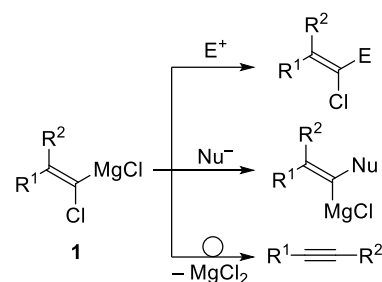


## Experimental and DFT Study on Electrophilic and Carbene-Like Reactivity of Magnesium Alkylidene Carbenoids

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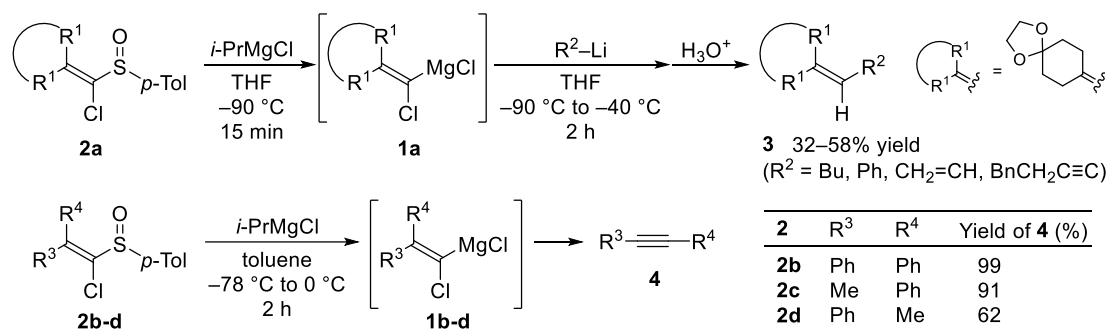
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Magnesium alkylidene carbenoids **1** are reactive intermediates in which magnesium and chlorine atoms are connected to a vinylic carbon atom (Scheme 1). Magnesium alkylidene carbenoids **1** have an ambiphilic reactivity, namely, magnesium alkylidene carbenoids **1** act not only as nucleophiles but also as electrophiles. Furthermore, as the name suggests, magnesium alkylidene carbenoids **1** have a carbene-like reactivity. We studied on the electrophilic reactivity and carbene-like reactivity of magnesium alkylidene carbenoids **1**.



**Scheme 1.** Reactivity of magnesium alkylidene carbenoids **1**.

Magnesium alkylidene carbenoid **1a** was generated from 1-chlorovinyl *p*-tolyl sulfoxide **2a** and *i*-PrMgCl via the sulfoxide/magnesium exchange reaction (Scheme 2). Nucleophilic substitution of magnesium alkylidene carbenoid **1a** with organolithium reagents occurred at the vinylic carbon atom to give substituted alkenes **3** in 32–58% yield. Reaction mechanism of nucleophilic substitution at the vinylic carbon atom was studied by DFT calculations. Activation energy for the reaction of magnesium alkylidene carbenoid with acetylide via the 1,2-metallate rearrangement was estimated to be 20.0 kcal/mol, and it was lower than that of the S<sub>N</sub>2 reaction of chloroalkene with acetylide by 7.7 kcal/mol. When magnesium alkylidene carbenoids **1b–d** were left without organolithium reagents, 1,2-rearrangement occurred to give terminal alkynes **4** in 62–99% yield.



**Scheme 2.** Nucleophilic substitution of magnesium alkylidene carbenoid **1a** with organolithium reagents and 1,2-rearrangement of magnesium alkylidene carbenoids **1b–d**.

1) T. Kimura, *Synthesis* **2017**, 40, 3835.