A Computational Investigation on Gas-Phase Molecular Structures of Ethylene and Propylene Adsorbed on Pd and Pt Dimers

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Abstract: At 298 K, adsorption mode structures (π and/or di-σ) are obtained for palladium and platinum dimers (Pd_2, Pt_2 and PdPt) using density functional (B3LYP) theory calculations in the GAMESS-US suite of package. In all cases, LANL08 basis sets with ECP are used for the metal atoms, while 6-31G and 6-31G* are used for the H and C atoms respectively. Abstraction of a hydrogen atom is observed from Pt and Pt_2's interaction with the methyl group of propylene which was not observed from Pd and Pd_2's interaction with the same group using the method described above. The two central important aspects (adsorption and activation) in the catalysis of C=C containing compounds such as ethylene and propylene by transition-metal clusters are determined. For each case, optimized geometries with vibrational frequencies are obtained.

1. Introduction

Transition metals are important ingredients of cluster complexes in use today for the economical production of a variety of petro- and commodity chemicals [1], and computational methods have found widespread use to describe the molecular interactions of the transition-metal cluster complexes. New opportunities had been provided by computer codes to explore and understand the catalytic properties of transition-metal clusters ranging from a single atom to nanoparticles [2]. Therefore, to answer the question,

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"How do palladium and platinum metal clusters catalyze alkene reactions (such as hydrogenation)?", practical quantum chemical calculations of the structures and properties of palladium and platinum dimers and their interactions with ethylene and propylene are done.

This study serves to qualitatively describe the system above using density functional theory (DFT) calculations. DFT is found to provide accurate results at reasonable computational costs but, because of the approximations introduced in many exchange-correlation functional, verification of the results of DFT calculations against experiments has been found to be necessary.

In the last two decades, density functional theory (DFT) has been applied to small clusters of group 10 metals such as palladium (Pd) and platinum (Pt). The common objective is to determine how large a cluster is needed to realistically simulate a metal surface, in order to permit investigation of chemisorption and catalytic processes [3]. Transition metals are important ingredients of heterogeneous catalysis [1]. The study of their reactivity at the molecular level not only had been useful to relate or explain their macroscopic properties but also had allowed the investigation of the reactivity [4] and use as catalyst of small transition metal clusters. The unique geometric and electronic characteristics of the clusters, such as the presence of high density under-coordinated surface atoms are often pointed out as the reason for their distinct catalytic properties. Due to the synergistic way that theory [2, 3, 5] and experiment [4, 7, 8, 9] had interacted in this particular field in the last few decades, clusters of variable sizes had been synthesized and several of their properties had been probed.

This study aims to: (a) show the two adsorption modes (π and di-σ adsorption mode) of ethylene on Pd_n and Pt_n (n=2), as well as Pd_nPt_m (n+m=2) clusters; (b) see the activation of the methyl group in propylene by the metal atoms and dimers and (c) use LANL08 basis sets from a basis set database with effective core potentials (ECP) from a software package for the metal atoms and dimers.

The ethylene and propylene adsorption on Pd_n, Pt_n (n=2) and Pd_nPt_m (n+m=2) clusters are discussed, followed by the activation of propylene methyl group using hybrid density functional B3LYP method. The B3LYP functional has been found to closely mimic these types of systems [10] although the use of new functionals had appeared in literature [8]. Relativistic effective core potentials (ECP) without the inclusion of spin-orbit coupling (SOC) are used for the metal atoms and dimers.

Transition-metal clusters of Pd and Pt, and cluster complexes with Pd and/or Pt are important catalysts in a variety of chemical reactions. This study serves to obtain a description of how these transition metals catalyze alkene reactions computationally with the least computational cost. Understanding of the interaction of palladium and platinum with double bond containing compounds is done which in the future can aid in molecular investigation and preparation of variety of catalysts from these transition metals and other alkenes.

2. Methods

The hybrid method (B3LYP) combining five functionals: Becke + Slater + HF exchange (B3), with LYP + VWN5 correlation functionals (LYP) was used in the DFT calculations for obtaining the optimized structures of the molecules under study. This method is implemented in the General Atomic and Molecular Structure System (GAMESS-US) package GAMESS, 2012 and 2013 versions.

For the optimization of the metal atoms and dimers, the associated non-contracted basis set LANL08 was used for the 18 valence electrons of Pt and Pd [17]. The basis sets were taken from the Basis Set Exchange Library. The relativistic effective core potential (ECP) was utilized to describe the core electrons. This accounts for the relativistic effects important for Pd and Pt atoms. The Hay and Wadt ECP for palladium and Stevens/Basch/Krauss/Jasien/Cundari (SBKJC) ECP for platinum were used. The ECPs were incorporated in the GAMESS-US package.

