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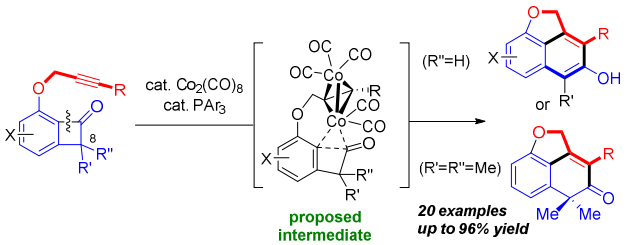
Cobalt-Catalyzed Intramolecular Alkyne/Benzocyclobutenone Coupling: C−C Bond Cleavage via a Tetrahedral Dicobalt Intermediate

Zixi Zhu, † Xinghan Li, ‡ Sicong Chen, † Peng-hao Chen, ‡ Brent A. Billett, † Zhongxing Huang,†,‡ and Guangbin Dong*†,‡

†Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, United States

‡Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States

Supporting Information Placeholder

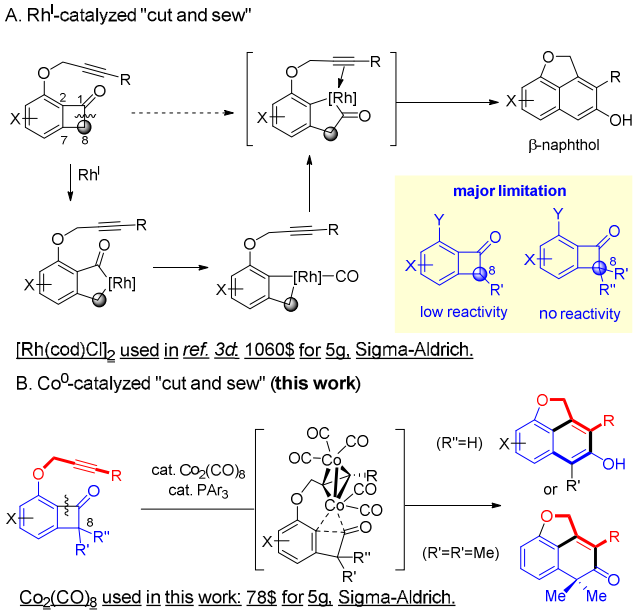


ABSTRACT: A Co(0)-catalyzed intramolecular alkyne/benzocyclobutenone coupling through C−C cleavage of benzocyclobutenones is described. $Co_2(CO)_8$/P[3,5-$(CF_3)_2C_6H_3]_3$ was discovered to be an effective metal/ligand combination, which exhibits complementary catalytic activity to the previously established rhodium catalyst. In particular, the C8-substituted substrates failed in the Rh system, but succeeded with the Co catalysis. Experimental and computational studies show that the initially formed tetrahedral dicobalt-alkyne complex undergoes C1−C2 activation via oxidative addition with Co(0), followed by migratory insertion and reductive elimination to give the β-naphthol products.

KEYWORDS: *C−C activation, benzocyclobutenones, cobalt catalysis, cyclization, β-naphthol.*

Catalytic carbon−carbon bond (C−C) activation has emerged as a useful tool for quickly building molecules with high complexity.[1] Numerous elegant C−C activation transformations have been developed to date; however, the majority of them require the use of noble transition metals (TMs), such as Rh, Ru, Pd and Ir. Clearly, it would be highly desirable if the same transformations can be catalyzed by earth abundant first-row TMs, which would offer a more cost effective option. In addition, complementary reactivity could be expected due to distinct properties of first-row TMs from noble metals. Despite the recent advance of Ni catalysis in various C−C activations,[1r-u] using other first-row TMs as catalysts has been rare.[2] Our laboratory has been focusing on developing catalytic methods based on activation of ketone α-C−C bonds, and our prior works exclusively relied on using Rh catalysts.[3] Herein, we disclose the first Co(0)-catalyzed C−C activation of ketones,[4] in which an intramolecular coupling between benzocyclobutenones and alkynes was realized with an inexpensive cobalt precatalyst (**Scheme 1**). Preliminary mechanistic study suggests that the reaction is promoted by a tetrahedral dicobalt-mediated C−C cleavage.

