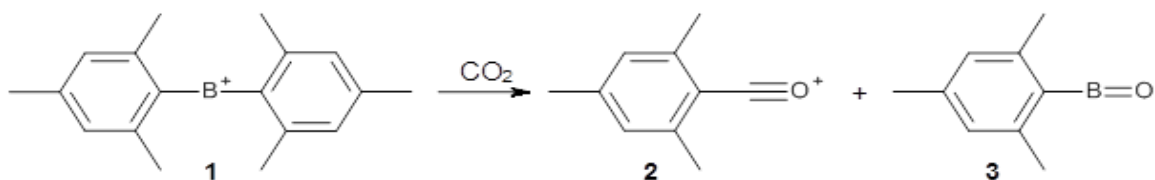


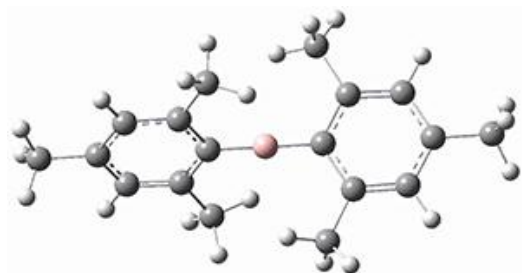
SPLITTING CO₂ WITH A TWO-COORDINATE BORON CATION

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 CO₂, which gives **2** and organoboranes that are not identified, though presumably derived from **3**.



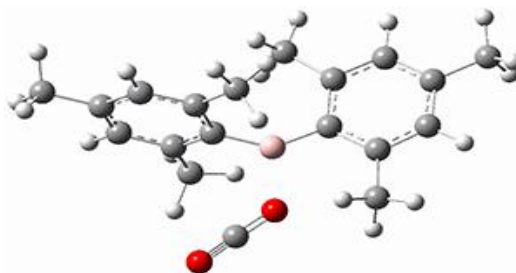
M06-2x/6-311+G(d,p) computations support a hypothetical mechanism whereby first a complex between **1** and CO₂ is formed (**CP1**), that is 4.4 kcal mol⁻¹ above isolated reactants. Then passing through **TS1**, which is 4.2 kcal mol⁻¹ above **CP1**, an intermediate is formed (**INT**), which is almost 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.



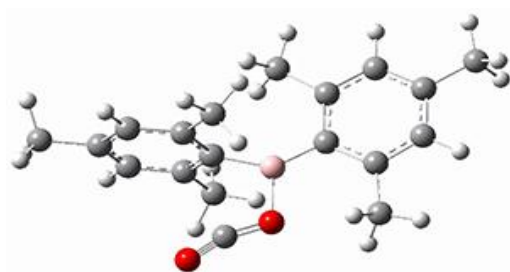
1

(0.0)



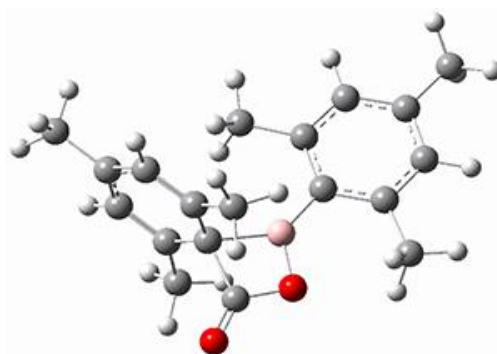
CP1

(4.4)



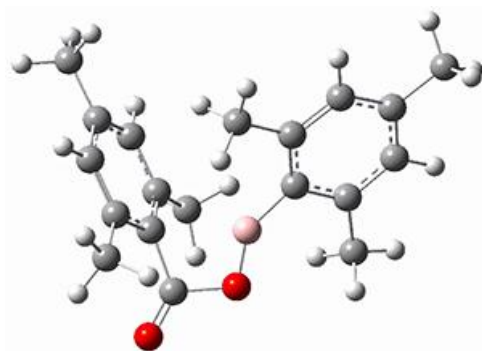
TS1

(8.6)



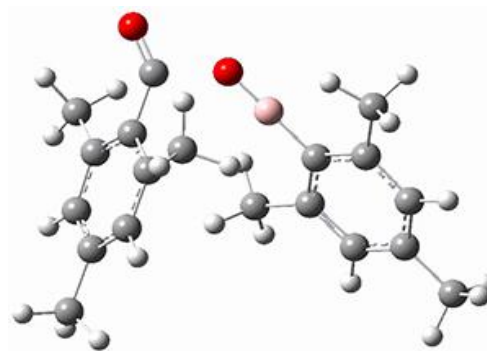
INT

(-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://comporgchem.com/blog/?p=3177>