Sodium-Metal-Promoted 1,2-Dimagnesiation and 1,2-Dialumination of Alkynes

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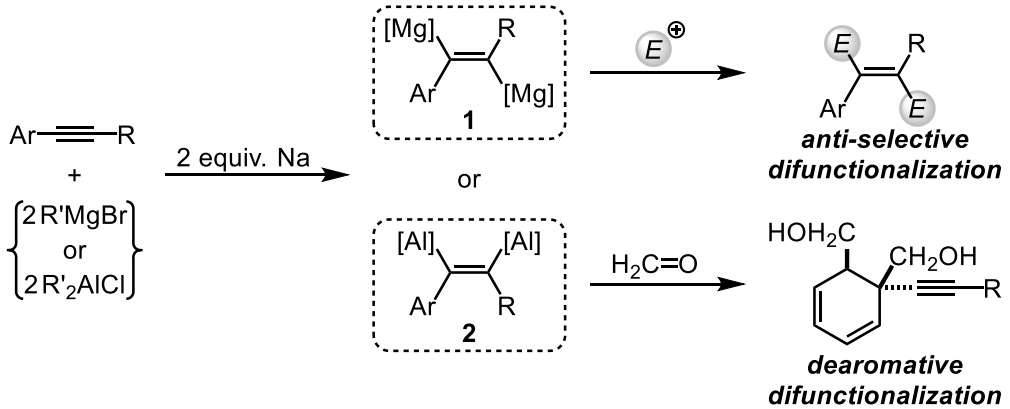
Recently, we have been interested in the development of sodium-metal-promoted functionalizations of unsaturated hydrocarbons.[1] For example, the 1,2-*syn*-diboration of arylacetylenes proceeds with the aid of sodium metal and trimethoxyborane.[1c] The key to the success of these reactions is the use of reduction-resistant electrophiles such as trimethoxyborane. In this context, we envisioned that organomagnesium or organoaluminium compounds would also be suitable electrophiles and that the resulting 1,2-dimetalloethenes would show unique reactivities. Here, we report that arylacetylenes undergo the sodium-metal-promoted 1,2-dimetallation to give the corresponding 1,2-dimagnesioethenes **1** or 1,2-dialuminoethenes **2**.

In the presence of 2 equivalents of alkylmagnesium bromide, arylacetylenes reacted with 2 equivalents of sodium metal to afford **1**. The subsequent one-pot addition of electrophiles gave 1,2-*anti*-difunctionalized ethene derivatives with high stereoselectivity. When dialkylaluminium chlorides were used instead of alkylmagnesium bromides, the subsequent one-pot addition of paraformaldehyde to the resulting 1,2-dialumino-1-arylethenes **2** induced an unexpected dearomatization of the aryl moiety to provide the corresponding dearomatized 1,4-diols. The mechanism of the dearomatization was investigated by means of DFT calculation.



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