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Cobalt(III)-Catalyzed Functionalization of Unstrained Carbon—Carbon Bonds through β -Carbon Cleavage of Alcohols

Erhan Ozkal, Bastien Cacherat, and Bill Morandi*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Mülheim an der Ruhr, Germany

Supporting Information

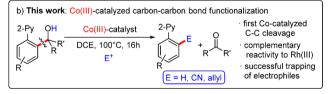
ABSTRACT: We demonstrate that a simple Co(III)-complex can efficiently catalyze the cleavage of unstrained C–C bonds via the β -carbon elimination of secondary and tertiary alcohols bearing a directing group. The cobalt-aryl intermediate generated under the reaction conditions can be trapped by different electrophiles to generate a new carbon–carbon bond. Some essential features of this new Co-based mechanistic manifold were revealed by preliminary mechanistic studies.

KEYWORDS: cobalt, C-C bond activation, base metal, β -carbon elimination, alcohols

The catalytic activation of inert bonds is an important challenge in transition metal catalysis. 1 C-H and C-C bonds are ubiquitous in organic compounds, and their transformation provides complementary routes to efficiently functionalize hydrocarbon skeletons. Rh, a rare and expensive noble metal, has provided a platform for the discovery of powerful C-H^{2,3} and C-C⁴⁻⁷ bond functionalization reactions (Scheme 1a). However, the high cost and low sustainability of

Scheme 1. Context of the Work

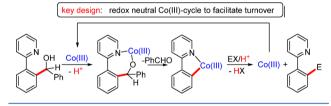
a) Approaches to catalytic hydrocarbon functionalization using Rh/Co



rhodium catalysts has recently stimulated the discovery of alternative, cobalt-based catalysts for several important transformations. Separations of Cobalt-catalyzed C–H functionalization, in particular, is a blossoming research area that provides many new sustainable reactions once exclusively reserved to Rhcatalysis. Excitingly, rather than simply serving as a rhodium substitute, cobalt exhibits distinct and complementary reactivity when compared to its noble metal counterpart. It can thus be expected that the discovery of cobalt complexes able to catalyze C–C bond cleavage reactions will significantly impact the area of C–C bond functionalization. In this Letter, we report the first example of an efficient Co-catalyzed C–C bond cleavage reaction (Scheme 1b).

A limited number of reports have previously described *stoichiometric* cobalt-mediated C–C bond cleavage reactions. ¹⁴ The majority of these reactions rely on the oxidative addition of strained or polarized (C–CN) C–C bonds onto Co(I)-species. We reasoned that a distinct approach relying on a β -carbon elimination step ⁶ would offer the possibility to perform a redoxneutral C–C cleavage process. Catalytic turnover should be possible through simple ligand exchange and protonation steps (Scheme 2). Additionally, circumventing the need for sensitive

Scheme 2. Proposed Redox-Neutral Co(III)-Catalyzed C–C Bond Cleavage/Functionalization



Co(I) intermediates, this redox-neutral strategy will enhance the compatibility of the catalytic system with external electrophiles.

To realize our strategy, we selected secondary arylmethanol 1 as a test substrate in order to evaluate the propensity of our transformation to cleave selectively the C–C bond over alcohol oxidation through β -hydride elimination. The presence of a directing group should (1) facilitate β -carbon cleavage and (2) stabilize the intermediate Co-aryl species against premature protodemetalation prior to electrophile trapping. We initially focused our attention on the development of a direct cleavage reaction of secondary alcohols to generate the corresponding

Received: August 11, 2015 Revised: September 23, 2015 Published: September 25, 2015

products, namely, 2-phenylpyridine and benzaldehyde. The goal of this transformation is to identify suitable catalysts and assess the feasibility of our mechanistic hypothesis using the simplest electrophile, H^{\dagger} . Initial attempts using a range of different cobalt salts did not afford any of the desired products (Table 1, Entries 2–5). Gratifyingly, $[Cp*Co(CO)I_2]$, when

