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A Comparative Study of the Carbonyl Positioning Mechanism in the Mn (CO) 5 CH2F and Mn (CO) 5CHF2 Complex through Quantum Chemistry

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Abstract

In this study, quantum computation was performed by density functional theory (DFT) on carbon monoxide CO placement in Mn (CO) 5CH2F and Mn (CO) 5CHF2 complexes, and all structures were geometric optimization and the CO deposition mechanism in different states on They were evaluated. The pathway for locating the reaction in both complexes was through the migration mechanism of the alkyl group. The initial complex will have four different paths to reach the product.

The computational result shows that a path is preferable to other paths, which is attributed to spatial and electron effects

Keywords: Mn (CO) 5CH2F, Reaction Reaction, DFT, Mn (CO) 5CHF2.

1. Introduction

A placement reaction involves the placement of a ligand (typically unsaturated) in the transplant [1], a metal-ligand in a complex. As shown in Scheme (1-1) and (1-2) [2], there are two main types of placement reaction. One placement of 1,1 [3] in which the metal and ligand X are attached to an atom of the ligand of type L (a 2e ^ ligand - such as CO) represented as A = B [4] and the other is the placement 2.1 [5] in which the metal and X ligand are placed on adjacent atoms in this type of ligand (such as C2H4) [6]. In this paper, the CO placement in the Mn (CO) 5X complex (X = CHF2, CH2F) is studied based on the migration mechanism [7] of the alkyl group [8].

Fig (1). Response Placement 1.1

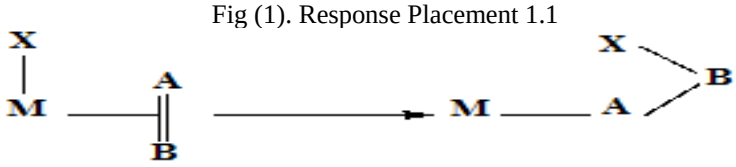


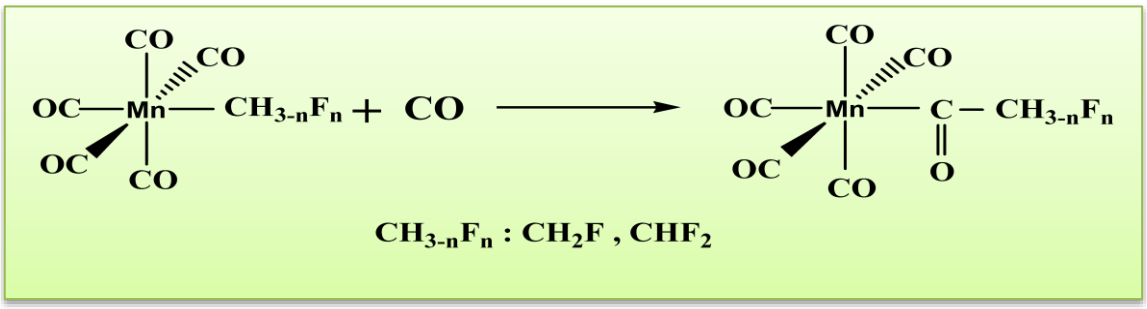
Fig (2). Response Placement 1.2

2 .Computational method

All calculations were performed using Gaussian software 03 [9]. The calculations have been used for all interfaces and transition states using the functional density theory (DFT) with three applied parameters (B3) plus Lee, Young, and Par (LYP). For all standard series atoms 6-31G has been used and for the central metal atom, LANL2DZ has been used.