We have been engaged in the systematic development of "cut and sew" transformations[1p] for building bridged and fused rings, which involves oxidative addition of a TM into a C−C bond, followed by 2π-insertion and reductive elimination. A suite of methods has been demonstrated for intramolecular "cut and sew" reactions with benzocyclobutenones,[3a,b,d,m] where insertion occurred selectively at the C1-C2 position. For example, the coupling with alkynes generates fused β-naphthols (Scheme 1A).[3d] The DFT study by Liu and coworkers suggests that the reaction first

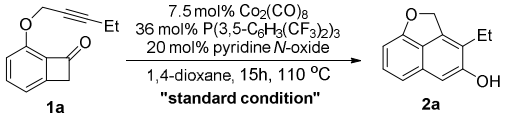


Scheme 1. "Cut and Sew" reaction between alkynes and benzocyclobutenones.

cleaves the C1-C8 bond, and then through a decarbonylation/reinsertion sequence delivers Rh to the C2 position.[5] Hence, *one major limitation* with the Rh system is that substitution at the

C8 position is not well tolerated due to the steric constrain in the initial C−C cleavage step, which became a motivation to discover alternative catalytic systems. During our total synthesis of cycloinumakiol, a trace amount of the desired "cut and sew" product was detected when stoichiometric $Co_2(CO)_8$ was used.[6] While the reaction was not catalytic, it inspired us to explore the use of $Co_2(CO)_8$ as the precatalyst for the intramolecular alkyne/benzocyclobutenone coupling (Scheme 1B).

Table 1. Control Experiments.



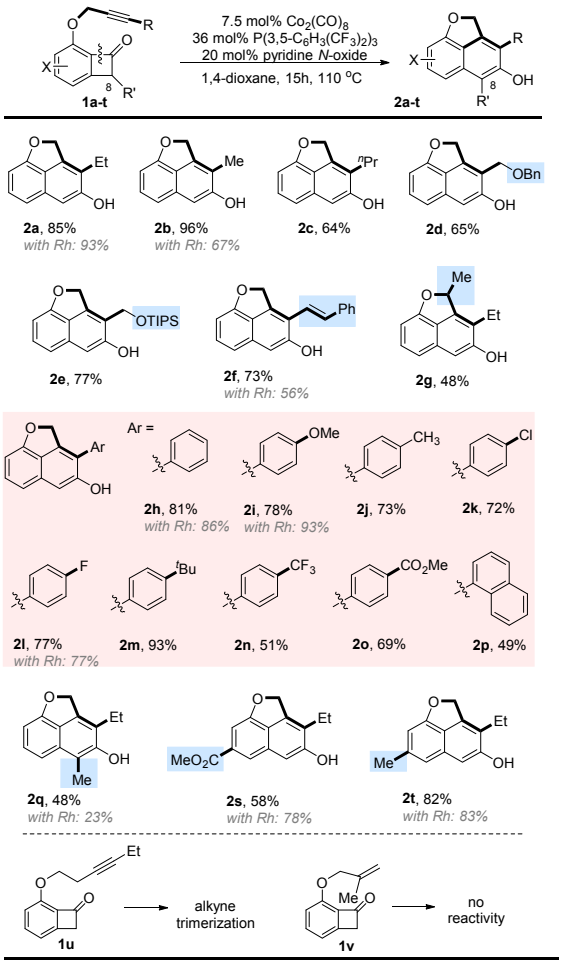
entry	change from "standard condition"	yield[a] (%)
1	none	88
2	w/o $Co_2(CO)_8$	0
3	w/o pyridine *N*-oxide	46
4	w/o $P(3,5\text{-}C_6H_3(CF_3)_2)_3$	52
5	$CoBr_2$ instead of $Co_2(CO)_8$	0
6	SalenCo(II) instead of $Co_2(CO)_8$	0
7	Co nanoparticles[b] instead of $Co_2(CO)_8$	0
8	dppb[c] instead of $P(3,5\text{-}C_6H_3(CF_3)_2)_3$	trace
9	PPh_3 instead of $P(3,5\text{-}C_6H_3(CF_3)_2)_3$	75
10	SPhos instead of $P(3,5\text{-}C_6H_3(CF_3)_2)_3$	75
11	90 °C instead of 110 °C	76
12	130 °C instead of 110 °C	55[d]
13	with 1.2 equiv $ZnCl_2$	33

