The CCSD(T) Calculation of Large Transition Metal Complexes with Frontier Orbital Consistent Quantum Capping Potential Method

Yu-ya Ohnishi, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki*

Department of Molecular Engineering, Kyoto University, Kyoto, 615-8510, Japan

E-mail: Yuya.Ohnishi@t12.mbox.media.kyoto-u.ac.jp

Chemically reasonable models of PR_3 (R = Me, Et, ^{i}Pr, and ^{t}Bu) were constructed to apply the CCSD(T) method to large transition metal complexes. In this model, R is replaced with the H atom including the frontier orbital consistent quantum capping potential (FOC-QCP) which reproduces well the frontier orbital energy of PR_3. The steric effect is incorporated well by the new procedure named steric repulsion correction (SRC), which was not incorporated in the usual QM/MM methods.

To examine the performance of this FOC-QCP method with the SRC, the activation barriers and reaction energies of the reductive elimination reactions of C_2H_6 and H_2 from $M(R^1)_2(PR^2_3)_2$ (M = Ni, Pd, or Pt; R^1 = Me for R^2 = Me, Et, or ^{i}Pr, or R^1 = H for R^2 = ^{t}Bu) were evaluated with the DFT[B3PW91], MP4(SDQ), and CCSD(T) methods. The FOC-QCP method reproduced very well the DFT[B3PW91]- and MP4(SDQ)-calculated energy changes of the real complexes with PMe_3. For more bulky phosphine, the SRC is crucially important to present correct energy change, in which the MP2 method presents reliable steric repulsion correction like the CCSD(T) method because the systems calculated in the SRC do not include transition metal element.

Also, the coordination energies of CO, H_2, N_2, and C_2H_4 with a large dinuclear complex $[RhCl(P^iPr_3)_2]_2$ were theoretically calculated by the CCSD(T) method combined with the FOC-QCP and the SRC. The CCSD(T)-calculated energies agree well with the experimental ones, as shown in Figure. On the other hand, the DFT[B3PW91]-calculated energies of the real complexes considerably deviate from the experimental ones.

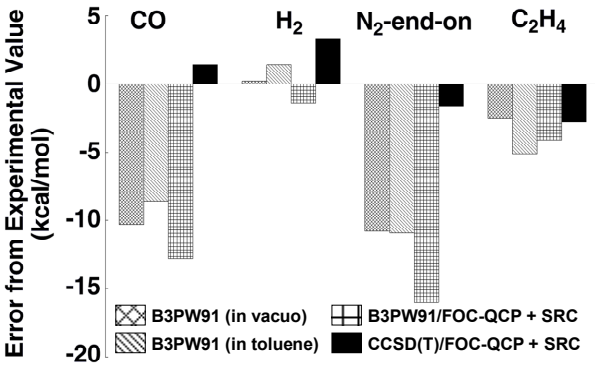

Figure. The error of the coordination energies (kcal/mol) of CO, H_2, N_2-end-on, and C_2H_4 to $[RhCl(P^iPr_3)_2]_2$ from the experimental values.