# A Computational Study of Complexes Relevant to the Mechanism of the Friedel-Crafts Reaction

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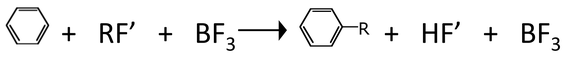
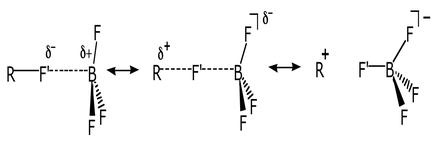
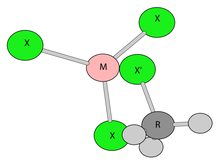
## Introduction:

- Fundamental question: What are the structural and bonding properties of the intermediates in the Friedel-Crafts[1, 2] reaction?




- Is this a weak complex or an ion pair?






- R is an organic group (e.g., $CH_3$-)
- X is a halogen (F, Cl) on M
- X' is a halogen bonded to R group
- M is a group III element (B, Al)

- **How do changes in M, X and X' affect structure and bonding intermediate?**

## Methods:

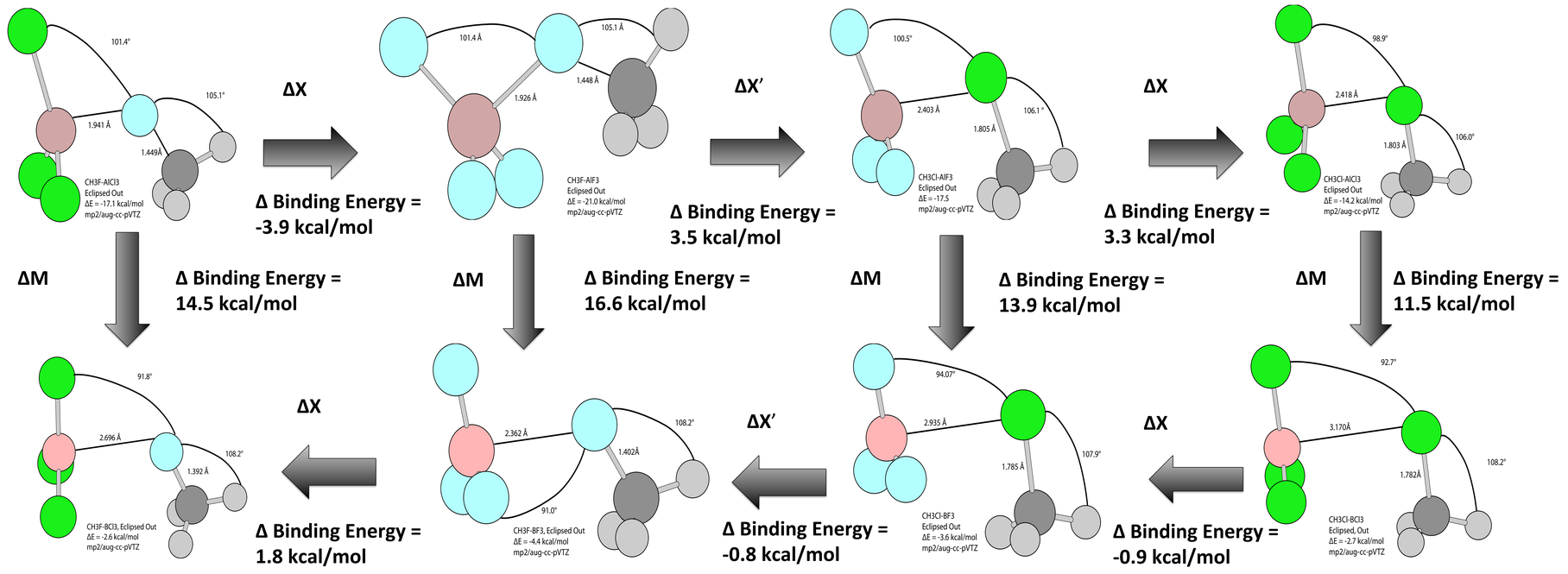
- Computational study of structural and energetic properties of RX-$MX_3$ complexes

- Gaussian 09 version B.01 was used for all computations:

- Methods: MP2, ωB97X-D, X3LYP
- Basis set: aug-cc-pVTZ

We computed

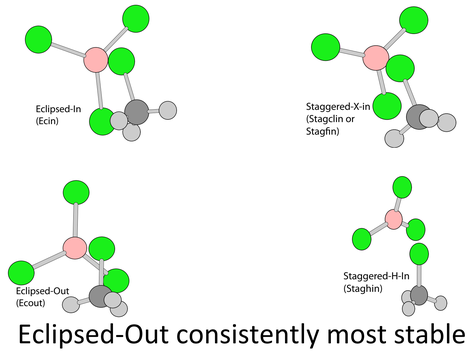
- Frequencies (freq)
- Binding energies
- Molecular structures (Opt = tight, int=ultrafine)
- Charge Distributions (pop=npa, aim=cp)




## Results:

### Conformations

- Four different conformations
- We titled them eclipsed-in, eclipsed-out, staggered- H-in, and staggered-X-in.




- Eclipsed-Out consistently most stable conformation by binding energy. (As such, all complexes in above graphic in eclipsed-out conformation.)

### Trends in Structure and Binding Energy

- Changing M atom from B to Al produces marked increase in stability
- Changing X on C from F to C decreased dative bond strength slightly
- Changing X on M from F to C also decreased dative bond strength by comparable amount

### Bonding Analysis: Charges

- Charge transfer greater for M = Al than M = B (parallels Δ E)

- Charge on R less for R-Cl compounds than for R-F compounds, part of that is due to greater electronegativity of F

| | MX3 Charge | X' Charge | R Charge |
|---|---|---|---|
| CH3Cl-AlCl3 | -0.197 | 0.025 | 0.171 |
| CH3Cl-AlF3 | -0.159 | -0.014 | 0.173 |
| CH3Cl-BCl3 | -0.013 | -0.080 | 0.092 |
| CH3Cl-BF3 | -0.016 | -0.085 | 0.101 |
| CH3F-AlCl3 | -0.109 | -0.385 | 0.493 |
| CH3F-AlF3 | -0.096 | -0.393 | 0.489 |
| CH3F-BCl3 | -0.012 | -0.376 | 0.388 |
| CH3F-BF3 | -0.022 | -0.383 | 0.405 |

## Conclusion:

- Changing M produces most dramatic change in binding energy
- Effect of changing X or X' less important to binding energy
- R-F has some carbocation character (large positive charge)

### Future Work

- Compute using larger R groups and study effects of solvents on energies
- Take low temperature liquid phase IR spectra of complexes

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## Literature Citations:

1. Knauf, R. R.; Helminiak, H. M.; Wrass, J. P.; Gallert, T. M.; Phillips, J. A.; *J. Phys. Org Chem.* **2011**. 25, 493-501.
2. Olah, G.A. *Friedel-Crafts and Related Reactions;* Wiley/Interscience: New York, 1963.