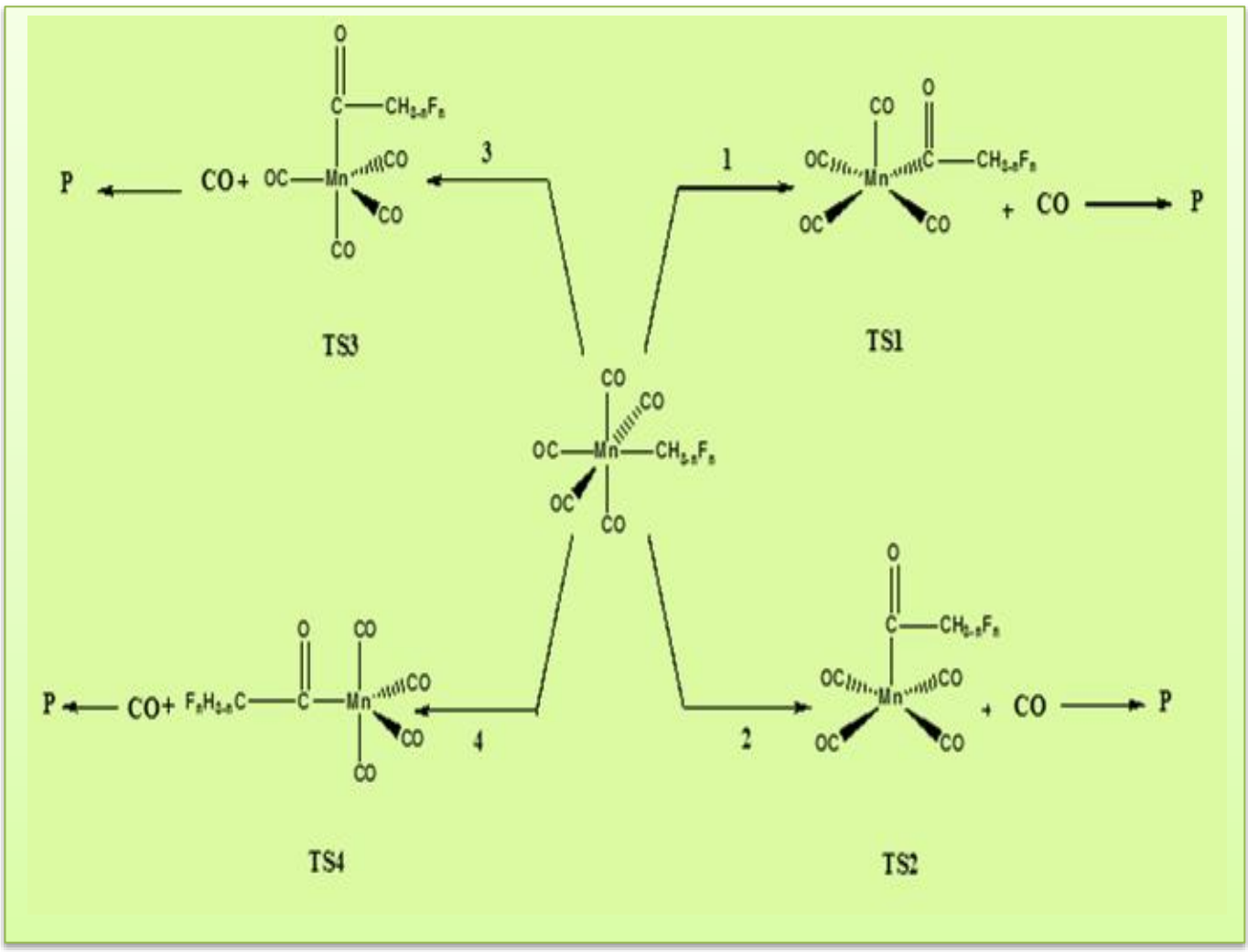
3. Job description and calculations:

In the following sections, the carbon monoxide CO positioning in the metal-alkaline bond, which is an example of the placement-removal reaction of the ligand, is discussed. This reaction is a key step in some catalytic processes. The placement will take place so that after completion of the process, CO is introduced into the metal-alkaline bond. The CO reaction with the complexes studied in this research work Mn (CO) 5X (X = CHF2, CH2F) is an indicator of the carbonyl position.



Schema (3) Carbonyl Positioning Response

If we only consider the reaction equation, it may be assumed that CO is directly related to the Mn-CH3-nFn bond, such a view is entirely in line with the name CO (CO), but other mechanisms with the same stoichiometry For other input ligands other than CO. In this paper, the results of initial quantum mechanics methods were evaluated to evaluate carbonyl residue reaction in Mn (CO) 5CH2F and Mn (CO) 5CHF2. Energy is calculated and structural parameters and results are obtained using the methods mentioned in the tables. In this reaction, a reactive species reacts with CO and CO is produced by CO. Carbon monoxide shows a great tendency to be placed on a metal-alkaline bond. The reaction of the reactive species begins with Mn (CO) 5CH3-nFn. In the reagent, manganese has a quasi-octagonal makeup, and manganese metal in the composition has an electron d6 arrangement and six corundum. This composition has 18 electrons. In the first-order placement reaction, the migration of the methyl group to the CO group at the position of the Cis is faster and more reversible. In this migration, the Acyl group is formed and an intermediate 5 Curtain that can have a triangular borehole structure (TBP) and a square pyramid, which has an empty site for entering the CO. In the next step, the CO enters the empty site and produces the Mn (CO) 5COCH3-nFn product.



