

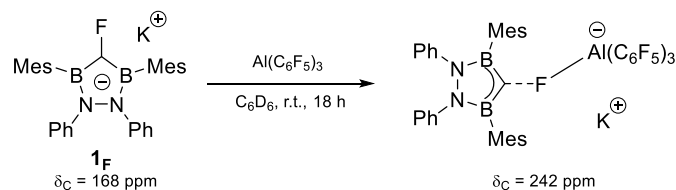
## Reactivity of diborylcarbenoid and properties as an equivalent to diborylcarbene

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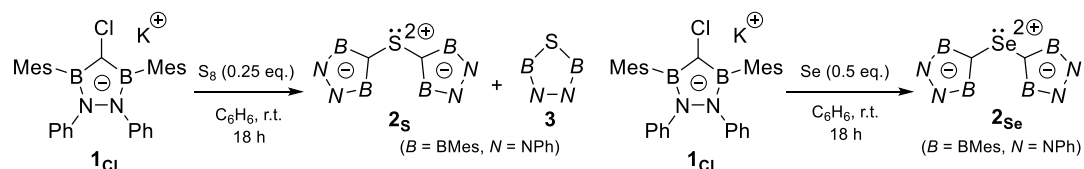
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Carbene is a neutral divalent carbon species possessing six valence electrons. Singlet carbene can exhibit both Lewis basicity and acidity. Looking at the chemistry of carbene, although various persistent carbenes have been studied, they are known to be strongly Lewis basic because they all have  $\pi$ -donating substituent(s) on the carbene carbon to stabilize the p-type vacant orbital. In a sharp contrast, diborylcarbene (DBC) where the carbene carbon is substituted by two boryl groups has long been discussed as a Lewis acidic carbene. However, its property has never been explored except for theoretical studies and trapping reactions.<sup>[1]</sup>

In this work, we synthesized K/X-diborylcarbenoids **1<sub>X</sub>** (X = F, Cl) as stable equivalents to DBC, and studied their reactivities. When **1<sub>F</sub>** reacted with Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in benzene-*d*<sub>6</sub>, the <sup>13</sup>C NMR chemical shift of the carbenoid carbon shifted from 168 ppm to 242 ppm (Scheme 1). ESI(+)-TOFMS spectrum of this reaction solution showed peaks corresponding to the DBC-proton or potassium cation adducts, which were not found in the absence of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. These observations strongly suggest the interaction between aluminum atom and fluorine atom on the carbenoid carbon. We also examined the reactivity of synthesized diborylcarbenoid **1<sub>Cl</sub>** toward elemental chalcogens (Scheme 2). When **1<sub>Cl</sub>** reacted with elemental sulfur at ambient temperature in benzene, two kinds of products **2<sub>S</sub>** and **3** were obtained. Both **2<sub>S</sub>** and **3** were characterized by single crystal X-ray diffraction analysis. Reaction of **1<sub>Cl</sub>** with elemental selenium also gave C–Ch–C type compound **2<sub>Se</sub>**.



**Scheme 1.** F atom abstraction from **1<sub>F</sub>** with Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.



**Scheme 2.** Reactions of **1<sub>Cl</sub>** with elemental chalcogens (S, Se).

[1] D. Bourissou, O. Guerret, F. P. Gabbaï, and G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.