[a]Unless otherwise noted, yields were determined by ^{1}H NMR. [b] Obtained by heating $Co_2(CO)_8$ alone in 1,4-dioxane at 130 °C for 6h. [c]18 mol% of dppb was used. [d]Isolated yield.

Benzocyclobutenone **1a** with an alkyne moiety was employed as the model substrate. After a careful survey of the reaction parameters (See Table S1, Supporting Information), the desired β-naphthol product (**2a**) was afforded in 88% yield using $Co_2(CO)_8$/P[3,5-$(CF_3)_2C_6H_3$]$_3$ as the metal/ligand combination and pyridine *N*-oxide as the additive. Control experiments were carried out to understand the role of each reactant (Table 1). In the absence of $Co_2(CO)_8$, no desired product was observed (entry 2). The reaction without pyridine *N*-oxide or the ligand still afforded the desired product albeit in a lower yield (entries 3 and 4). Their roles are proposed to create open coordination sites[7] and assist catalyst dissociation. Co(II) complexes, such as $CoBr_2$ and salen Co complex, are not reactive (entries 5 and 6). On the other hand, cobalt nanoparticles, obtained from the decomposition of $Co_2(CO)_8$, showed no catalytic activity (entry 7), suggesting that the reaction is likely catalyzed by homogeneous Co species. The use of other mono-dentate phosphine ligands, such as PPh_3 or SPhos, slightly lowered the yield (entries 9 and 10); in contrast, bidentate ligands, such as dppb, significantly inhibited the reaction, probably through blocking reactive sites on Co (entry 8). Lowering the reaction temperature to 90°C slightly decreased the yield (entry 11). Surprisingly, raising the reaction temperature to 130°C gave a much lower yield (entry 12), likely due to the accelerated decomposition of the Co catalyst or competitive alkyne trimerization reaction.[8] In the previous Rh system, adding $ZnCl_2$ was found to be beneficial to the reactivity;[3d] however, it was detrimental to the Co catalyst, though the exact reason remains unclear (entry 13).

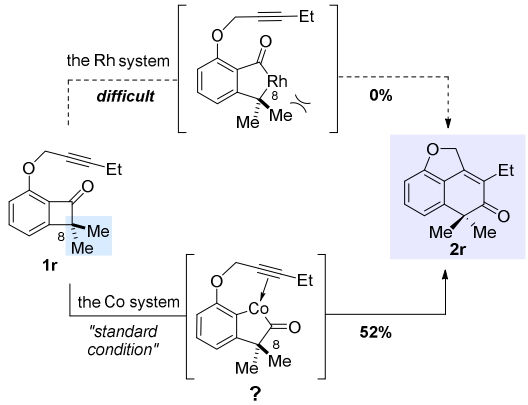
With the optimized conditions in hand, the scope of this reaction was examined (Table 2). Similar to the $[Rh(cod)Cl]_2$-dppp system,[3d] substrates containing alkyl, aryl, or alkenyl alkynes were converted into the corresponding β-naphthols in good to excellent yields. Numerous functional groups, such as aryl chloride (**2k**), ethers, esters (**2o**), olefins (**2f**), benzyl-protected alcohols (**2d**), and triisopropylsilyl (TIPS) ethers (**2e**) were well tolerated. Introducing a methyl group at the propargylic position decreased the yield, which is possibly caused by the steric hindrance around the alkyne (**2g**). In general, less bulky and more electron-rich alkyne moieties gave higher yields. Both electron-donating (**2t**) and withdrawing (**2s**) substituents on the benzocyclobutenone rings were well tolerated. Unfortunately, substrates with a longer tether (**1u**) did not undergo the "cut and sew" transformation, instead only giving alkyne trimerization products.[8] Unsurprisingly, the less reactive olefin-tethered substrate (**1v**) gave no reaction under the catalytic conditions.[3a]

