1P123 Theoretical Studies on Trimerization of Acetylene in the Presence of the Rhodium Catalysts.
The Effect of changing the Ligand

○ AbdelRahman Dahy and Nobuaki Koga

Graduate School of Human Informatics and Graduate School of Information Science,
Nagoya University

Trimerization of alkynes as a method of preparation of benzene derivatives and benzenoid structures has been studied extensively by experimentalists. Since preparation of benzene derivatives by trimerization of alkynes in presence of nickel catalyst by Reppe et at. in 1948, trimerization of alkynes takes place in presence of many transition metal catalysts such as Ti, Zr, Ta, Fe, Ru, Co, Rh, Ir, Ni and Pd catalysts. In order to understand this type of reactions and obtain more information useful in designing such reactions, we studied theoretically in a previous work the trimerization of acetylene in presence of cobalt catalyst. Also, trimerization of acetylene in presence of ruthenium catalysts was studied theoretically by Kirchner et al. and Yamamoto et al. In this work, we will present theoretically the trimerization of acetylene in presence of rhodium catalyst. Also, the effect of changing of the ligands coordinated to the rhodium atom on the reaction mechanism will be presented. The two models used for the catalyst here are CpRh and $RhCl(PH_3)_2$ and the model used for the alkyne is acetylene molecule. The method used is DFT/B3LYP with basis sets; LANL2DZ + f polarization function on rhodium atom, 6-31G** for C and H, and 6-31+G** for Cl and P. For trimerization of acetylene in presence of CpRh as a catalyst, it was found that the oxidative addition of bis(HCCH)Rh complex to rhodacyclopentadiene, **1**, takes place with the activation energy of 14.1 kcal/mol. Also, the intramolecular mechanism for the addition of the third acetylene molecule to **1** through acetylene complex **3** is more favorable compared to the intermolecular mechanism. The activation energy of 2.9 kcal/mol for the former is smaller than that of 16.8 kcal/mol for the latter. In the case of $RhCl(PH_3)_2$ as a catalyst, there are three isomers of rhodacyclopentadiene, **2a**, which formed by the direct addition of acetylene to acetylene rhodium complex, and **2b** and **2c**, formed by the oxidative addition of bis(HCCH)Rh complex. The activation energies for the formation of these three isomers are different, 33.5, 9.2 and 12.9 kcal/mol, respectively. The addition of the third acetylene molecule to **2s** passes through acetylene complexes **4a** and **4b**. The activation energies of benzene formation from **4a** and **4b** are 6.3 and 2.7 kcal/mol, respectively. In the case of the CpRh as a catalyst, the coordination energy for the acetylene to **1** is 26.3 kcal/mol, while that for coordination of acetylene to **2c** is 20.6 kcal/mol. The coordination of acetylene to complex **2a** or **2b** to give complex **4a** is weaker (**4a** is more stable than **2a** + HCCH and **2b** + HCCH by only 3.2 and 9.7 kcal/mol) because of the differences in trans influence. Comparing the formation of benzene complex via acetylene complex **3** with that via acetylene complex **4b** shows that the formation of benzene complex via intramolecular mechanism in presence of CpRh as a catalyst is more favorable than that in the case of $RhCl(PH_3)_2$ catalyst.

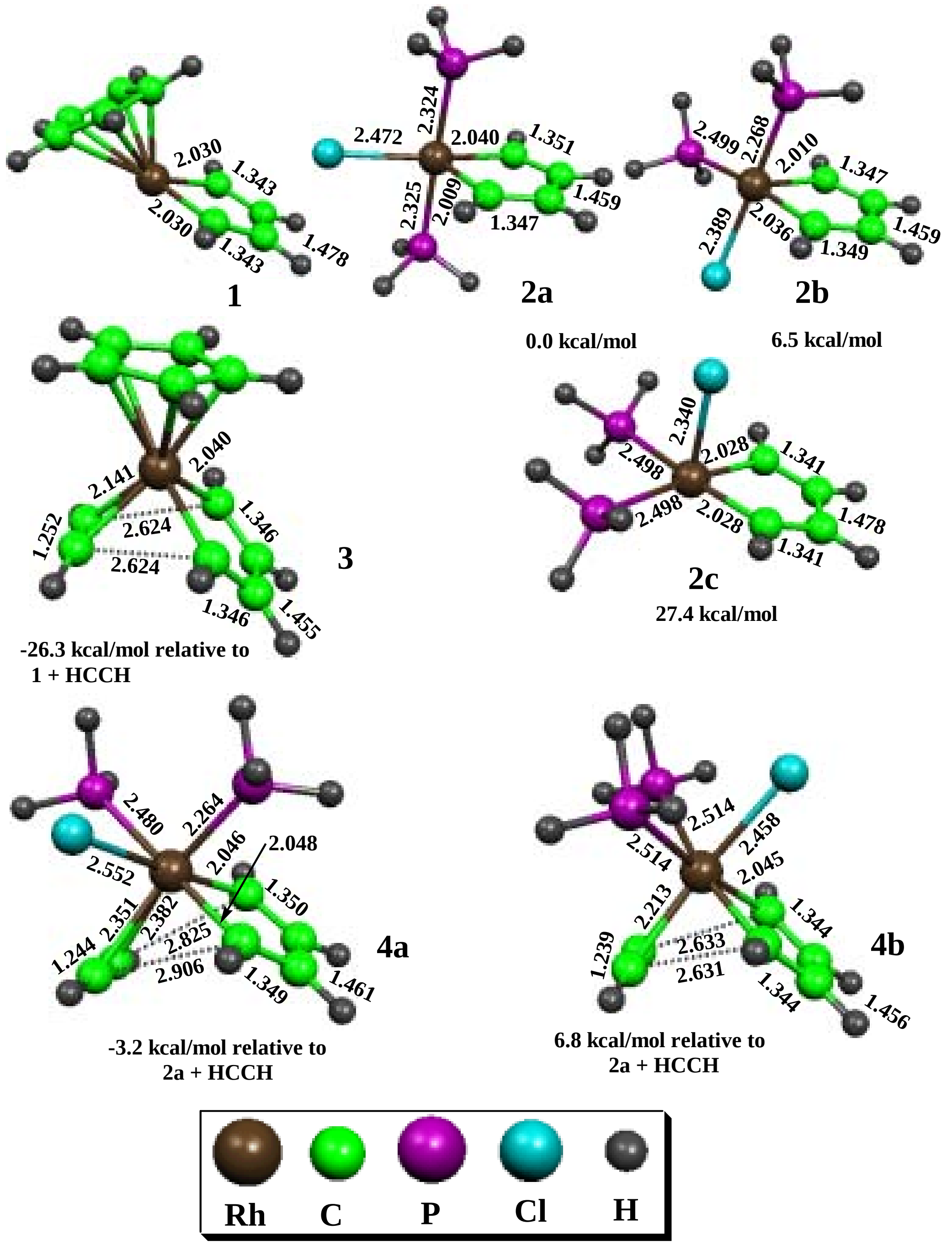

Figure 1. The optimized structures of rhodacyclopentadiene complexes, **1**, **2a**, **2b** and **2c** and those of the rhodacyclopentadiene acetylene π-complexes **3**, **4a** and **4b**. The energies of **2b** and **2c** are relative to **2a**. The energy of **3** is relative to **1** + HCCH. The energies of **4a** and **4b** are relative to **2a** + HCCH. All the energies are in kcal/mol and bond lengths are in angstroms.