction conditions, we investigated various substrates. First, we tested the substituents on the phenyl group (Scheme 2). The results indicated that the decarbonylation was not very sensitive to the electron density of the phenyl group (**2b**–**k**). Both electron-donating (**2b** and **2c**) and electron-withdrawing groups (**2e**–**k**) provided good results. However, a strong electron-donating group (e.g., **2o**) slightly decreased the efficacy. Various functionalities, including AcO (**2h**), MeO (**2c**), and different halides (**2e**–**g**) were tolerated, and thus offered the possibility for additional functionalization.[16] Steric hindrance did not significantly affect the efficiency of the reaction. For example, *para*- (**2b**), *meta*- (**2l**), and *ortho*-methyl (**2m**) groups gave similar yields. Heteroaryl groups such as thiophenyl, were tolerated. Moreover, the decarbonylation of the styryl ketone worked well and the corresponding stilbene derivative **2p** was isolated in excellent yield.

We further examined alkyl aryl ketones (Scheme 2). Various alkyl groups were suitable for this transformation (**2s**–**2x**). When starting from methyl and ethyl ketones, the corresponding arenes were obtained in excellent yields (**2s** and **2t**). A long-chain alkyl group is suitable for this decarbonylation (e.g., **2u**). Notably, the isomerization of a normal alkyl group was not observed, therefore this method might be a complementary method of the Friedel–Crafts reaction for the alkylation of arenes. Secondary alkyl groups were also feasible and the corresponding decarbonylated products were isolated in good yields (**2v** and **2w**). Starting from a phenethyl substrate, direct decarbonylation took place (**2x**), which partially ruled out cationic and radical intermediates.

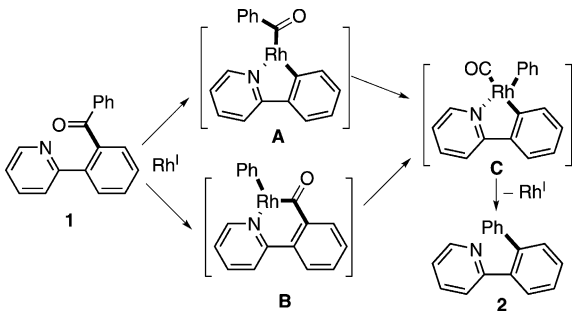
The functionality tolerance of the pyridinyl unit was further surveyed (Scheme 3). The decarbonylation of the substrates having different substituents were carried out. Both electron-donating (**3e, 3f**) and electron-withdrawing groups (**3c**) offered good results. Similarly, the halide functionality (**3b**) is tolerated and offers the potential for orthogonal transformations.[16] The substrates with or without a substituent at the 4-position of the phenyl ring (**3h, 3l, 3j**) gave good results, and surprisingly contained a trace amount of the *ortho*-diarylated by-product and the unsubstituted 2-arylpyridine. When other solvents were used, trace amounts of the *ortho*-diarylated by-product was also observed, thus indicating that the second aryl group derives from phenyl scrambling rather than the solvent (PhCl).[17] To our delight, the aryl scrambling could be inhibited by using $[\{(CO)_2RhCl\}_2]$ instead of $[Rh(CO)_2(acac)]$ as the catalyst. Notably, the alcohol motif survived under the reaction conditions (**3d**). 8-Bezoylbenzoquinoline was introduced to these conditions and the decarbonylation worked well to produce the desired product **3m** in 91 % yield. Other N-based directing groups, such as quinolinyl, pyrazolyl, and oxazolyl were effective although a prolonged reaction time was required to achieve moderate yields (**3l**, **3n,** and **3o**). Finally, we tested the diketone at two *ortho* positions. Both carbonyl groups were extruded and 2,6-biphenylphenyl pyridine **4** was isolated in an 89 % yield, thus showing the high efficiency of this transformation [Eq. (1)].



