

# HYDROGEN MOLECULE INTERACTION WITH $\text{CpCr}(\text{CO})_3$ CATALYST

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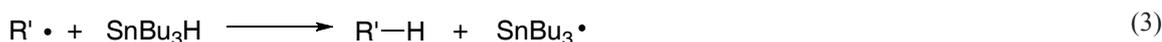
## In Memory of Ion Vatamanu For His Scientific Contributions

**Abstract.** The hydrogen molecule interaction with  $\text{CpCr}(\text{CO})_3$  catalyst has been studied using the B3LYP, B86 functionals and the 6-311++G\*\*, LACV3P basis sets. The best results in the testing calculations of the analyzed reaction have been obtained by using the B86/6-311++G\*\* DFT version giving quite good agreement between experimental and theoretical calculated enthalpies. The dispersion corrected DFT Grimme's and Head-Gordon and coworkers' functionals have been attempted without any improvement of the results. The free energies of the initial reactants, transition states, intermediate compounds and final products of the typical six-ring bond modification mechanism have been calculated. The energy barriers of the reaction pathways are too high in the DFT approximation.

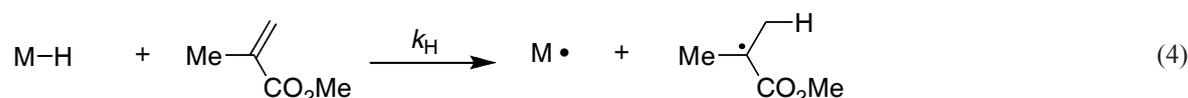
**Keywords:** catalysis, electronic structure, DFT methods, reaction mechanisms

### Introduction

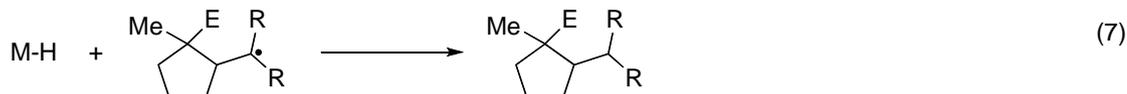
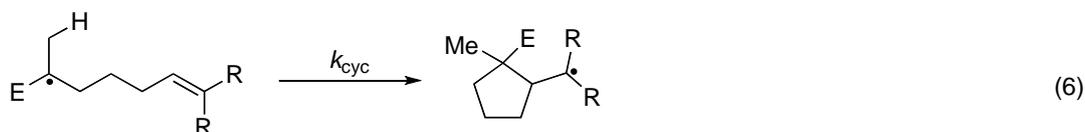
The H• transfer between metallo-hydrides and organic substrates is essential for the catalysis of chain transfer during radical polymerization<sup>1-6</sup>. Such hydrogen radical transfer is commonly used for radical cyclization compounds preparation as a first step in the modeled polymerization process. Moreover, they are often included in reaction cascades for assembling many natural products<sup>5-10</sup>. However, a major limitation of radical chemistry, which has prevented its use on an industrial scale<sup>11-14</sup> has been its reliance on trialkyltin hydrides. In a typical cyclization a tin radical generates the organic radical  $\text{R}\cdot$  by abstracting  $\text{Br}\cdot$  (eq 1) or its equivalent,  $\text{R}\cdot$  cyclizes to  $\text{R}'\cdot$  (eq 2), and  $\text{R}'\cdot$  abstracts  $\text{H}\cdot$  from the tin hydride to regenerate the tin radical (eq 3).



Special procedures are required to handle, remove, and discard the tin reagents (which are toxic). Standard purification techniques often leave levels of tin in the final product that are still toxic, precluding the use of tin-based radical reactions in the production of pharmaceuticals. The problems associated with trialkyltin hydrides have given rise to publications with such titles as "Flight from the Tyranny of Tin".<sup>12</sup> Furthermore, such reactions are stoichiometric not only in tin but in the other heavy element (bromine in eq 1, iodine or sulfur – or selenium-containing moieties in related reactions) abstracted by the tin to generate  $\text{R}\cdot$ . Considerable waste is thus generated, i.e., the "atom economy"<sup>15,16</sup> of  $\text{Bu}_3\text{SnH}$ -based methods for generating radicals is poor. The importance of finding a way to generate radicals without tin is demonstrated by the number of alternatives to the stoichiometric use of  $\text{Bu}_3\text{SnH}$  that have been published<sup>13</sup>. Studer has remarked that "transition metal based hydrides are promising alternatives to the tin hydrides"<sup>13</sup>, and  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$  has been used for the cyclization of halo acetals<sup>17</sup>. Transition metal based hydrides are not only tin-free but catalytic, with  $\text{H}_2$  as the only stoichiometric reagent. The weak metal-hydrogen bond (usually between 55 and 65 kcal/mol) in transition-metal hydrides allows the generation of radicals by the transfer of  $\text{H}\cdot$  to alkenes, eliminating the need for radical precursors that contain heavy atoms. Such  $\text{H}\cdot$  transfer reactions are already currently used in the catalysis of chain transfer during radical polymerizations of methyl methacrylate:



The sequence in eqs 5–8 is a schematic catalytic process involving transition metal compounds as catalysts<sup>18,19</sup>:



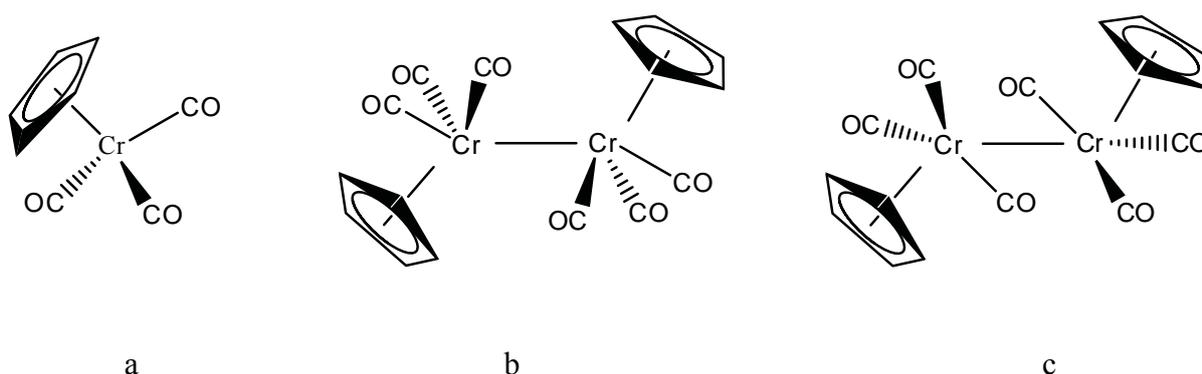
Here E is an electrophilic group and R is an aliphatic radical. Cr, V, Co transition metal compounds have been used as catalysts for the substrate hydrogenation in the last decades<sup>1-19</sup>. The weak M-H bond in the metal hydrides can make the H-radical transfer between metallo-hydrides and substrates a powerful tool in preparing hydrogen storage materials. Although, the efficiency of the above mentioned transition metal catalysts depends also on their ability to dissociate the hydrogen molecule and to give the respective hydride products. On the other hand, the primary reaction mechanism of the hydride formation is still extremely poorly known due to the insufficient number of theoretical contributions. This paper is dedicated to the electronic-structure-based study of the CpCr(CO)<sub>3</sub> catalyst interaction with molecular hydrogen.

### Computational details

Density Functional Theory, DFT, calculations were made with the 09 version of the GAUSSIAN suite of programs (Gaussian, Inc.)<sup>20</sup>. The calculations have been performed on the NCSA cluster and the CSI CUNY supercomputers. Several DFT functionals and basis sets have been used in order to find the most reliable approximation for electronic calculations of CpCr(CO)<sub>3</sub> hydrogenation. As previously found<sup>21,22</sup>, there is an equilibrium of radical-monomer CpCr(CO)<sub>3</sub> and dimer [CpCr(CO)<sub>3</sub>]<sub>2</sub> in solution (eq. 10).



Therefore, the geometry optimization of monomer-radical CpCr(CO)<sub>3</sub>• and of two dimer isomers, anti and gauche [CpCr(CO)<sub>3</sub>]<sub>2</sub>, respectively, have been performed.



**Figure 1.** Illustration for the structure of the monomer CpCr(CO)<sub>3</sub>• and dimer [CpCr(CO)<sub>3</sub>]<sub>2</sub> systems: a) Monomer radical CpCr(CO)<sub>3</sub>•; b) Dimer [CpCr(CO)<sub>3</sub>]<sub>2</sub> in anti configuration; c) Dimer [CpCr(CO)<sub>3</sub>]<sub>2</sub> in gauche configuration

The anti structure has an angle of 180 degrees, while the gauche structure has 60 degrees of molecule-components rotation (Fig. 1).  $\Delta H$  was chosen for comparison of the theory and the experiment. The calculated  $\Delta H$  values of reaction 10 are listed in Table 1.

