A Computational Study of Friedel-Crafts Intermediates: RX'–MX3

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Friedel-Crafts processes are an important class of carbon-carbon bond forming reactions and among the most common involve an alkyl halide and a Lewis acid catalyst. We are interested in the intermediates of these processes, which are alkyl halide acid-base complexes: RX'–MX_3. Using a variety of computational methods (ω-B97X-D/aug-cc-pVTZ preferred) we obtained equilibrium structures and binding energies for RX'–MX_3 compounds where R = CH_3; M = B, Al, or Ga; and X = F or Cl. We considered four distinct conformations for each complex, with the conformation shown below consistently being the most stable. Binding energies from aluminum compounds were the most stable, followed by gallium and finally boron, which were generally weak. Using an NPA charge analysis, we assessed the charge on the R group as well as the extent of charge transfer from the R-X' group to the MX_3 group. In addition, we mapped the M-X' potential curves for several representative complexes in this family, including CH_3Cl-$AlCl_3$, CH_3F-BF_3, CH_3Cl-AlF_3, CH_3F-$AlCl_3$ via ω-B97X-D/aug-cc-pVTZ. Future work will assess the effect of dielectric media on the potential curves.

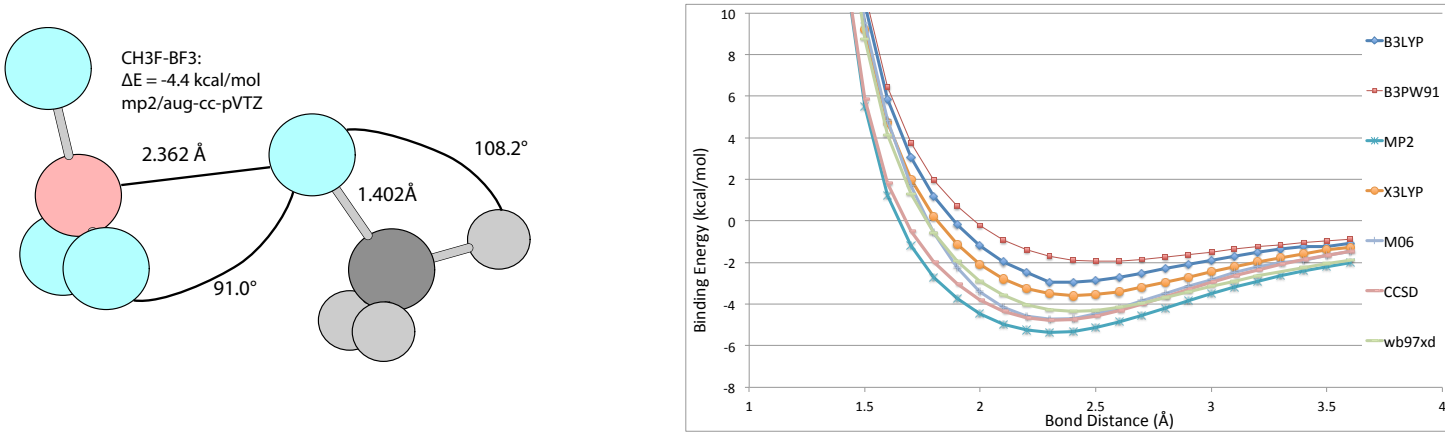

Figure 1: On left is equilibrium structure for complex CH_3F-BF_3 in the most stable conformation. On right is a curve of bond potential vs. distance for the complex using nine different methods to determine most accurate method as compared to CCSD.