DFT Studies of Interaction between Methane and Single Metal Atoms:
Co, Rh, Ir, Ni, Pd, and Pt

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Abstract

Density functional theory (DFT) calculations were performed to study the interactions between methane and single atom of six metals, Co, Rh, Ir, Ni, Pd, and Pt. Understanding the metal initiated activation of C-H bonds is important as the metal-methane interaction can lead to the production of hydrogen molecules from methane as well as the detection of methane. The energies associated with the sigma interactions between methane and the metal atom were obtained with B3LYP. The different possible orientations and electronic interactions for each metal-methane interaction were analyzed and weighted using the population distribution to determine the average binding energy for the complex. The relative binding energies of each metal were compared and the metal with the greatest degree of binding is Palladium. The molecular orbitals were also analyzed to gain an understanding of how strongly the metal was interacting with methane. The distances between the atoms in the complex were studied to determine whether the interactions formed a sigma complex and the type of coordination the interactions formed.

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1. Introduction

A large amount of research has been conducted in order to better understand the characteristics of metal-C-H σ interactions, especially in metal-methane systems.[1-26] Although metal-methane complex was discovered in the late sixties or early seventies of the twentieth century,[27-29] and potential applications of methane as ligands, however, data on metal-methane σ-complexes are extremely limited because of the nature of the interaction is difficult to describe accurately and the computational methods to such studies are only available recently.

In metal-σ interactions the electrons of a σ bond, such as C-H in methane, interact with a metal resulting in an elongated bond.[30,31] The σ electrons in the C-H bond are donated to the empty d orbitals of the metal, the metal then back donates to the antibonding σ* molecular orbitals of the bond. The back donation of electrons to the antibonding molecular orbital causes the σ bond to destabilize and become elongated. This characteristic can be beneficial in organic compounds because it increases the reactivity of otherwise stable carbon-hydrogen bonds,[32] as this is the first step of any C-H bond activation[33-65] or sensing.[66] Increasing the acidity of the hydrogen in methane makes it more favorable for further reactions to take place; this can lead to the development of methods used to produce hydrogen from naturally abundant methane gas, as well as develop devices, i.e. sensors, capable of detecting low concentrations of methane.

In the density functional theory (DFT) studies of methane adsorption on Pd atom and clusters, Zhang et al found that the three CH_4-Pd adducts with weak Pd and methane interactions.[67] Bullock et al. studied the σ bonds formed between hydrocarbons and low valence shell metals.[12] Formation of σ complexes has been observed in alkane-metal complexes.[5] There are a great demand on understanding the neutral metal-methane interactions.[6] The metal-

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methane complexes can be formed via several different coordination configurations, including η^1; η^2-H,H; η^2-C,H; η^3, which are shown in Figure 1.[68]

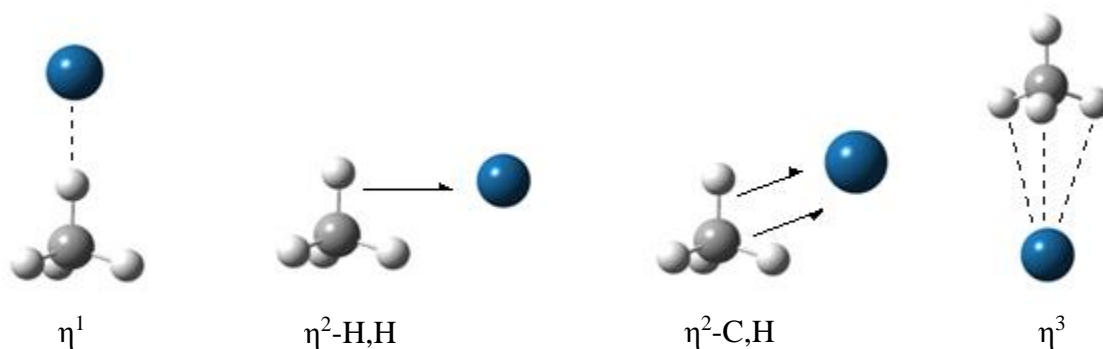| η^1 | η^2-H,H | η^2-C,H | η^3 |

Figure 1. Configurations of interaction between methane and a metal atom. The blue, gray, and white balls represent metal, carbon, and hydrogen atoms, respectively.