Table 1

**Experimental and calculated enthalpy values (Kcal/mol) for the  $[\text{CpCr}(\text{CO})_3]_2 = 2 \text{ CpCr}(\text{CO})_3 \bullet$  dimer-monomer equilibrium**

Functional	Basis set	Theory	Experiment <sup>21</sup>	Experiment <sup>22</sup>
B3LYP	6-311++G**	-11.01	12.7	14.8
BP86	6-311++G**	11.54		
BP86	mixed(LACV3P)	10.90		

Mixed basis set (Table 1) includes LANL2DZ for Cr atom and 6-311++G\*\* for light elements and is similar but superior to LACV3P, which includes LANL2DZ for metals and 6-31G\*\* for light elements. The basis set doesn't have a serious impact on  $\Delta H$  values according to our calculations. Instead, the functional are contributing to  $\Delta H$  change in our functional and basis sets trial, as observed from Table 1. This can be explained by different exchange interaction contribution of two different functionals. The calculated values are made in vacuum and can differ somehow from the experimental one. In conclusion, one can observe that BP86 functional and 6-311++G\*\* basis set theory level give the best results and can be chosen for next steps of our calculations. The gauche  $[\text{CpCr}(\text{CO})_3]_2$  isomer concentration is less than 1% in solution, according to Boltzmann population at 298.15 K temperature, due to the higher value of the enthalpy and, therefore, of the free energy.

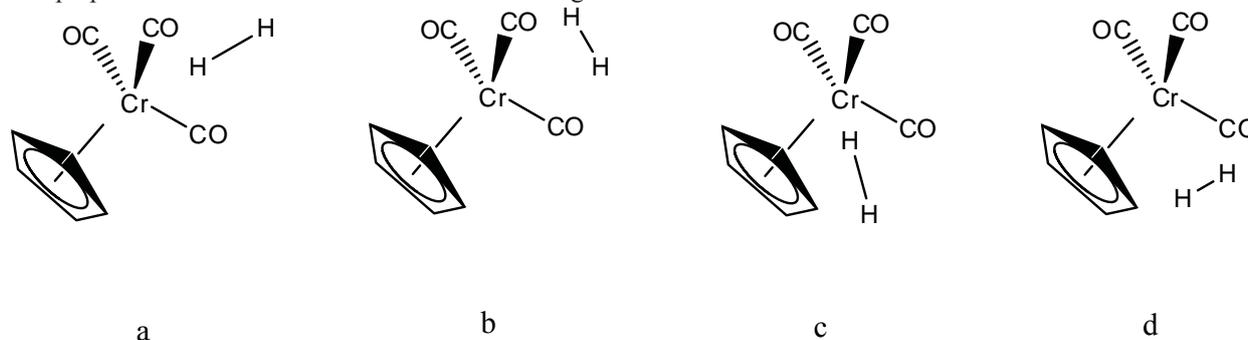
### Results and discussions

The DFT electronic structure calculations have been continued by using BP86 functional and 6-311++G\*\* basis set and has been focused on the hydrogen molecule interaction with the monomer radical system and dimer into anti and gauche structure configurations. We have, therefore, examined the enthalpy balance of eq. 9.



The geometry optimization has been performed for the reaction pathways of  $\text{H}_2$  molecule interaction with the monomer radical at the first step, since the radicals are generally more reactive. The whole analysis can be generally considered into four geometries of reaction pathways (Fig. 2):

In Fig. 2a is showing the hydrogen molecule, oriented by one of its H atoms to Cr atom of  $\text{CpCr}(\text{CO})_3 \bullet$  system, and entering in between three  $\text{Cr}-\text{C}\equiv\text{O}$  bond structures; **b** geometry configuration has the hydrogen molecule side oriented to Cr atom with two equal  $\text{Cr}-\text{H}$  distances, entering in between three  $\text{Cr}-\text{C}\equiv\text{O}$  bond structures; **c** geometry configuration of hydrogen molecule is oriented by one H atom to the Cr atom with H-H bond parallel to carbon five-member ring; **d** the approaching hydrogen molecule is side oriented to Cr, with two equal  $\text{Cr}-\text{H}$  distances and with H-H bond perpendicular to the five-member red carbon ring.