In Scheme 2, four paths are proposed to examine the mechanism. This reaction has been investigated with the interfaces of the square pyramid and the two pyramidal triangles, in which each of these structures was considered as substrates in two tropical and axial positions.

4. Directions Examined Reactions:

Route number 1:

The reaction of the reactor Mn (CO) 5CH3-nFn begins and goes toward the TS1 transition state; the migration of the CH3-nFn group occurs on one of the carbonyls located in the Cis position relative to the alkyl group and the group CH3-nFn CO-forming. During this migration, the TS1 transition mode, which has an appropriate CO space entry point, is formed. This intermediate has a square pyramid structure, in which the acyl group is in a tropical position.

In the next step, the CO enters the space and the product Mn (CO) 5COCH3-nFn is obtained.

Route No. 2:

This reaction is in accordance with the mechanism of path number 1 and goes towards the TS2 transition state, and like the pre-intermediate path has a quadrilateral pyramid structure, with the

difference that the acyl group is in a pivotal position. This route also gives us the Mn (CO) 5COCH3-nFn product line 1.

Route No. 3:

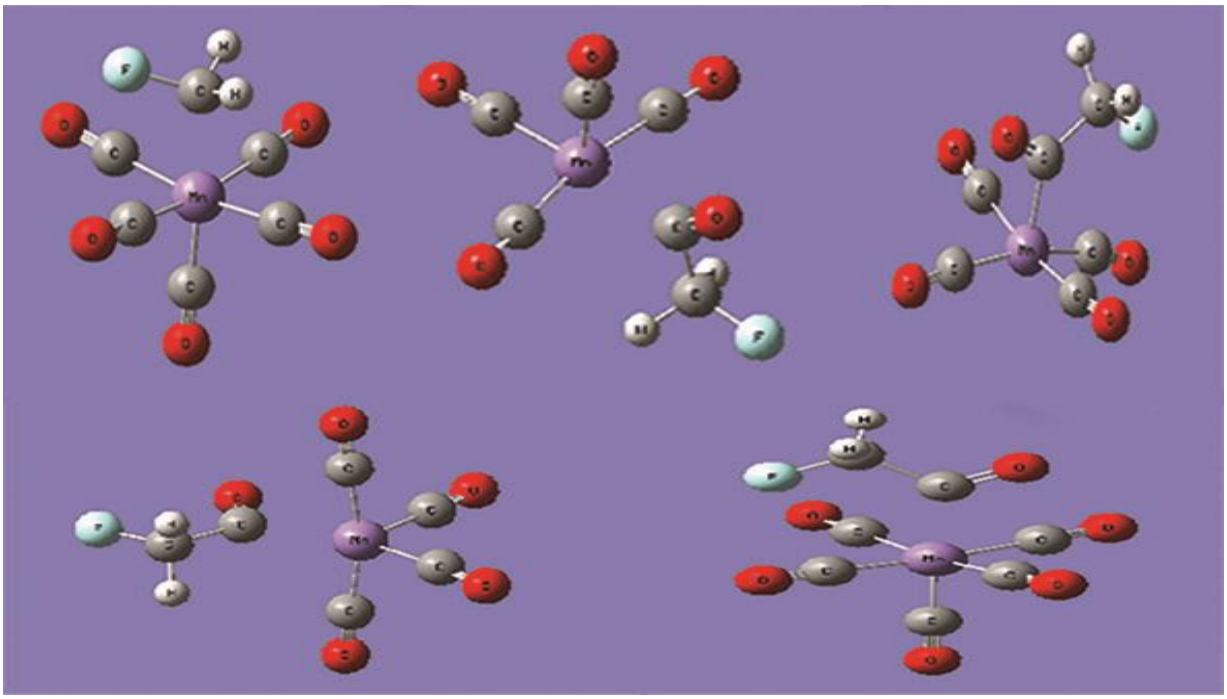
This path starts at the same path as the above mentioned reactor and goes on to the TS3 transition state, and it should be noted that the TS3 has two triangular pyramidal structures and the acyl group is located in a pivotal position.