Table 2. Substrate scope[a]



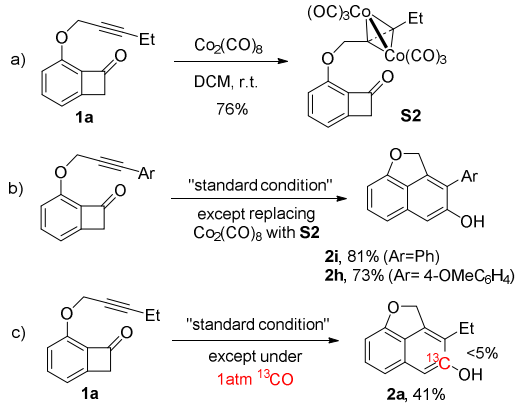
[a] All yields are isolated yields. The yields with Rh are from ref. 3d. Others are all new substrates.

Compared to the Rh system, the Co catalysis gave comparable yields but at a lower reaction temperature (110 vs 130 °C). However, *one most significant difference is in the case of C8-substituted benzocyclobutenones*. Using $[Rh(cod)Cl_2]_2$-dppp, 8-methyl-substituted substrate **1q** exhibited low reactivity and only afforded 23% yield; in contrast, the Co system gave a more than doubled yield of product **2q**. In addition, 8,8-dimethly substituted substrate **1r** was completely unreactive with the Rh system owing to the bulkiness of the C1−C8 bond; however, the Co catalysis successfully provided the corresponding benzocyclohexenone product (**2r**) in 52% yield (Scheme 2). The enhanced reactivity of the Co catalyst with 8-substituted benzocyclobutenones suggests that the reaction with Co is unlikely initiated by cleavage of the C1−C8 bond; therefore, it may operate through a different mechanistic pathway from the Rh system.



Scheme 2. Unique reactivity with the 8,8-dimethly substituted substrate

The unique reactivity of the Co system motivated us to explore the reaction mechanism. Consequently, a number of experiments were carried out. Analogous to the Pauson−Khand reaction,[9] mixing of $Co_2(CO)_8$ and the substrate (**1a**) at room temperature rapidly generated a tetrahedral dicobalt-alkyne adduct (**S2**) (Scheme 3a). This species was found to be catalytically active for the intramolecular benzocyclobutenone alkyne coupling, giving comparable yields as those with $Co_2(CO)_8$ (Scheme 3b). Considering the established high stability of the dicobalt-alkyne adduct,[10] it is reasonable to assume that this intermediate may be involved in the catalytic cycle. On the other hand, running the reaction under a ^{13}CO atmosphere yielded the desired product without much ^{13}C incorporation. Given that the exchange between free CO and the coordinated CO on $Co_2(CO)_8$ is known to be facile,[11] if the reaction proceeded through cleavage of the C1−C8 bond first, the subsequent CO desertion and re-insertion would have introduced substantial ^{13}C into the product. The absence of significant ^{13}C incorporation disfavored the pathway involving cleavage of the C1−C8 bond.