For the description of the H atom, the all electron split-valence 6-31G basis set was used, while for the C atom, the 6-31G basis set supplemented with *d*-type functions (6-31G*) was used and referred to as B3LYP/6-31G* for the alkenes. The objective of geometry optimization was to find an atomic arrangement which makes the molecule most stable.

Frequency calculations during optimization at the same basis sets and level of theory to check the geometry were done. Frequencies of the optimized molecules were obtained.

Input files contained all or more the following:

- Type of calculation
- Level of theory and basis set
- Memory requirement
- Molecule Specification

MacMolPlt [25] molecular viewer was used to visualize the molecules. After successful optimization, the output was saved as a log file and can be observed using the downloadable MacMolPlt.

3. Results and Discussion

Bond lengths (in Angstroms, Å) and bond angles (in degrees) are obtained from the optimized geometries of ethylene and propylene (Figure 3.1) and then compared with experimental values.
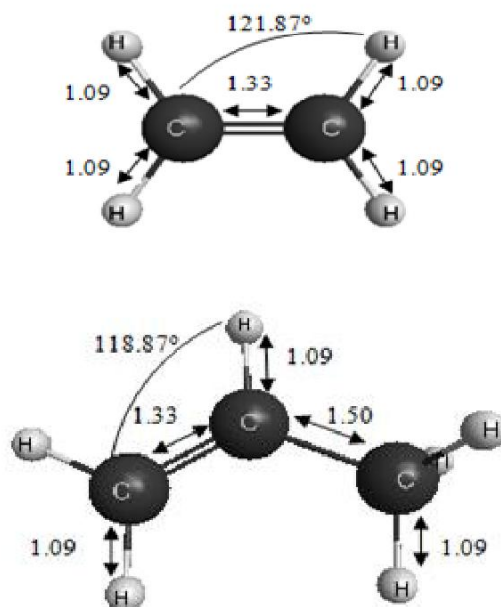
Figure 3.1. Optimized Geometries (Ethylene and Propylene Respectively) Using B3LYP/6-31G*.

Results in the calculation of ethylene bond distances and angles are near experimental values as shown below (Table 3.1)

Table 3.1. Some Data from C_2H_4 Optimized Geometry as Compared with Experimental Values

| Equilibrium Geometry	B3LYP/6-31G* Results	Experimental values[a]
Distance (CC) (Angs.)	1.3312	1.337 ± 0.003
Angle (HCC) (°)	121.87	121.35 ± 1
Angle (CH2-C) (°)	180.00	180.00

[a]H.C. Allen, E.K. Plyler, J. Am. Chem. Soc. 80 (1958) 2673 [19].

3.1. Optimized Adsorption Mode Structures

The term π adsorption mode is used when ethylene molecule interacts with a single metal atom in a surface and di-σ adsorption mode when ethylene molecule interacts with two metal atoms in a surface [19]. These terms are used when referring to the interaction of ethylene with transition metal clusters of two or more atoms [18].

In Figure 3.2, π adsorption mode structure of Pd$_2$-ethylene can be seen. The double bond in ethylene was converted to a single bond during adsorption. There is therefore an elongation of the CC bond of ethylene. There is also a bending away of hydrogen atoms from the metal surface. The

Dewar-Chatt-Duncanson mechanism explains the coordination of ethylene with the transition metal atoms. In all cases, the main interaction is through the electrons in the CC bond. The hybridization of the carbon atoms changed from sp^2 to between sp^2 and sp^3.
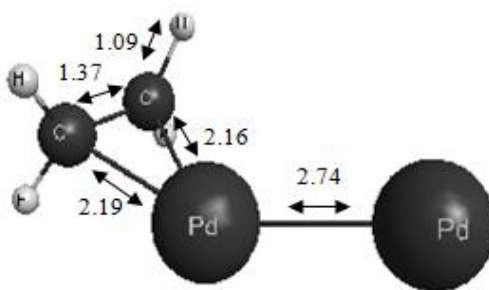
Figure 3.2. Pd$_2$-Ethylene (π adsorption mode) Optimized Structure.

For Pt$_2$-ethylene, difficulty was encountered in obtaining a π adsorption mode optimized structure. This agrees with experiment since there was no reported experimental Pt$_2$-ethylene π adsorption mode structure. Only di-σ complexes are formed experimentally on Pt(100) at low temperatures ($T \cong 100$ K) [19].