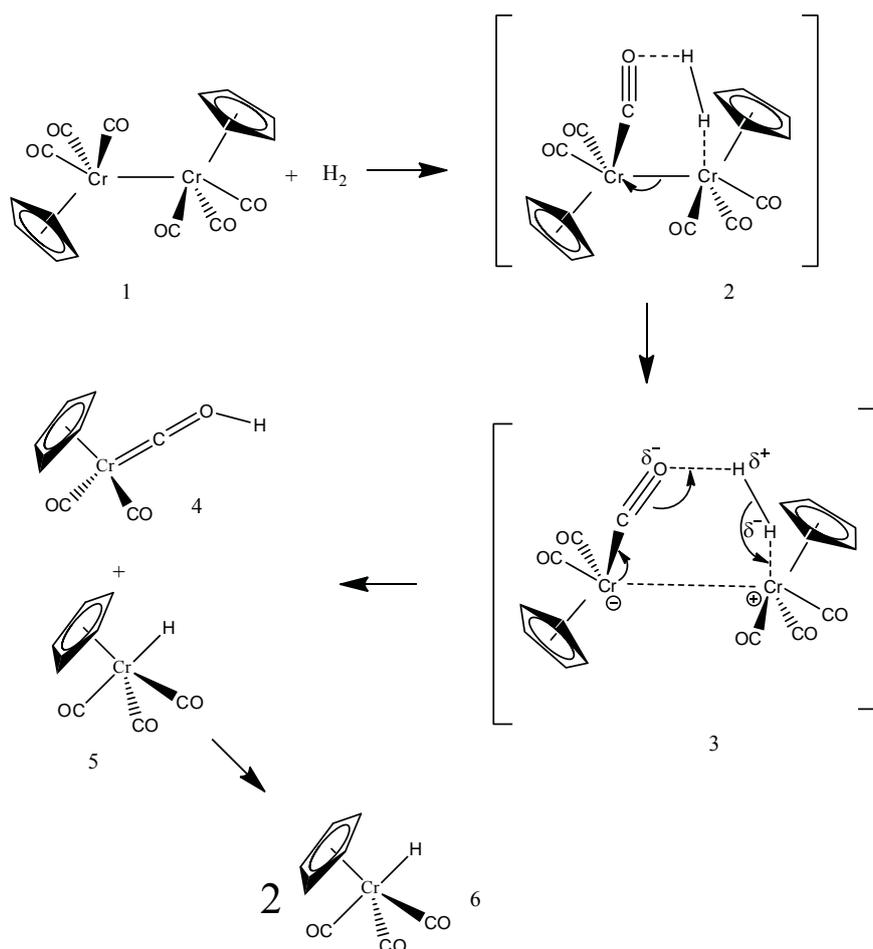
**Figure 2.** Illustration for the possible reaction pathways for  $\text{H}_2$  molecule with the  $\text{CpCr}(\text{CO})_3 \bullet$  monomer (see the text)

The reaction pathway shows the lowest uphill slope during geometry optimization process along the decreasing distances between reagents, although, without any minimum of total energy during the whole "reaction pathway". The total energy difference between the initial "infinite" distance and final distance of about 1.60 Å is equal to 1.03 eV. In conclusion, the hydrogen molecule interaction with  $\text{CpCr}(\text{CO})_3 \bullet$  radical can be excluded from consideration because of a high energy barrier (more than 2 eV for every of **a**, **b**, **d** configurations) as well as because of a lack of the total energy minimum (**c** configuration).

As above mentioned, there is a reversible equilibrium between two monomer  $\text{CpCr}(\text{CO})_3 \bullet$  radicals from one side and the two dimer isomers, anti and gauche, from another side in the solution. Therefore, the hydrogen molecule interacting with  $[\text{CpCr}(\text{CO})_3]_2$  dimer is obvious as an alternative to hydrogen molecule-monomer interaction. The contribution of hydrogen molecule interaction with gauche structure of the dimer is too low to be considered from two points of view: a) Its concentration is less than 1% in solution compared to anti; b) The energy barrier found by us for hydrogen molecule interacting with this isomer is about 1.5 times larger compared to the energy barrier in the case

of hydrogen molecule interacting with the anti system. Therefore, two factors show the negligible share of the gauche system participation in the hydrogenation reaction.