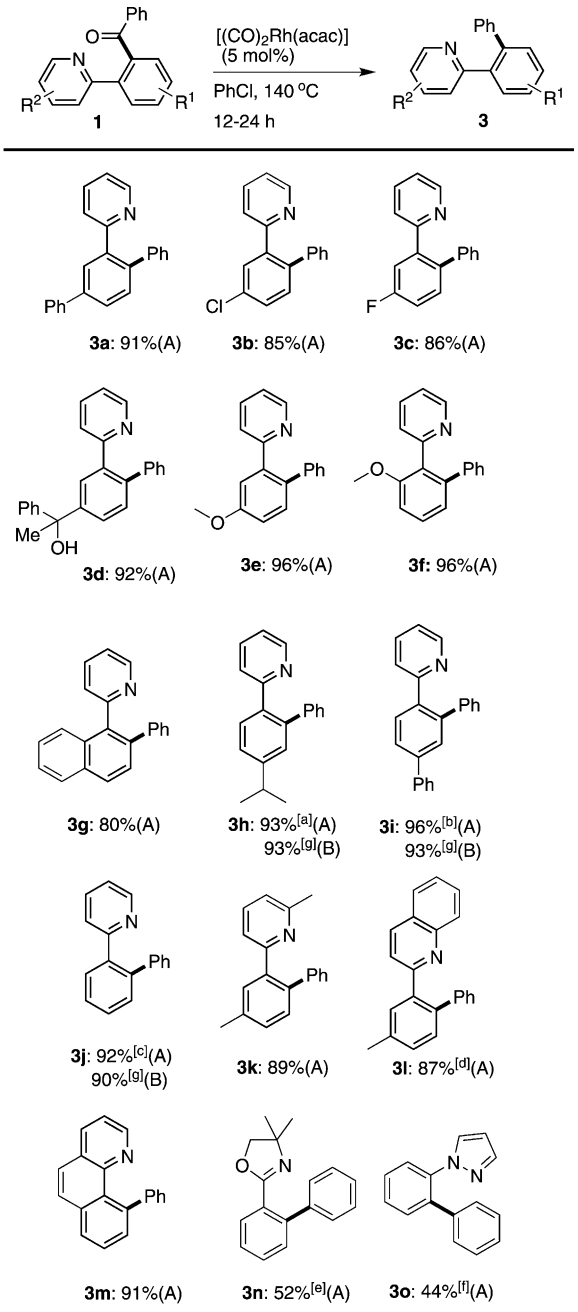
(1)

Given that photoirradiation can initiate decarbonylation in a bridged ring system,[10] we investigated the potential role of the light in this transformation. Actually, the decarbonylation took place in the dark with a comparable efficiency, whereas it was completely shut down in the absence of the rhodium catalyst. Thus, the rhodium complex is the real catalytic species performing this decarbonylation.

The proposed reaction pathway is shown in Scheme 4. The decarbonylation is initiated from the oxidative cleavage of the carbon–carbon bond in the square-planar Rh^I complex with



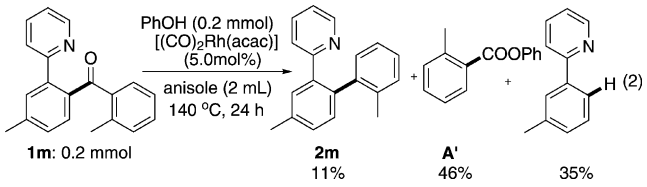
Scheme 4. Proposed mechanism.



Scheme 3. Extrusion of CO by pyridine-directed rhodium(I)-catalyzed carbon–carbon bond activation. Method A: 0.2 mmol of **1** in the presence of 5.0 mol % $[(CO)_2Rh(acac)]$ in 2.0 mL of PhCl at 140 °C. Method B: 0.2 mmol of **1** in the presence of 2.5 mol % $[\{(CO)_2RhCl\}_2]$ in 2.0 mL of toluene at 140 °C. For experimental details see the Supporting Information. Reported yield is that of the isolated product; method used is indicated in parentheses. [a] *ortho*-substituted monoaryl/diaryl ratio > 20:1 as determined by crude ^{1}H NMR analysis of the crude reaction mixture. [b] *ortho*-substituted monoaryl/diaryl ratio = 16:1 as determined by ^{1}H NMR analysis of the crude reaction mixture. [c] *ortho*-substituted monoaryl/diaryl = 20:1 as determined by ^{1}H NMR analysis of the crude reaction mixture. [d] 36 h. [e] 36 h and 79 % starting material was consumed. [f] 36 h and 67 % starting material was consumed. [g] Yield of the isolated product; only the monoarylated product was obtained.

the assistance of the pyridine group to form the octahedral acyl/Rh^{III} species **A** or **B**.[6,12] After the reverse migratory insertion, reductive elimination produces the desired product **2** with the regeneration of the Rh^{I} catalyst which re-enters the catalytic cycle. The acyl/Rh^{III} species **A** was trapped by phenol to afford the phenyl benzoate **A′** in addition to the desired product [Eq. (2);reported yield is that of isolated product],[18] thus suggesting that **A** could be the key intermediate of the catalytic cycle. However, the intermediate **B** could not be ruled out at this stage.

In conclusion, we have developed a novel and efficient rhodium(I)-catalyzed decarbonylation process through double C–C cleavage with the assistance of an N-containing



directing group. Various functionalities are compatible with the reaction conditions. This method not only offers an alternative way to synthesize biaryls, and alkenyl and alkyl benzenes, but also is fundamentally important to understanding the reactivity of the inert carbon–carbon bonds. Additional investigations aimed at exploring this chemistry and understanding the real catalytic pathway are underway in our laboratory.

Experimental Section

$[(CO)_2Rh(acac)]$ (0.01 mmol, 2.6 mg) in 2 mL of anhydrous PhCl was added by syringe to a Schlenk flask containing ketone **1** (0.2 mmol). After degassing three times, the reaction mixture was subsequently heated at 140 °C in Wattecs Parallel Reactor for the proper time with stirring. After cooling down to room temperature, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc (15:1→5:1) to afford the desired product **2.**

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