Route No. 4:

The path to this transition towards the TS4 transition mode has a transition mode with a two-pronged triangular pyramidal structure and the acyl group is in a tropical position. It should be noted that in all of the studies, the path No. 3, which was preceded by the TS3 transition, was removed due to spatial and electron effects, and these structures changed to the TS4 direction.

5. Discussion on the results.

In this research, all the basic structures, interfaces and products are optimized. Calculations that include zero point energy (ZPE), the total calculated energy (E0) and electron energy (Eele), which are arranged in tables and charts.



The schema (3) of the optimized shape of the molecules is from the upper left: Reactor, TS1, TS2, TS4 and product for Mn (CO) 5CH2F

Table 1 shows the total calculated energy (E0), zero point energy (ZPE) and electron energy (Eele) for Mn (CO) 5CH2F

B3LYP/6-31G			
Kcal/mol / $Mn(CO)_5CH_2F$	ZPE	E_{ele}	E_0
react	45.89168883	-508124.0281	-508078.1364
CO	3.15763032	-71102.81610705	-71099.65847673
TS1	45.64946997	-508097.6332	-508051.9837
TS2	45.89419887	-508100.2649	-508054.3707
TS4	45.39219087	-508095.5266	-508050.1344
P	51.81663825	-5792422.237	-579190.207

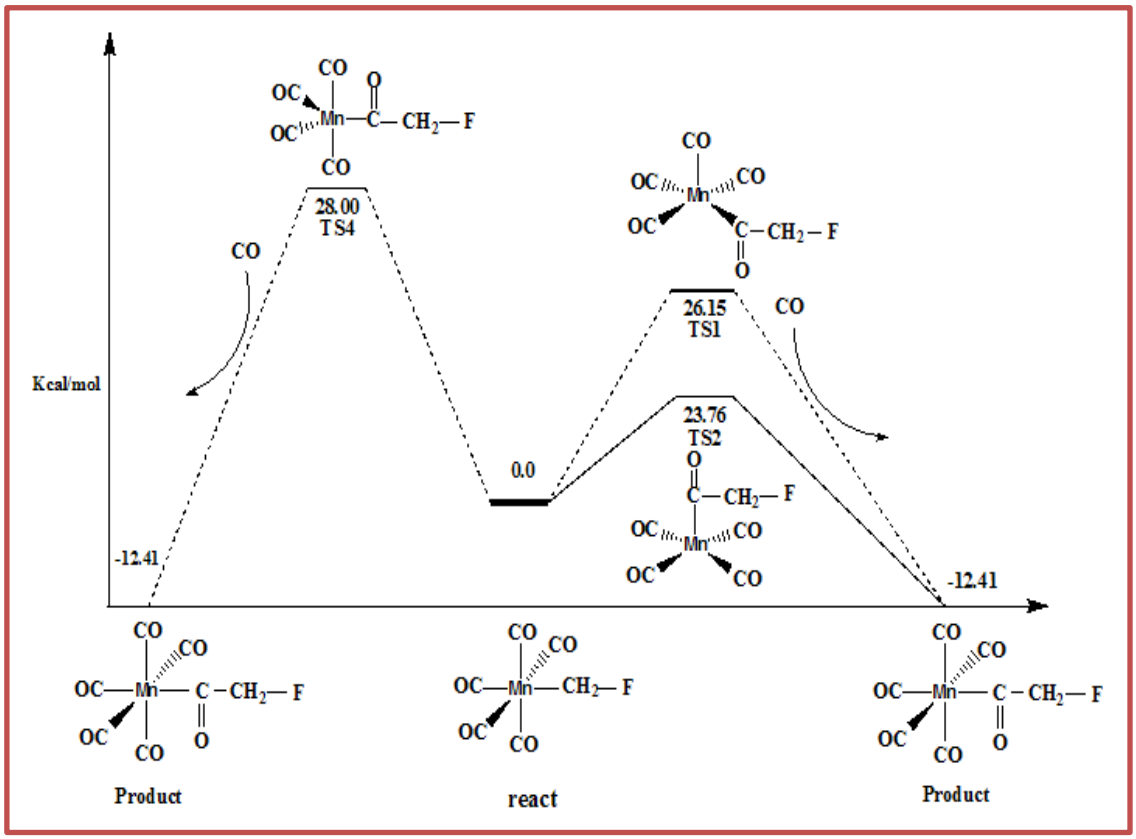
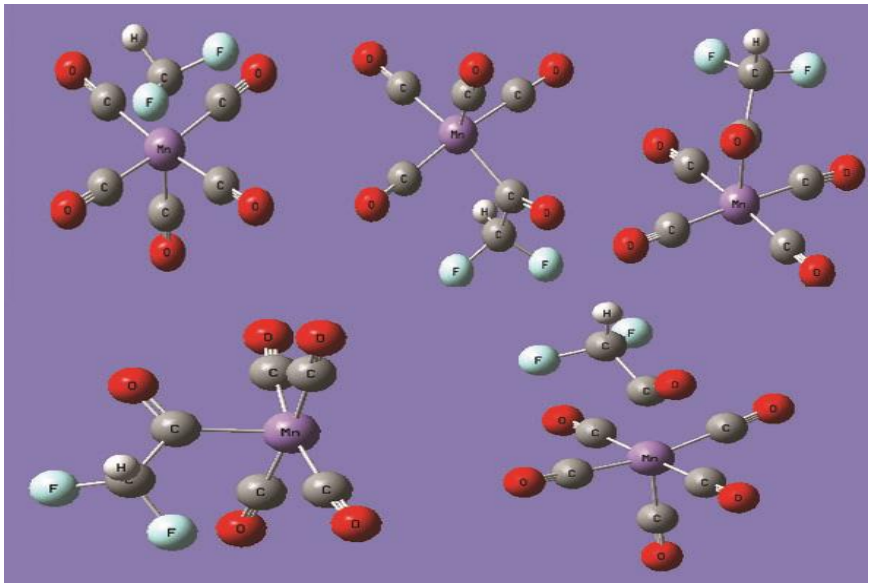


