Theoretical Studies on the Reaction Mechanism for Formation of Benzene Complex from Cobaltacyclopentadiene and Allene in Presence of CpCo as

a Catalyst

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Compounds containing benzene nucleus are important industrially and academically. This led many authors to prepare benzene more than 100 years ago. First substituted benzene is prepared thermally by trimerization of substituted alkynes molecules. Although this reaction is highly exothermic, its energy barrier is very high. So, this reaction needs high temperature and gives many isomers. Therefore, it has no synthetic utility. Since the preparation of substituted benzene by Reppe et al. from trimerization of alkynes in presence of nickel system as a catalyst, substituted benzenes have been prepared from trimerization of alkynes catalyzed by many transition metal systems. One of the most used transition metal systems for preparation of substituted benzene was cobalt systems. The CpCoL₂ was used as a catalyst where L = CO, PPh₃, olefins. It was found recently that the highly chemo- and regioselective substituted benzene can be prepared from metallacyclopentadiene and allene where M=Co, Ni, and Pd systems. The reaction of bisalkyne with substituted allene in presence of $CoI_2(PPh_3)_2$ as a catalyst gives only meta-isomers in good yield without the formation of ortho-isomer (cf.scheme 1).

In this work, to get more information about this reaction, we investigated theoretically the formation of substituted benzene from cobaltacyclopentadiene and allene in presence of CpCo as a catalyst according to the suggested mechanism by Cheng et al. DFT with LANL2DZ for Co, 6-31G for Cp and CH₂OCH₂ and 6-31G(d) for the rest of atoms are used to get qualitative results. We found that the formation of cobaltacyclopentadiene from propynyl butynyl ether and CpCo takes place with low energy barrier, 9.1 kcal/mol, and high exothermicity, 12.9 kcal/mol. Then, both ortho- and meta-cyclohexadiene complexes are formed by first coordination of allene in the coordination sphere of Co(III) in cobaltacyclopentadiene, then insertion into the weaker Co-C_a bond and finally cyclohexadiene complex formed according to the suggested mechanism by Cheng et al (cf. scheme 2). From the point energy profile with zero-point correction, we found the energy barriers for the rate determining step for formation of the two isomers are small. In the case of *ortho*-isomer the energy barrier was 6.1 kcal/mol, while in the case of *meta*-isomer the energy barrier was 15.3 kcal/mol. This difference in energy barriers is ascribed to the fact

that the intermediate complex in the case of meta-isomer is more stable than that in the case of ortho-isomer by 9.3 kcal/mol. So, although ortho-isomer path is favorable kinetically, thermodynamically the meta-isomer path is favorable. So, our results agree with the experimental result that the thermodynamic factor is the main factor of controlling this reaction. Also, the effect of substituted groups on allene such as methyl and phenyl groups on the reactions is studied.



-40.1 kcal/mol

Scheme 2. B3LYP results for model reactions for the mechanism proposed by Cheng et al.