Table 1. Evaluation of Reaction Conditions^a

$$\begin{array}{c} \text{O-Catalyst} \\ \text{AgSbF}_6 \\ \text{DCE, } 100 \, ^{\circ}\text{C} \\ \end{array} \begin{array}{c} \text{N} \\ \text{H} \end{array} \begin{array}{c} \text{O} \\ \text{H} \end{array}$$

entry	catalyst (5%)	AgSbF ₆	2-Ph-py	PhCHO ^b
1	-	-	<5%	<5%
2	$Co(OAc)_2 \cdot 4H_2O$	-	<5%	<5%
3	$CoCl_2$	10%	<5%	<5%
4	Co(acac) ₃	-	<5%	<5%
5	$[Cp*Co(CO)I_2]$	-	<5%	<5%
6	$[Cp*Co(CO)I_2]$	10%	90%	90%
7	-	10%	<5%	<5%
8	$[Cp*Co(CO)I_2]$	5%	53%	53%
9 ^c	$[Cp*Co(CO)I_2]$	10%	76%	78%

 a 0.1 mmol 1, 5 mol % catalyst, 1,2-dichloroethane, 16 h, 100 °C. b GC-yield, dodecane used as an analytical standard. c at 80 °C. 2-Ph-py = 2-phenylpyridine.

combined with a silver salt, gave the two cleavage products in 90% yield, respectively (Entry 6). Decreasing the amount of the silver salt to one equivalent relative to cobalt led to a significant decrease in yield (53%), suggesting the importance of forming a more active dicationic Co-species in situ (Entry 8). Finally, the reaction could also tolerate a slight decrease of the temperature to 80 $^{\circ}$ C (Entry 9, 76%).

In order to probe the generality of the cleavage reaction, we evaluated the different substrate structural features on the reactivity (Scheme 3). It was demonstrated that electronic and steric effects had little influence on the transformation. Electron-rich (2, 75%, and 3, 78%) and electron-deficient

Scheme 3. Effect of Structural Changes on the Transformation (Isolated Yields)

substituents (5, 90%, and 6, 71%) on both the western and eastern part of the substrate were well tolerated. A sterically more hindered (4) and a naphthyl-substituted substrate (7) also provided the desired product in good yield (74% and 84% respectively). Finally, different types of alcohols were probed. Although aliphatic alcohols are prone to alkene formation via acid-mediated elimination, substrate 8 gave the product in high yield (82%) with no detection of alkene byproduct. When tertiary alcohols were used, the corresponding cleavage products were also isolated in good yields for both an alkyl/ aryl (10, 90%) and a dialkyl-substituted tertiary alcohols (9, 87%), thus significantly increasing the generality of the reaction. Only the triarylmethanol substrate 11 afforded a reduced yield (38%), probably due to substrate decomposition via acidmediated generation of a stable triaryl carbocation. In all cases, full regioselectivity for the cleavage of the aromatic moiety bearing the directing group was observed.

We next performed preliminary experiments to reveal mechanistic aspects of this intriguing catalytic process. We evaluated the reversibility of our Co-catalyzed reaction using a competition experiment (Scheme 4). Product 5 was not

Scheme 4. Mechanistic Study of the Cleavage

detected in any significant amount (<1%) by GC and NMR-analysis of the crude reaction mixture, a result suggesting the irreversibility of the β -carbon elimination step under Cocatalysis.

We next performed competition experiments between substrates bearing different substituents on the eastern phenyl ring by quenching the reaction mixture prior to completion. These qualitative experiments clearly revealed that electron-donating substituents accelerate the cleavage, whereas electron-withdrawing substituents retard it. This electronic effect suggests the buildup of a positive charge in the transition state.