Scheme 3. Preliminary mechanistic study

Having ruled out the pathway involving C1−C8 bond cleavage, a plausible catalytic cycle is proposed for the alkyne insertion (Figure 1). The reaction begins with decarbonylation of dicobalt-alkyne complex **A**, which is accelerated by pyridine *N*-oxide[7], and followed by coordination of the ketone carbonyl to form complex **B**. At this stage, two pathways are possible. **Path a** involves cyclometalation between the alkyne moiety and the carbonyl to form intermediate **C** that can undergo subsequent β-carbon elimination, reductive elimination and tautomerization to give the β-naphthol product and re-generates the catalyst. **Path b** involves direct oxidative addition into the benzocyclobutenone C1−C2 bond with one cobalt center. The resulting cobaltacycle **D** then undergoes migratory insertion into the alkyne to afford intermediate **E**, which upon reductive elimination and tautomerization forms the β-naphthol product and re-generates the catalyst.

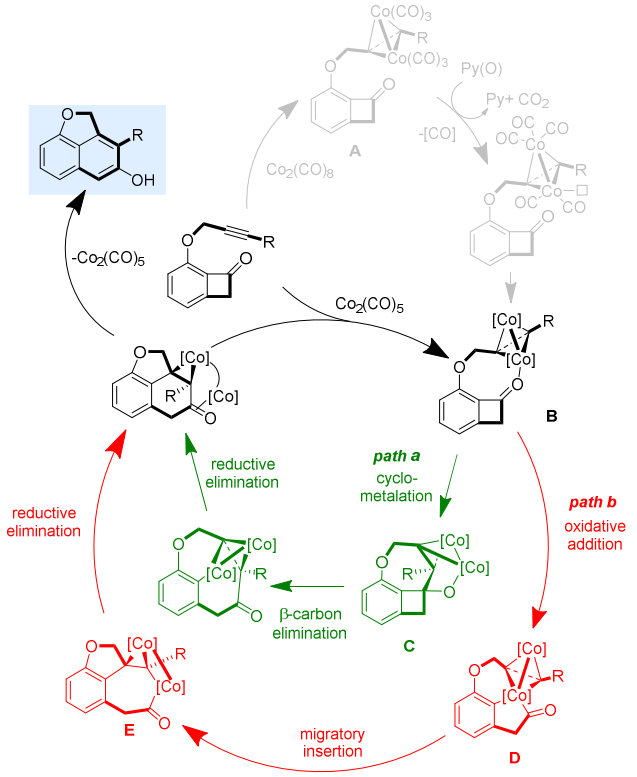


Figure 1. Plausible catalytic cycle.

To further explore the reaction mechanism, preliminary DFT study was conducted (without considering pyridine *N*-oxide and the phosphine ligand).[12] The computation started from the active tetrahedral dicobalt complex, and the energy diagram is depicted in Figure 2 with 3D structures of key transition states **TS1** and **TS2** included. The computational study shows that oxidative addition into the distal C1−C8 bond exhibits extremely high activation barrier (**TS1'**, 50.5 kcal/mol) due to a highly strained transition state. The cyclometalation pathway (**path a**) also shows a high activation energy (**TS1''**, 56.7 kcal/mol), which is attributed to a non-coplanar structure of Co−C−C−O four-membered ring and consequently less efficient orbital overlap. In contrast, the direct cleavage of the C1−C2 bond has a much lower energy barrier (**TS1**, 29.9 kcal/mol), supporting ***path b*** to be a more favorable pathway.[13] The migratory insertion step was found to exhibit the highest overall activation energy (**TS2**, 36.6 kcal/mol) to give **Int3**. The following reductive elimination readily takes place to form the second C−C bond with a lower activation barrier. The two cobalt centers in the resulting intermediate (**Int4**, -28.7 kcal/mol) are stabilized by both C=C and C=O π-bond to form a dicobalt/enone complex via a μ^2-carbonyl bridge.[14] As a potential competitive pathway, decarbonylation from **Int3** would lead to a six-membered cobalt cycle, the activation energy of which (**TS3',** 8.2 kcal/mol) is 11.5 kcal/mol higher than the one of the reductive elimination step; in addition, the free energy of the subsequent intermediate (**Int4'**, -1.6 kcal/mol) is 27.1 kcal/mol higher than **Int4**. Thus, the CO de-insertion pathway is neither thermodynamically nor kinetically favorable. This observation is consistent with the result of the ^{13}C-labelling study (*vide supra*), in which CO exchange was not significant. Computational methods and detailed information regarding each intermediates and transition states are available in the Supporting Information.

