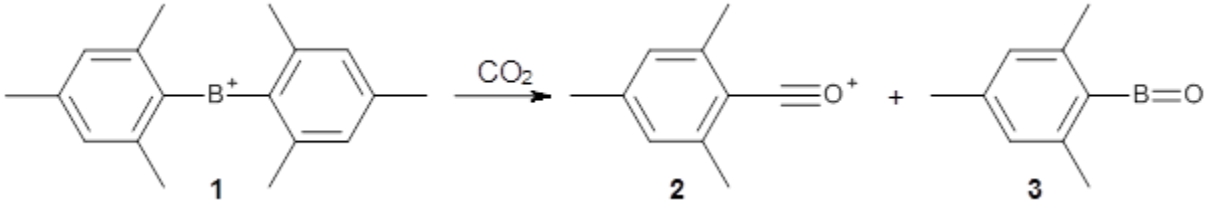
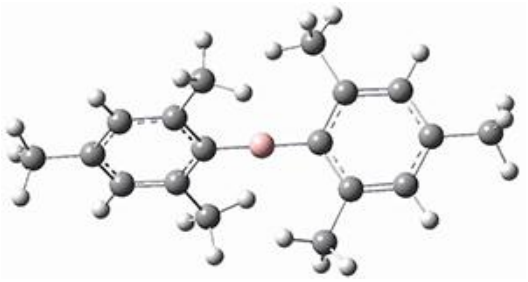
A TWO-COORDINATE BORON CATION FEATURING C–B+–C BONDING

This paper is a bit afield from the usual material I cover but this is an interesting reaction. Shoji and coworkers have prepared the two-coordinate boron species **1**,[1] and confirmed its geometry by an x-ray crystal structure. What I find interesting is its reaction with CO_2, which gives **2** and organoboranes that are not identified, though presumably derived from **3**.

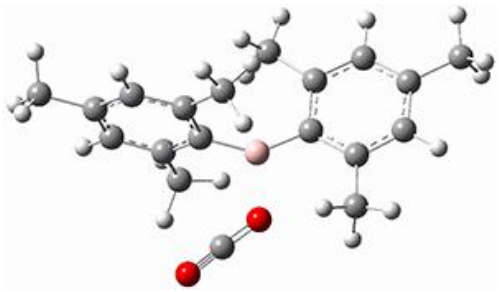


M06-2x/6-311+G(d,p) computations support a hypothetical mechanism whereby first a complex between**1** and CO_2 is formed (**CP1**), that is 4.4 kcal mol^{-1} above isolated reactants. Then passing through **TS1**, which is 4.2 kcal mol^{-1} above **CP1**, an intermediate is formed (**INT**), which is almost 6 kcal mol^{-1} below starting materials. A second transition state is then traversed (about 1 kcal mol^{-1} below starting materials), to form an exit complex between **2** and **3**, which can then separate to the final products with an overall exothermicity of 10.6 kcal mol^{-1}. The structures of these critical points are shown in Figure 1.



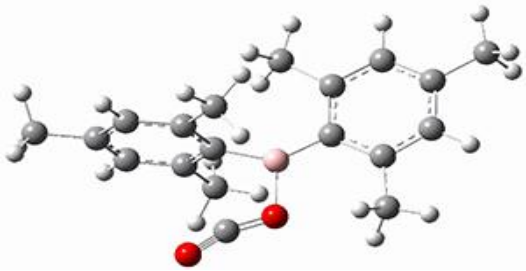
1

(0.0)



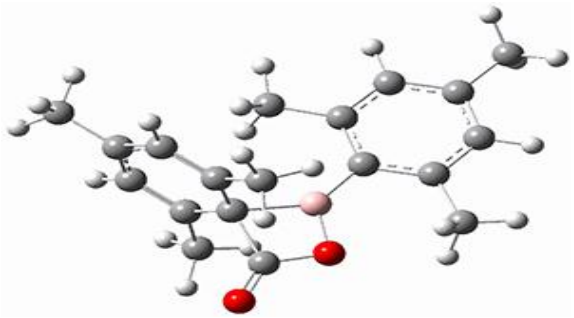
CP1

(4.4)



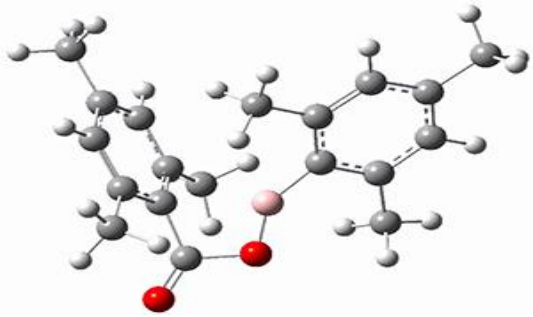
TS1

(8.6)



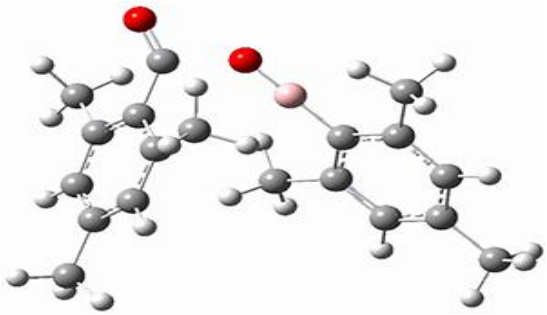
INT

(-5.7)



TS2

(-1.1)



CP2

(-9.0)

Figure 1. M06-2x/6-311+G(d,p) optimized structures. Relative energy in kcal mol^{-1}.

Source: http://www.compchemhighlights.org/2014/08/a-two-coordinate-boron-cation-featuring.html