Having demonstrated catalytic competency with our simple model electrophile, H+, we next turned our attention to whether the β -carbyl elimination-derived organocobalt species could be intercepted with carbon-based electrophiles under analogous reaction conditions (Scheme 5). Such a process would be an important proof of concept that the catalytic reactivity developed herein could lead to the discovery of a myriad of efficient cobalt-catalyzed carbon-carbon functionalization reactions. We selected a cyanating reagent (N-cyano-Nphenyl-p-toluenesulfonamide, NCTS) as an electrophile, because this reagent has shown promising reactivity toward Co-aryl intermediates in C-H functionalization reactions. 13b,g,l Additionally, a direct carbon-carbon cyanation via C-C bond cleavage has not been reported under Rh-catalysis. To our delight, cobalt-catalyzed C-C bond cyanation of both secondary and tertiary alcohol substrates provided 65 and 91% yield, respectively. To the best of our knowledge, this reaction is the first example of a catalytic C-C bond cyanation

Scheme 5. Co-Catalyzed C-C Bond Functionalization

via the β -carbon elimination of alcohols. Importantly, when a Cp*Rh(III)-complex was used instead of Co, a mediocre yield (23%) of the desired product and significant amounts of the 2phenylpyridine (75%) side-product were observed, a result that points toward an inefficient trapping of the Rh-aryl species by the cyanating reagent. 16 This result is in accordance with previous C-H functionalization reports describing the enhanced polarization of the Co-aryl bond, when compared to the corresponding Rh-aryl bond, a feature that leads to enhanced nucleophilicity of the Co-aryl species. 11d Additionally, an allylation reaction could be performed in moderate yield, giving the monoallylated product in pure form. This result is interesting because inseparable mixtures of mono- and bisallylated products are commonly obtained in the C-H functionalization of phenylpyridines.¹⁷ Overall, these results both demonstrate that Co can catalyze C-C bond cleavage/ functionalization reactions difficult to achieve under Rhcatalysis and showcases the possibility to trap the transiently formed Co-aryl intermediate with suitable electrophiles, a mechanistic manifold that is likely to fuel the discovery of a wide range of novel Co-catalyzed reactions.

In the cobalt-catalyzed carbon—carbon cyanation, two mechanistically distinct pathways could lead to the formation of the desired product (Scheme 6a). First, the Co-aryl intermediate **A**, generated by the initial β -carbon elimination, can be directly trapped by the cyanating reagent (Path **A**) or can be first protonated to form phenylpyridine prior to

Scheme 6. Mechanistic Study of the Cyanation

undergoing a Co-catalyzed C–H functionalization pathway to form the desired product (Path B). Accordingly, we tested whether C–H functionalization is a possible secondary pathway (Scheme Sb). With C–H functionalization, 37% and 15% yield, respectively, of cyanated products were obtained, confirming that C–H functionalization is possible under standard reaction conditions. To probe whether a C–H activation pathway is responsible for the C–C cyanation process, we conducted a competition experiment employing CF₃-phenylpyridine (14) and our standard test substrate 1. The C–H activation-derived cyanated product 15 was neither detected in the crude reaction mixture nor isolated, suggesting that direct trapping of the initially generated Co-aryl bond by the reagent is likely the dominating pathway generating the product (Path A).

In conclusion, we have described the first efficient cobalt-catalyzed cleavage of carbon—carbon bonds via β -carbon elimination. Importantly, we demonstrated that the Co-aryl intermediate can be trapped by a suitable electrophile to form a new C–C bond. The cobalt catalyst proved superior to the corresponding Rh-based system in a cyanation reaction. In a broader context, the discovery that a simple cobalt complex can efficiently catalyze carbon—carbon functionalizations via β -carbon elimination will provide a platform for the design of sustainable carbon—carbon cleavage/functionalization reactions for organic synthesis.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01753.

General information, materials, instrumentation, and procedures (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: morandi@kofo.mpg.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Generous funding from the Max-Planck-Society/Max-Planck-Institut für Kohlenforschung is acknowledged. We thank Prof. Benjamin List for sharing chemicals and analytical equipment, and our MS-department for technical assistance.

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