An exhaustive number of attempts have been performed for modeling the hydrogen molecule anti-dimer  $[\text{CpCr}(\text{CO})_3]_2$  molecule interaction with an exhaustive number of various geometry configurations. Two different reaction pathways lead to hydrogen molecule dissociation and the reform to the metal complex hydride products. The first reaction pathway with the higher comparative energy barrier is the absorption of hydrogen molecule during the reaction geometry, when the H-H bond line is moved inside, toward Cr-Cr bond line, in parallel fashion. The hydrogen molecule starts dissociating at a distance of about 2.55 Å from the Cr atoms and when reaching this distance the hydrogen atoms are absorbed irreparably into dimer space until a hydride compound is formed. The distance Cr-Cr dramatically increases under influence of the hydrogen molecule absorption from 3.27 Å to 6.19 Å in an intermediate hydride structure. While the H-H distance increases from 0.74 Å to 3.24 Å in the same intermediate hydride system, proving that the hydrogen molecule has been dissociated. It is interesting to mention that the intermediate compound has the negligible gain of energy of about 1.5 Kcal/mol or 0.065 eV when compared to separate monomers. Evidently, such an unstable intermediate structure cannot be observed at standard condition in solutions, on the one hand, and is situated in the generally accepted error range of DFT methods, on the other hand. The difference between the total energy of the intermediate hydride and the total energy of the initial structures, when hydrogen molecule and dimer catalyst are separated at "infinite" distances, is equal to -10.9 kcal/mol. This shows that the reaction is energetically convenient. The Cr-H bond in both cases, e.g., in the intermediate hydride structure and monomer hydrides, is equal to about 1.59 Å; however, the reaction between  $\text{H}_2$  and a Cr-Cr bond is forbidden if it occurs with, and preserves,  $C_{2v}$  symmetry.<sup>23</sup> (The classic example of such a forbidden reaction is that between  $\text{H}_2$  and  $\text{I}_2$ ). Although neither of the two conformers of  $[\text{CpCr}(\text{CO})_3]_2$  in solution (anti and gauche) has  $C_{2v}$  symmetry, it seems unlikely that the Cr-Cr bond of any conformer can react with  $\text{H}_2$  in such a way, since it shows a relative large barrier of 1.29 eV.