Heterogeneous catalysis plays important roles in the refining of natural resources and in the synthesis of organic molecules that have many applications in energy and sensing industry.[69-78] Many studies have been conducted to investigate methane activation to form useful products[37,67,79,80] and other reactions[80-113] on various nanoparticles.[114-133] Reactions on Cu catalyst[134,135] and on single atom catalyst[136,137] have been active research area. In order for the σ interaction induced reactions to be useful two challenges must be addressed, these include activity and more importantly selectivity. The reaction needs to proceed quickly enough for it to be useful and there should be minimal formation of side products. To overcome these challenges, understanding the σ complex formation is critically important. As such, in this research the interactions of six metals with methane molecule were analyzed to determine the most effective metal for the activation of C-H bonds. The most efficient metal catalyst is one that is able to activate the C-H bonds most significantly and not lead to the breaking of carbon-

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hydrogen bonds.[1] To evaluate the adsorption strength of various single metal atoms in methane adsorption, we performed DFT calculations to obtain the relative binding energy of each metal-methane complex and analyze the bond distances of the elongated C-H bonds. The relative binding energy is useful in predicting which metal will have the strongest interactions with methane. The elongated bond distances will provide insight into the characteristics of the interactions, whether they are σ interactions and the type of coordination they have.[1]

2. Computational Details

The DFT calculations performed in this experiment were completed using Gaussian 09 software, calculations were setup using Gauss View 3.09. The interactions were studied by optimization and frequency calculations of metal-methane complexes in gas phase using B3LYP. In order to account for all possible metal-methane interactions, combinations of three different orientations (shown in Figure 1) and three electronic configurations for each metal were considered. A split basis set was used with Lanl2DZ for metal atoms and 6-311g+(d,p) for C and H atoms. To determine the relative accuracy of the basis set, a single basis set calculations, b3lyp/lanl2dz, was used for all elements. The convergence criteria of calculations were default and have been used in our other DFT studies.[138-142]

Some of the interactions proved to be difficult for Gaussian to solve, in order to complete some of the calculations a quadratically convergent SCF was used and write connectivity was selected. When a calculation would terminate without finding an optimized structure the output file was saved as an input file and the calculation was continued where it had ended. There were calculations that would determine an optimized structure that does not exist, resulting in negative vibrational frequencies. The arrangement of the atoms in these structures would be altered;

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generally the metal was moved towards the direction of the vibration vector given by the output file. The calculation process was continued until an optimized structure was obtained with no negative frequency values. The structures of the output files were then analyzed to ensure the orientation of the metal was not significantly different than the input file.

3. Results and Discussion

The metal-methane complexes were analyzed by calculating the binding energies associated with the sigma interactions for each metal and investigated the optimized structures of the complexes including C-H bond distances. The binding energies provided theoretical data used to predict the most effective metal catalyst for the activation of C-H bonds in methane. The bond distances gave further insight into the magnitude of the interaction and whether the interaction resulted in broken carbon-hydrogen bonds, which was unfavorable.[1]
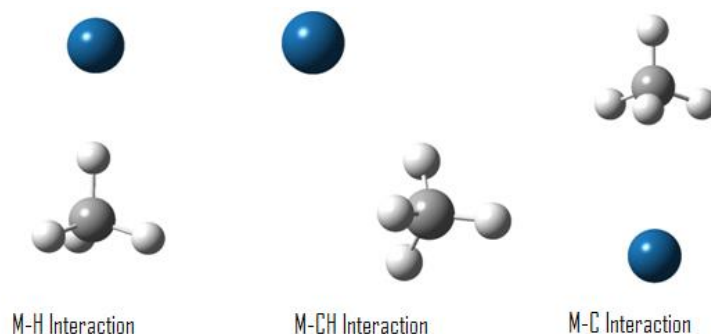

M-H Interaction   M-CH Interaction   M-C Interaction

Figure 2. Metal-Methane orientations and notation of the complexes.