In conclusion, we discovered a simple Co system that can catalyze β-naphthol synthesis via an intramolecular alkyne/benzocyclobutenone coupling. To the best of our knowledge, this reaction represents the first example of Co-catalyzed C−C activation of ketones. Compared to the Rh system, the Co-

catalyzed reaction not only operates at a lower temperature with similar yields, but also effectively tolerates C8-substituted substrates. Its unique mechanistic feature disclosed here should have broad implications for developing more efficient and economical C−C activation methods in the future.

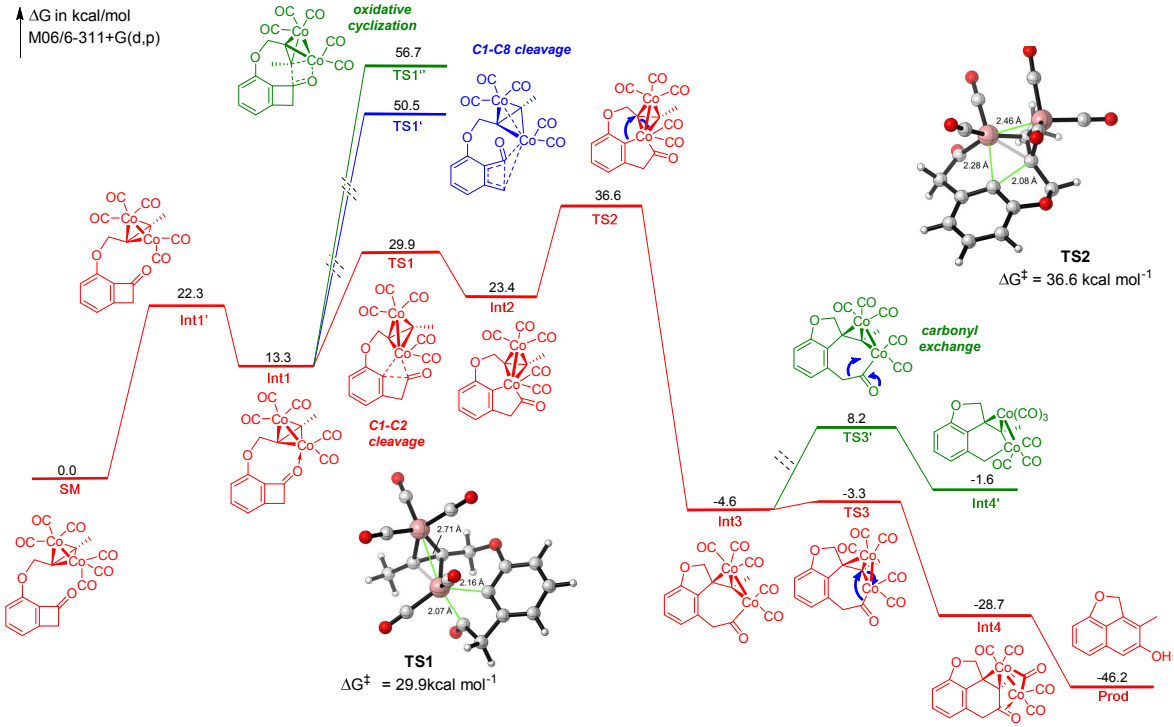


Figure 2. DFT calculated pathways for the intramolecular alkyne insertion.

AUTHOR INFORMATION

Corresponding Author
*Email: gbdong@uchicago.edu

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Detailed experimental procedures, characterization of products, and computational discussion and data.

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