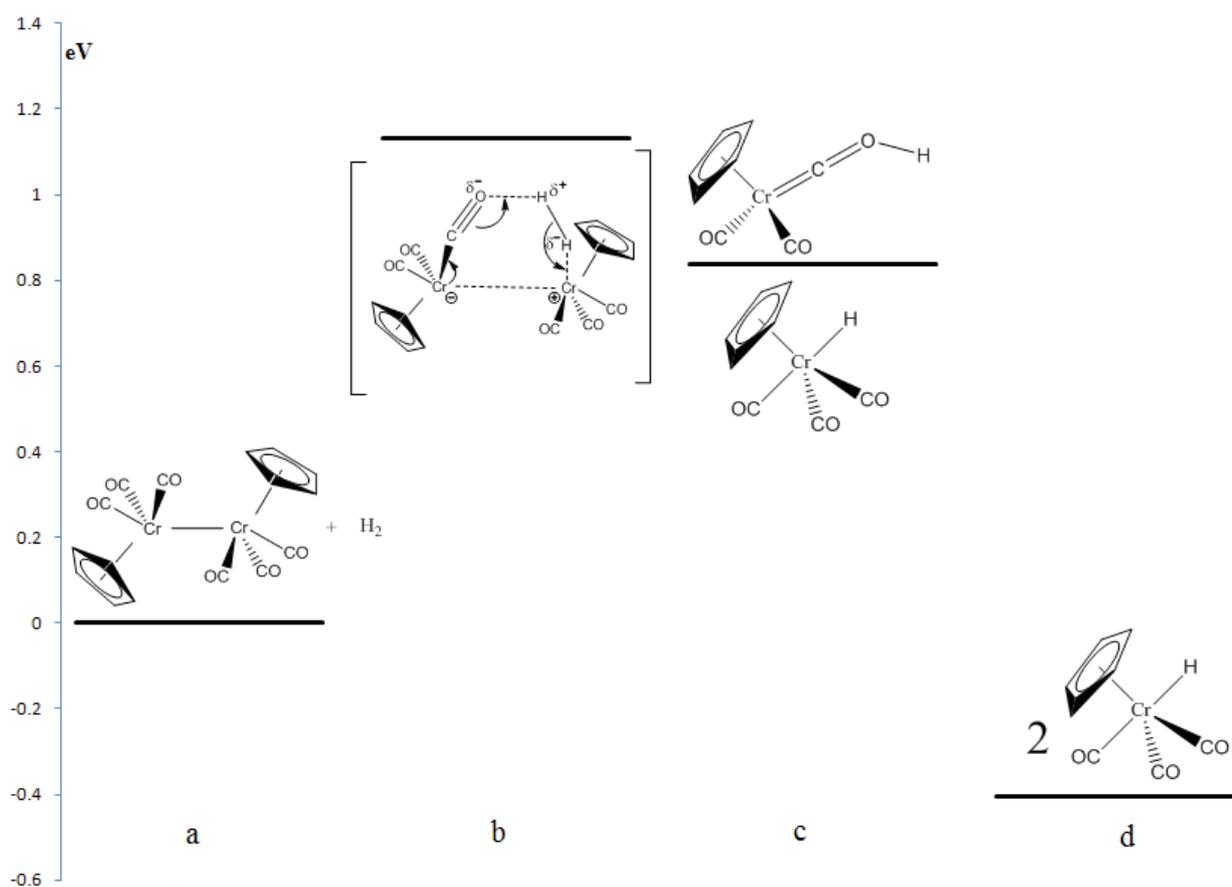


The second reaction pathway with the final hydrogen molecule dissociation during the geometry optimization is the  $\text{H}_2$  molecule moving toward one of the chromium centers. As in the previous case, the distance Cr-Cr is dramatically increased under influence of the hydrogen molecule absorption up to 6.29 Å. The hydrogen molecule is polarized between one Cr atom and one O atom and gradually dissociates. The energy barrier for such a reaction pathway is equal

to about 1.09 eV or about 25 Kcal/mol, and is lower than the previously found energy barrier for the first reaction pathway. We consider the heterolytic cleavage of H-H bond to be more acceptable for this reaction since it gives a lower energy barrier and since such a mechanism is more common for hydrogen molecule dissociation by metal complexes. The mechanism, which can be inferred from our calculations includes the formation of a six-member ring (-Cr-Cr-H-H-O-C-) at the first stage, followed by stepwise electron transfers (see below), plus the respective process of H-H bond cleavage, C≡O bond modification and formation of two new Cr-H and O-H bonds:

The  $\ominus$  sign shows the position, where the extra-electron is temporary situated and doesn't mean the charge of the atom, while the  $\oplus$  sign shows the position, from where the electron has been removed. Two chromium atoms in the transition state 3 have Mulliken charges equal to about +2 and +4, respectively. The  $\text{Cp}(\text{CO})_2\text{CrCOH}$  (4) intermediate compound undergoes the rearrangement, transferring the hydrogen atom to metal atom or to another  $\text{Cp}(\text{CO})_3\text{Cr}$  radical, since the  $\text{Cp}(\text{CO})_3\text{CrH}$  (5, 6) system is lower in energy by about 1.19 eV (see Fig. 3), comparing to  $\text{Cp}(\text{CO})_2\text{CrCOH}$  (4) system.

The above described analysis of two reaction pathways show, that the energy barrier is too high for a thermal reaction. The dispersion corrected DFT Grimme's and Head-Gordon and coworkers functionals<sup>20</sup> have been tried, therefore, to recalculate the above mentioned transition states together with the initial reagents and final products. However, such improved DFT approximation does not lower the energy barrier for the analyzed here reaction, according to our calculation data.



**Figure 3.** The relative total energies of the reaction components: a) Initial compounds; b) Transition state; c) Intermediate compounds; d) Final products.

## Conclusions

The B86/6-311++G\*\* DFT approximation lead to the best agreement between experimental and calculated enthalpy of the  $[\text{CpCr}(\text{CO})_3]_2 = 2\text{CpCr}(\text{CO})_3\cdot$  dimer-monomer equilibrium. The DFT calculations with the chosen functional and basis set show, that the hydrogen molecule doesn't interact with  $\text{Cp}(\text{CO})_3\text{Cr}$  radical, since the  $\text{Cp}(\text{CO})_3\text{CrH}_2$  system has a significantly higher free energy comparing to initial compounds. Instead, it is showing a convenient free energy value of the hydride formation reaction and, therefore, is interacting with  $[\text{CpCr}(\text{CO})_3]_2$  anti isomer. The homolytic hydrogen molecule dissociation by anti isomer lead to the two  $\text{CpCr}(\text{CO})_3\text{H}$  hydride molecules with significant gains in free energy, while the heterolytic cleavage of the hydrogen molecule leads to the intermediates compounds, which undergo internal rearrangement to the same final products. The full mechanism can be, therefore, drawn; however,

the still too large energy barrier suggests, that DFT approximation is not adequate for calculating energy barriers for catalytic processes with transition states of the reaction, accompanied by bond cleavage and new bond formation due to its limitations<sup>24</sup>. A multi-reference method then might be necessary for the calculation of such reactions.

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