In Figure 3.3, the structure has lesser energy than the π adsorption mode structure in Figure 3.2.
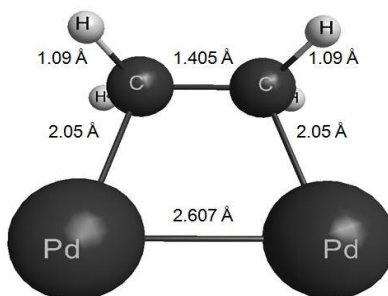
Figure 3.3. Pd$_2$-Ethylene (di-σ adsorption mode) Optimized Structure.

As can be seen in figures 3.2 and 3.3, the complexes have longer CC bond lengths (1.40 Å for di-σ adsorption mode and 1.37 for π adsorption mode) than ethylene alone (see Table 3.2). The order for the CC bond length is ethylene < ethylene (π adsorption mode) < Pd$_2$-ethylene (di-σ). The di-σ adsorption mode is said to be more stable than the π adsorption mode.

Table 3.2. Comparison of CC Bond Lengths, Å in Ethylene and Pd_2-Ethylene Complexes

MOLECULE	LEVEL OF THEORY	BASIS SET	CC bond length, Å
C_2H_4	B3LYP	6-31G*	1.33
Pd_2-C_2H_4	B3LYP	6-31G* and LANL08 with ECP	1.37
Pd_2-C_2H_4	B3LYP	6-31G* and LANL08 with ECP	1.40

The Pd-Pd bond length is shorter (1.607 Å in di-σ adsorption mode) compared to the dimer alone and to the π adsorption mode structure. The order is Pd dimer > Pd_2-ethylene (π adsorption mode) > Pd_2-ethylene (di-σ).

Table 3.3 shows the CC bond lengths and the dimer bond lengths in the di-σ adsorption modes. The bare dimers have longer bond lengths than in the complexes. The CC bond lengths are greater than in the ethylene molecule. The double bond character of carbon atoms have disappeared during the adsorption.

Table 3.3. Optimized di-σ Adsorption Modes and Their Corresponding CC and Dimer Bond Lengths

MOLECULE	LEVEL OF THEORY	BASIS SET	CC Bond Length, Å	Dimer Bond Lengths, Å
Pd_2-C_2H_4	B3LYP	6-31G* and LANL08 with ECP	1.40	2.61
Pt_2-C_2H_4	B3LYP	6-31G* and LANL08 with ECP	1.51	2.54
$PdPt$-C_2H_4	B3LYP	6-31G* and LANL08 with ECP	1.49	2.58

Upon the three complexes, ethylene molecule bonded strongly to the Pt dimer. Also, C-Pt bond lengths are shorter than C-Pd. The geometric and electronic structures of ethylene are found to be highly perturbed by the adsorption process. These results are in agreement with electron energy loss spectroscopy (EELS) results which showed that ethylene is more strongly bound on Pt(111) than on Pd(111) [19].

3.2 Activation of Propylene Methyl Group

Figure 3.4 below shows that Pd atom was not able to activate C-H bond in the methyl group of propylene. This is because the ground state of Pd atom has a closed shell d^{10} configuration which was easily predicted by the B3LYP method which calculates and predicts ground electronic states. The open shell s^1d^9 (^3D) state is 21.9 kcal/mol above for Pd [5]. In contrast to Pt atom where the s^1d^9 (^3D) state is the ground electronic state, while the d^{10} configuration is 11.1 kcal/mol higher in energy, Pd is not able to break C-H bond in the methyl group of propylene as can be seen in the figure. This is also an optimized structure obtained when Pd is oriented near the methyl group. Pd_2 also did not activate the methyl group of propylene as shown in Figure 3.5, although there is an interaction with one Pd and C atom.
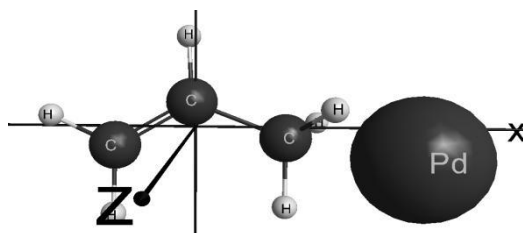

