Mechanistic Study on Chromium-catalyzed Ring-opening Arylation of 7-Oxabenzonorbornadiene Derivatives with Aryl Grignard Reagents

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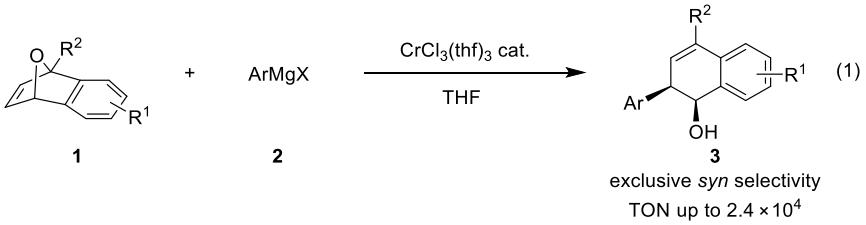
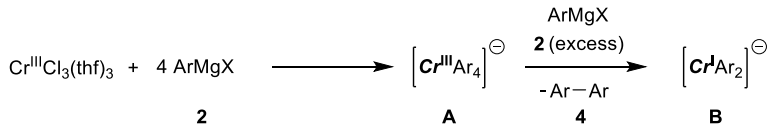
Stereoselective synthesis of multi-functionalized 1,2-dihydronaphthalen-1-ols has attracted interest due to their intrinsic applicability as building blocks for derivatizing to biologically active compounds.[1] Ring-opening of 7-oxabenzonorbornadiene derivatives with organometallic reagents in the presence of suitable transition metal catalysts is one of the straightforward methods to obtain the 1,2-dihydronaphthalen-1-ol skeleton.[2] Herein, we report chromium-catalyzed *syn*-selective ring-opening arylation of 7-oxabenzonorbornadiene derivatives **1** with aryl Grignard reagents **2**, giving *syn*-2-ary-1,2-dihydronaphthalen-1-ols **3** under ligand-free conditions (eq. 1). Several control experiments were carried out to clarify the active species for this ring-opening arylation starting from commercially available $CrCl_3(thf)_3$. In the initial step, tetraarylchromate(III) species **A** is generated by the reaction of $CrCl_3(thf)_3$ and 4 equiv. of aryl Grignard reagent **2**, and subsequent two-electron reduction of **A** *via* reductive elimination of one equiv. of biaryl **4** affords diarylchromate(I) species **B** (Scheme 1), in which excess amounts of **2** are indispensable for the reduction of **A**. In addition, *in situ*-generated Cr(I) species **B** showed high activity at –20 °C, whereas the Cr(III) species **A** was inactive under the same reaction conditions.



Scheme 1. Proposed Mechanism for Generation of Catalytically Active Diarylchromate(I) Species **B**



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