Figure (1) Chart ΔE The migration-migration of CO in the Mn (CO) 5CH2F complex in terms of (kcal / mol)

The high energy graph has three paths. In the path where the TS4 with the formula Mn (CO) 5CH2F is two triangular pyramidal (TBP), the energy (Kcal / mol) is 28. On other paths TS1 and TS2 with the closed formula above, there is a square pyramid structure that is located on the plate TS1 in the plate and in TS2 in

the axial position, which has an energy of 26.25 Kcal / mol and 23.76 Kcal / mol respectively are. In all three ways, the product produced Mn (CO) 5COCH2F, which has an octahedral structure with energy (Kcal / mol) of 12.41. With regard to the energies mentioned and calculated, the path in which the medium is in the form of a square pyramid and the pivot point in the axial position (TS2) has the lowest energy, so the energy barrier is less in this reaction, and it can be concluded that this The route is thermodynamically preferred to the TS1 and TS4 paths [10].



The schema (4) of the optimized shape of the molecules is from the upper left: Reactor, TS1, TS2, TS4 and product for Mn (CO) 5CHF2

Table 2 shows the total calculated energy (E0), zero point energy (ZPE) and electron energy (Eele) for Mn (CO) 5CHF2

B3LYP/6-31G			
Kcal/mol $Mn(CO)_5CHF_2$	**ZPE**	**E_{ele}**	**E_0**
react	**41.03413392**	**-570400.49**	**-570359.4558**
CO	**3.15763032**	**-71102.81610705**	**-71099.65847673**
TS1	**40.8885516**	**-570371.6477**	**-570330.7592**
TS2	**41.16528351**	**-570372.9555**	**-570331.7902**
TS4	**41.039154**	**-570371.4375**	**-570330.3984**
P	**47.12286345**	**-641516.4248**	**-641469.3019**