The optimized structures and energies for each metal, methane, and the metal-methane σ complexes were determined. The metals studied in this work include Cobalt, Rhodium, Iridium, Nickel, Palladium, and Platinum. Three electronic configurations for each metal were accounted for; these included doublet, quartet, and sextet for Co, Rh, and Ir as well as singlet, triplet, and

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quintet for Ni, Pd, and Pt. With Cobalt as an example; the doublet, quartet, and sextet energies were calculated for the metal and compared to determine the lowest energy electronic state, the ground state electronic configuration for cobalt was the quartet. The optimized structure and energy for the Co-methane complex for the doublet, quartet, and sextet electronic configurations were calculated for each orientation. The characteristics of each interaction were analyzed by considering the interaction and bond distances, energy values, and orientations. Upon analysis of the various interactions many of the optimized structures were found to be duplicates. The duplicates were excluded from the binding energy calculations in order to accurately compare the catalytic ability of each metal; duplicates are indicated in Table 1 with a δ.

Table 1. The energy values (in Hartree) of the optimized sigma complexes

Metal Complexes	Doublet	Quartet	Sextet	Metal Complexes	Singlet	Triplet	Quintet
Co--H	-185.5225	-185.5120	-185.3973	Ni--H	-209.7067	-209.7631	-209.531
Rh--H	δ	-149.9512	δ	Pd--H	δ	-167.1899	-166.9573
Ir--H	-145.0772	-145.0956	δ	Pt--H	-159.4969	-159.5361	δ
Co--CH	-185.4990	-185.5325	-185.4008	Ni--CH	-209.7331	-209.7631	δ
Rh--CH	-149.9509	-149.9511	-149.7468	Pd--CH	-167.2294	-167.1896	-166.9660
Ir--CH	-145.0773	-145.0994	-144.9481	Pt--CH	-159.6422	-159.5937	δ
Co--C	-185.4992	-185.5327	-185.4009	Ni--C	δ	-209.7631	-209.609
Rh--C	δ	-149.9511	-149.7550	Pd--C	δ	-166.966	-167.2294
Ir--C	-145.0787	-145.1000	-144.9482	Pt--C	-159.6422	-159.5935	-159.4082

The binding energy, E_b, for the complexes was calculated using equation (1), where E_{comp} is the energy of the metal-methane complex, E_{meth} is the energy of methane, and E_M is the energy of the lowest energy electronic state for each metal. Using this calculation method the lower the binding energy is the more favorable the interaction.

$$E_b = E_{comp} - (E_{meth} + E_M) \qquad (1)$$

The energy values for each electronic configuration were weighted using population values determined by the Boltzmann equation, shown in equation 2 where N_j is the number of

particles in state j, g_j/g_o is equal to 1, k is the Boltzmann constant, T is temperature 298.15 K (room temperature), and E_j is the energy difference between states.

$$N_j/N_o = g_j/g_o * \exp(-E_j/kT) \qquad (2)$$

The lowest energy complex within each orientation was considered the "ground state" with a population value of 1. The energy difference between the lowest energy complex and higher energy complexes was used in the Boltzmann equation to calculate the relative population values. The populations were then used to weight the relative energy contribution to the overall metal-methane interaction by multiplying the population values and energy values. This calculation was performed for each orientation and electronic combination; the relative energy values for each orientation are listed in Table 2.

Table 2. Weighted average binding energies of metal-methane interactions

Metal Complexes	Energy (kcal/mol)	Metal Complexes	Energy (kcal/mol)
Co-H	-5.72	Ni--H	-0.63
Rh-H	-0.17	Pd--H	-19.64
Ir-H	-1.95	Pt--H	-35.61
Co-CH	-0.50	Ni--CH	-0.63
Rh-CH	-0.14	Pd--CH	-5.13
Ir-CH	-4.32	Pt--CH	-30.96
Co-C	-0.64	Ni--C	-0.62
Rh-C	-0.12	Pd--C	-5.13
Ir-C	-4.71	Pt--C	-30.96

The energy values for each orientation were also weighted using the Boltzmann equation, in order to determine the relative energies for each metal-methane interaction. The energy differences between the lowest energy state and the higher energy orientations were determined and used to calculate the population values for each orientation. The relative energies associated with each metal-methane complex are shown in Table 3. Based on the calculations Platinum had the lowest binding energy and has the strongest interaction with a methane molecue. However,

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structures of the complex must also be taken into account. The energy of dispersion was also determined by the x, y, z coordinates in the optimization calculations.