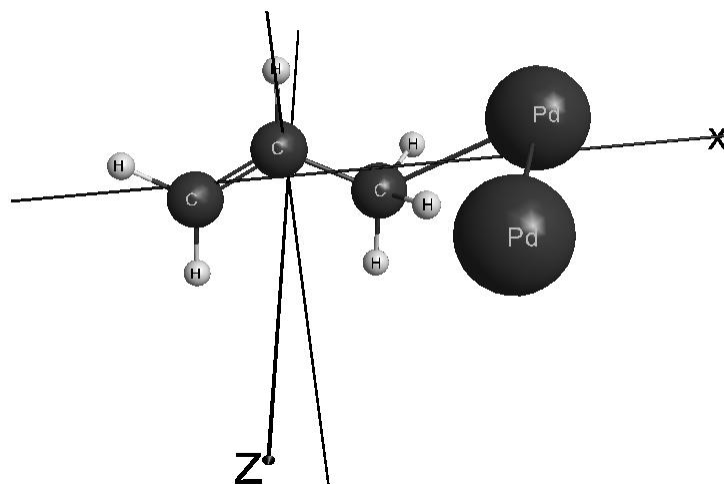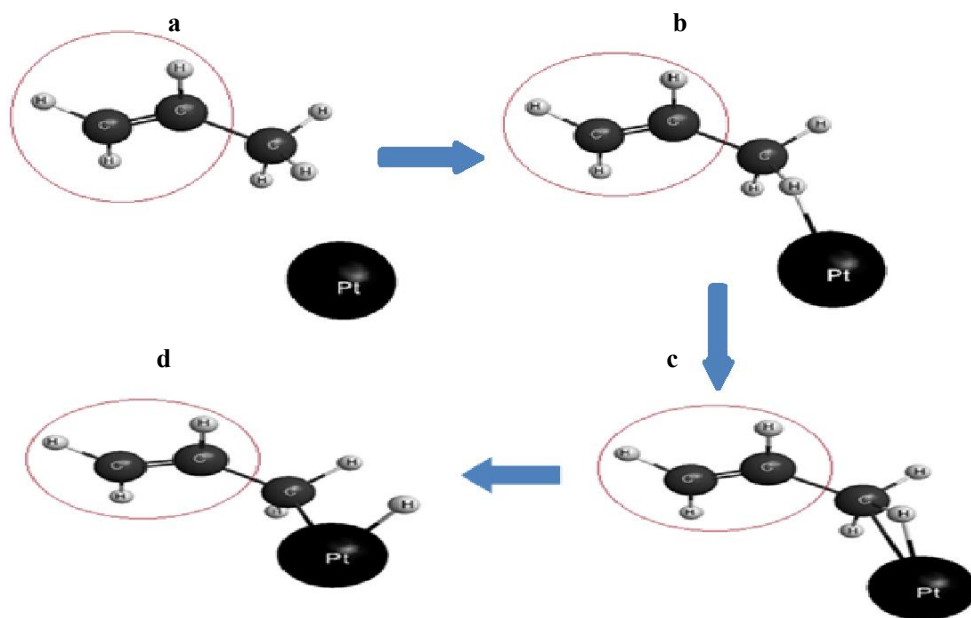**Figure 3.4.** Pd-propylene Optimized Structure. (The axes are shown.)

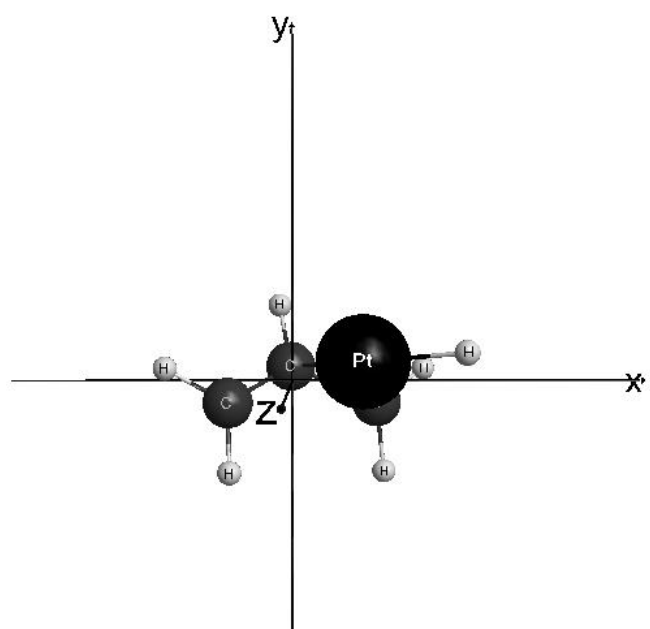**Figure 3.5.** Pd_2-propylene Optimized Structure. (The axes are shown.)