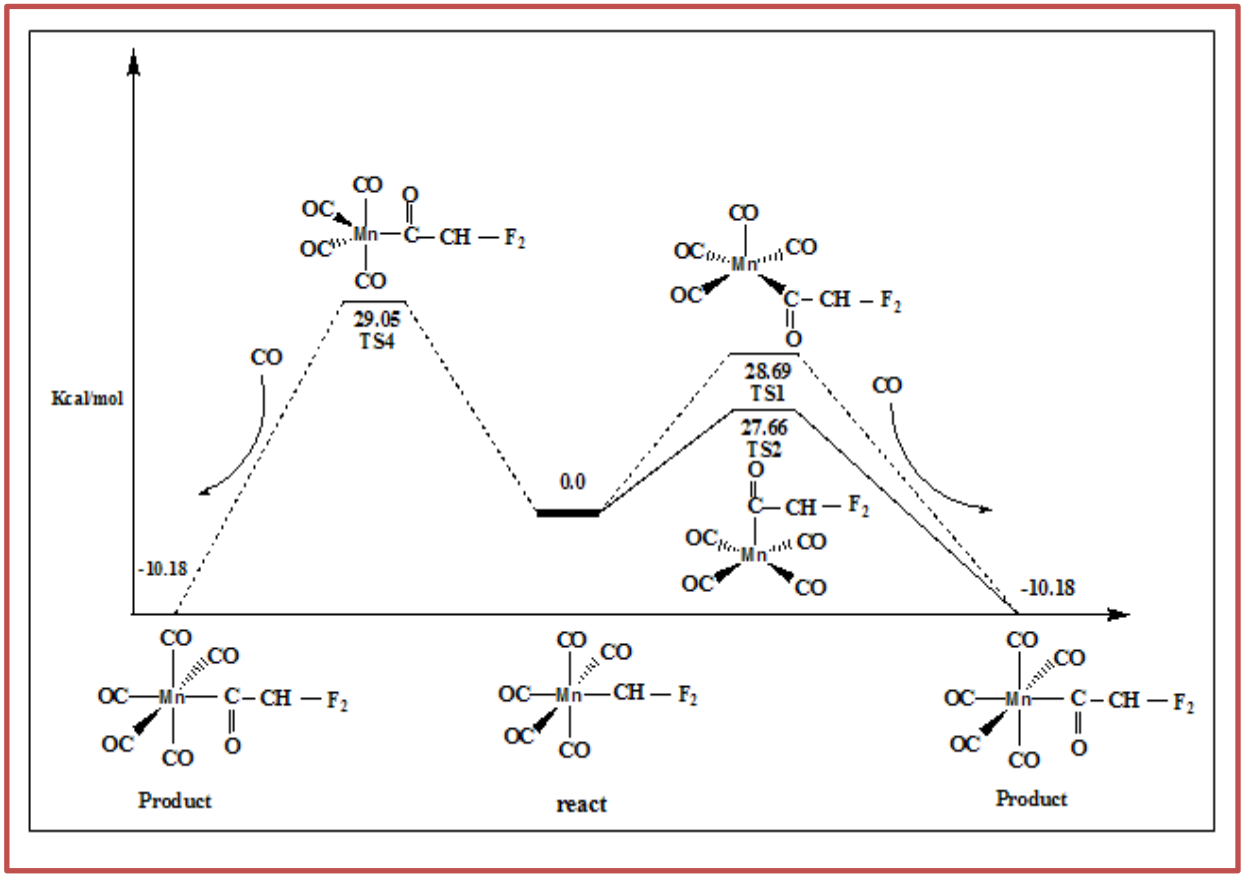


Figure (2) Graph ΔE of the CO-migration reaction in the Mn (CO) 5CHF2 complex in (kcal / mol)

The energy diagram in this reaction also has three paths. In the path where TS4 with the formula Mn (CO) 5CHF2 is two triangular pyramidal (TBP) energy (Kcal / mol) is 29.05. On other paths TS1 and TS2 with the closed formula above, there is a square pyramid structure that is in PS1 on the plate and in TS2 in the axial position, which has an energy of 28.69 Kcal / mol and 27.66 Kcal / mol respectively Are. On all three routes, the product produced Mn (CO) 5COCHF2, which has an octahedral structure with energy (Kcal / mol) of 10.18. With regard to the energies mentioned and calculated, the path in which the medium is in the form of a square pyramid and the pivot point in the axial position (TS2) has the lowest energy, so the energy barrier is less in this reaction, and it can be concluded that this The route is thermodynamically preferred to the TS1 and TS4 paths

6. Discussion and Conclusion:

From the quantum computation of the density function (DFT), the migration of the alkyl group in the Mn (CO) 5CH3-nFn complex,

)n = 1,2) and 4 paths of different transition modes 1, the path is deleted and from the remaining 3 tracks, only one path is considered, with less computational results, and is faster and preferred. The placement rate depends on the atom F, which is an electronegative atom and has more electronegative properties than H. In the CH3-nFn group, with increasing F and decreasing H, the metal-carbon bond is tightened and the migration of the alkyl group is more difficult and the rate of deposition is reduced.

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