Table 3. Binding energies of metal methane interactions

Metal Complexes	Average Energy (kcal/mol)
Cobalt-Methane	-1.04
Rhodium-Methane	-0.42
Iridium-Methane	-6.95
Nickel-Methane	-1.84
Palladium-Methane	-10.26
Platinum-Methane	-61.93

Previous work shown that inclusion of dispersion energy increases the binding energy but does not change the relative stability of absorption complexes.[67] The dispersion energies were also taken into account when calculating the average binding energy and the results are shown in Table 4. The overall trend of binding energies did not change however, the binding energies for palladium and iridium were much more similar when the dispersion energies are considered.

Table 4. Binding energies of metal-methane interactions with dispersion energy

Metal Complexes	Average Energy (kcal/mol)
Cobalt-Methane	-4.08
Rhodium-Methane	-3.54
Iridium-Methane	-9.57
Nickel-Methane	-4.15
Palladium-Methane	-9.68
Platinum-Methane	-63.82

The optimized structures for platinum resulted in the breaking of carbon-hydrogen bonds and the formation of Pt-C bonds and therefore they are not σ complexes. The weak interaction

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between Pt and methane atom was found in the previous work.[80] The metal with the lowest binding energy of σ complexes was palladium, the optimized structures for this metal was further analyzed and the results are shown in Tables 5-7 in details.

Table 5. Bond distances in Pd—H complexes

Singlet:	Distances (Å)	Triplet:	Distances (Å)	Quintet:	Distances (Å)
Pd-H3	2.164	Pd-H3	2.941	Pd-H3	4.39025
Pd-C1	2.567	Pd-C1	4.039	Pd-C1	5.487
C1-H3*	1.112	C1-H3	1.098	C1-H3	1.096
C1-H2*	1.112	C1-H2,H5,H4	1.095	C1-H2,H5,H4	1.096
C1-H4	1.094				
C1-H5	1.094				

Table 6. Bond distances in Pd—CH complexes

Singlet:	Distances (Å)	Triplet:	Distances (Å)	Quintet:	Distances (Å)
Pd-H3	2.165	Pd-H3	3.927	Pd-H3	3.182
Pd-H4	2.163	Pd-H4	3.789	Pd-H4	2.127
Pd-C1	2.567	Pd-C1	4.384	Pd-H5	3.185
C1-H2	1.094	C1-H2	1.096	Pd-C1	2.960
C1-H3*	1.112	C1-H3	1.096	C1-H2	1.097
C1-H4*	1.112	C1-H4	1.096	C1-H3	1.092
C1-H5	1.094	C1-H5	1.096	C1-H4**	1.141
				C1-H5	1.092

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Table 7. Bond distances in Pd—C complexes

Singlet:	Distances (Å)	Triplet:	Distances (Å)	Quintet:	Distances (Å)
Pd-H3	2.164	Pd-H3	4.102	Pd-H3	3.178
Pd-H4	2.166	Pd-H4	4.105	Pd-H4	3.182
Pd-H5	3.315	Pd-H5	3.890	Pd-H5	2.126
Pd-C1	2.569	Pd-C1	4.259	Pd-C1	2.957
C1-H2	1.094	C1-H2	1.096	C1-H2	1.097
C1-H3*	1.112	C1-H3	1.096	C1-H3	1.093
C1-H4*	1.112	C1-H4	1.096	C1-H4	1.093
C1-H5	1.094	C1-H5	1.096	C1-H5**	1.141

The bond distances showed which interactions resulted in the elongation of C-H bonds in methane and would be considered sigma interactions. The interactions with elongated bonds shown in Tables 4, 5, and 6 were Pd—H, Pd—CH, and Pd—C singlet interactions as well as Pd—CH and Pd—C quintet interactions. The molecular orbitals for these interactions were studied to determine the extent of orbital overlap between the metal and methane and the type of sigma coordination. The Pd—H, Pd—CH, and Pd—C singlet interactions resulted in a η^2-H,H coordination which caused the two hydrogen which interacted with the metal to become elongated. The Pd—CH and Pd—C quintet interactions resulted in η^2-C,H coordination. The η^2-C,H had a much larger degree of orbital overlap and caused the C-H bond the metal interacted with to break with an elongated distance of approximately 1.14 Å. Therefore from the bond distances and the molecular orbital overlap the only coordination modes that resulted in sigma interactions between palladium and methane were η^2-C,H, and η^2-H,H.