Calculation of the triplet state open shell Pd_2 with propylene may result to activation because the triplet state has a lower energy than the singlet state used here however for the atom of Pd, no activation can be observed even though the triplet state is used (the singlet state has lower energy).

PtC_3H_6 optimization showed an activation of inert C-H bonds of propylene. In the following figures below (Figure 3.6). Here, (a) as Pt was added near the methyl group of the optimized propylene, (b) a hydrogen from the methyl group becomes attached to Pt, and (d) Pt was found to break a C-H bond wherein the hydrogen (formerly attached to C) has now been attached to the Pt atom. Figure 3.6 shows that Pt is able to activate the propylene methyl group. The optimization shows that the metal atom abstracts a hydrogen molecule. During the process, C=C remains unaffected. The final optimized structure of Pt-propylene is shown in Figure 3.7 below.


Figure 3.6. During Optimization of Pt-propylene.

Figure 3.7. Pt-propylene Optimized Structure. (The axes are shown.)

Pt_2 is found to abstract hydrogen from the propylene methyl group in the same way the Pt atom. The optimized structure can be seen in Figure 3.8. Pt and Pt_2 can abstract a hydrogen atom from the methyl group unlike Pd and Pd_2. The interaction of Pt and Pt_2 with propylene methyl group is different with the interaction of Pd and Pd_2.
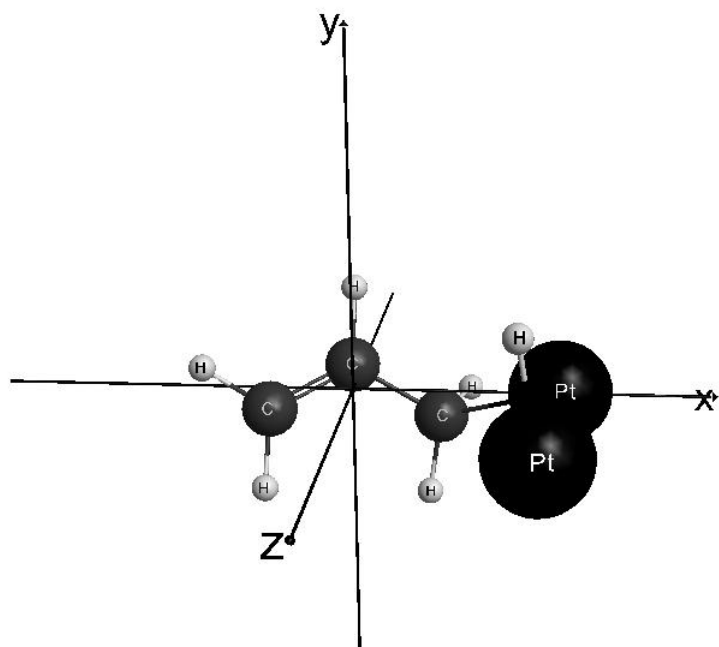
Figure 3.8. Pt_2-propylene Optimized Structure. (The axes are shown.)

4. Conclusion

Ethylene and the transition metal atom and dimers of Pd and Pt interactions were shown in this study. The ethylene molecule becomes adsorbed on Pd_2, Pt_2 and Pd-Pt via the two adsorption modes (π and di-σ). These adsorption modes had been achieved for Pd_2 and the di-σ adsorption mode for Pt_2 and Pd-Pt. The di-σ adsorption mode has lower energy (more stable) as compared to the π adsorption mode structure. Based on experiment, the ethylene molecule readily undergoes π adsorption with the Pd dimer as compared with Pt dimer. Ethylene was also found to be most strongly adsorbed on Pt_2 as compare to Pd_2 [19]. The main interaction of ethylene with transition metals is through the CC double bond.

The activation of C-H methyl group in propylene was also investigated for Pd and Pt. Pt atom and dimer abstracted a hydrogen atom from the methyl group of propylene which implied that platinum is a stronger catalyst than palladium. The Pd atom and dimer was unable to abstract a hydrogen atom from propylene methyl group.

Several studies that involve transition metal clusters and their interactions with different compounds had been done computationally, but the combination of ECP and basis set employed had not been used yet. Experimental data was found to coincide with the results obtained from the optimization procedures. This study had investigated the use of the basis set and ECP mentioned in the B3LYP functional for the transition metal clusters mentioned which is best for qualitative purposes (such as the adsorption modes of ethylene with Pd and Pt dimer and activation of methyl group by Pt atom and Pt dimer). Adsorption of ethylene on other small clusters of Pd and Pt can also be studied. Other higher level basis sets, as well as other methods can be used for comparison.

Acknowledgments

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