A High-Level Coupled-Cluster Study On The Substituent Effect in the H_2 Activation by Low Valent Aluminyl Anions

Nery Villegas-Escobar,[a,*] Preston R. Hoobler,[b] Alejandro Toro-Labbé,[c] Henry F. Schaefer III[d,*]

[a] *Quantum Chemistry and Molecular Modeling (QCMM) Group, Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción 4070386, Chile.*
[b] *Department of Chemistry, Covenant College, Lookout Mountain, Georgia 30750, United States*
[c] *Laboratorio de Química Teórica Computacional (QTC), Facultad de Química y de Farmacia, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, Santiago, Chile.*
[d] *Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602 USA.*

Aluminyl anions are electron-rich systems containing a low valent Al(I) center, which presents a lone electron pair and an empty-p orbital perpendicular to it. In this work, a high-level coupled-cluster study on the substituent effect in aluminyl anions toward activation of H_2 is carried out (Figure 1). Activation and reaction energies extrapolated at the complete basis set (CBS) were computed using Allen and co-workers' focal point analysis (FPA). The resulting energetics are comparable to CCSDT(Q)/CBS. Several corrections to the CBS energies were computed to get energetics with sub-chemical accuracy (<1 kcal mol^{-1}). To study the most important driving forces in the activation of H_2, a distortion/interaction model based on symmetry-adapted perturbation theory (SAPT) was performed.

The present work aims to provide a quantitative basis to discriminate the more suitable substitution and, therefore, rationally propose ligands to be used in H_2 activation applications.
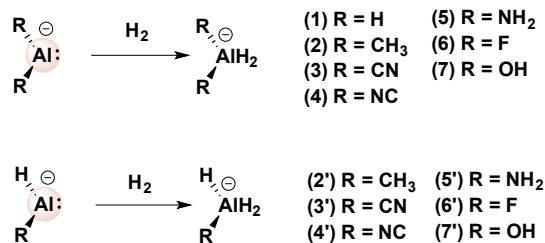
Figure 1: Reactions under consideration