In order to determine the accuracy of the data obtained using a dual basis set was used to calculate the binding energies for Palladium, Iridium, and Cobalt. Using DFT b3lyp/6-311g+(d,p) for C and H atoms and lanl2dz for the metal, these calculations provided a much

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more accurate binding energy and optimized structure. These values were compared with the values obtained from the single basis set calculations in order to ensure the accuracy of the results. The results of the calculations for the split basis set are shown in Table 8. The calculated binding energies for the metals in Table 8 displayed thermodynamically unfavorable interactions because the values were positive. Also the trend displayed from the single basis set calculations was not the same for the split basis set calculations. Once possible source of error was the calculations for the energy of methane, this would have resulted in a much larger energy for the separate metal and methane. Also several of the calculations for the different metal-methane interactions had not been completed, leaving a number of holes in the data that could have skewed the results.

Table 8. Binding Energies of Metal-Methane Interactions

Metal Complexes	Average Energy (kcal/mol)
Cobalt-Methane	-19.78
Iridium-Methane	-6.51
Palladium-Methane	-54.23

Finally, we discuss briefly the frontier orbitals of the σ complexes. As an illustration of the predicted σ-bonding, it is important to note the molecular orbitals of the structures. Though this trend is evident in many of the complexes, a few have been selected to emphasize the interaction. Figure 3 illustrates the electron distribution of the Cu-methane complex in the η^2-C,H configuration. It can be seen in Figure 3 that there is definite metal-carbon interaction, indicated by the red electron density. Additionally, metal-hydrogen interaction can be observed by the large green contour.
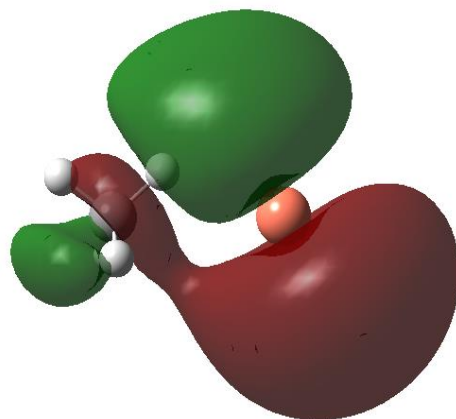
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Figure 3. The highest occupied orbital of the η^2-C,H Cu-methane complex.

Further illustration can be found in Figure 4, which depicts the electron distribution of Cu-methane complex with η^1 interaction. As seen in Figure 4, there is dz^2 σ-interaction interaction between the metal and the hydrogen which makes up the majority of the electron density of the complex. Figures 3 and 4 provide additional proof that the expected interaction is largely due to σ-interaction.
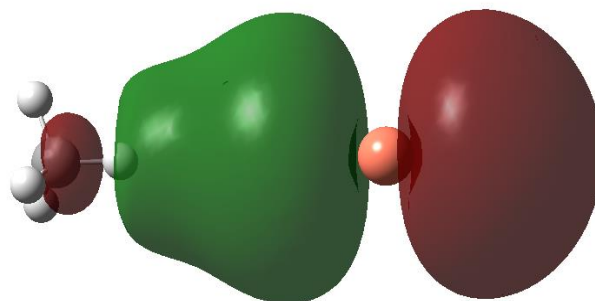

Figure 4. The highest occupied orbital of the η^1 Cu-methane complex.

4. Conclusions

The experiment showed that many of the metal-methane interactions resulted in the formation of a sigma complex. The most thermodynamically favorable interaction was between

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methane and palladium. The optimized structure with η^2-H,H coordination displayed the most ideal sigma interaction, though the metal also had several non sigma interactions as well as a η^2-C,H coordinate that resulted in the breaking of carbon-hydrogen bonds in methane. The results of the split basis set did not support the trends shown in the single basis set though there are possible errors in the calculations because none of the interactions were thermodynamically stable compared with the single basis set calculations. Further research is needed to be able to ensure the trend determined by the single basis set was accurate. Also the selectivity of the sigma complexes that result from the interaction with the metals needs to be investigated in order to determine if the metals will be useful as a catalyst for the activation of C-H bonds in methane.

Acknowledgements

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