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Interaction between a single Pt atom and a carbon nanotube studied by density functional theory

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Using density functional theory with the generalized gradient approximation, we have studied the interaction between a single Pt atom and a carbon nanotube. The bridge adsorption site on the outer wall of nanotube is favorable. The curvature affects the binding strength. Compared to the larger nanotube, Pt could bind stronger to the outer wall of a small radius nanotube. For zigzag nanotube, the most stable site on the outer wall is the bridge site with the underlying C-C bond being parallel to the axis of the nanotube, while for the armchair nanotube it is the bridge site with the underlying C-C bond being tilted to the axis of the nanotube. The energy in average differs by $\sim 1.5$ eV for adsorbing on both sidewalls of small radius nanotube, while it decreases much for the larger nanotube. Either by penetrating the wall or by substituting one C atom on the wall, the Pt atom is found to be hard to diffuse from the outside to the inside. The studied charge density suggests the weak covalentlike bonding between Pt and C atoms.

I. INTRODUCTION

The catalysis plays an innovative role in the development of new technologies to prevent pollution and in seeking new energy resources, which are becoming big issues accompanying the industrialization. Nanotechnology is believed to be important in heterogeneous catalysis for its peculiar properties and potential applications. Since its discovery, the carbon nanotube has received much attention in the study of interaction between a small particle and its wall. The beautiful tubular structure of a nanotube that could be coiled from a honeycomb graphene sheet has a large effective surface, which could facilitate the adsorption of small particles. Recently, some groups studied the applications of carbon nanotubes and carbon nanohorns as supports for catalyst in fuel cell.\(^{2-5}\) The polymer electrolyte fuel cell has aroused much research interest for its potential as a clean and mobile power source in the future.\(^{6-11}\) Pt and Pt-Ru materials are found to be the best catalysts of fuel cell, but are expensive and insufficient for commercializing. Using carbon nanotubes or nanohorns as supports the catalyst was reported to form small size particles, which were distributed dispersively and increase the reaction surface of catalyst per atom compared to the thin catalyst film, and then enhanced the cathode oxygen reduction reaction.

The carbon black has also been used as the support of catalyst. However, some catalyst particles trapped in deep cracks could not work as catalyst in fuel cell. Matsumoto et al.\(^ {2}\) using the multiwalled carbon nanotube produced by the catalytic decomposition of hydrocarbons, found that the Pt-deposited carbon nanotube reduced 60% Pt load per electrode area in a polymer electrolyte fuel cell below 500 mA/cm\(^2\) than the commercial Pt-deposited carbon black, and gained better electric power densities. Also using the multiwalled carbon nanotube, Li et al.\(^ {4}\) reported that the Pt particle size was in the range of 2–5 nm. The higher electrical property was also observed in their experiments. Yoshitake et al.\(^ {3}\) in experiment studied the Pt-deposited single walled carbon nanohorn. They found that Pt particles were homogeneously dispersed and the size was less than half of that in Pt-deposited carbon black.

However, to our best knowledge, the theoretical study of Pt-deposited carbon nanotube or nanohorn is processed much less until now. If the Pt could bind stronger to the wall of the tube than bind to the Pt particles, it would uniformly cover the wall of tube and form the coverage film instead of Pt particles, which could be denied by the experimental observations. The Pt atoms were found on experiments to cluster together into small particles. This indicates that the bonding between the Pt and sidewall of the nanotube may be weak, which needs the theoretical study to clarify the binding nature between the Pt and tube. Yuge et al.\(^ {5}\) reported that the adsorption of Pt on the outside wall of carbon nanohorn could give a better performance in heterogeneous catalysis. However, when the Pt content was 20% of the mixture, the experimental observations showed that the Pt particles appeared to be adsorbed on the inner wall of the carbon nanohorn. This raised another question besides the one on binding nature: could a Pt atom enter into the nanotube or nanohorn freely? The experimental studies call for better understanding of the interaction between Pt and the walls of nanotube or nanohorn, which in fact dominates the growth mechanism of Pt on the wall. In this paper, by the first-principles method, we study the interaction between a Pt atom and a single walled carbon nanotube in detail. We will focus on the adsorption of Pt on the wall of the tube, the diffusion energy barrier for Pt entering into the tube, and the binding nature, which could help us to better understand the experimental observations and could benefit the experimental study on catalysis in fuel cell.

II. SIMULATION DETAILS

The first-principles calculations are performed by using the Vienna \textit{ab initio} Simulation Package (VASP)\(^ {12,13}\) within the framework of density functional theory (DFT),\(^ {14,15}\) with generalized gradient correction in the form of Perdew-Wang 91.\(^ {16}\) The wave functions are expanded in a plane wave base with an energy cutoff of 287 eV. The ultrasoft pseudopotential\(^ {17}\) is used to describe the interaction be-
tween the core and the valence electrons. The solution of the Kohn-Sham equation is calculated by an efficient matrix diagonalization technique based on a sequential band-by-band residual minimization method\textsuperscript{12} and a Pule-like charge density mixing.\textsuperscript{18} The infinite one-dimensional nanotubes are simulated. We have applied the super tetragonal cells with the edge lengths of $a$ and $b$ lattices of 18.0 Å for (5,5) and (8,0) tubes, and 24.0 Å for a (10,10) tube, which are large enough to neglect the interaction between a nanotube and its periodic images. The $c$-lattice aligned with the axis of the nanotube is tuned to match the periodic condition. The irreducible Brillouin zone is sampled by three k-points generated by the Monkhorst-Pack technique.\textsuperscript{19} The structure optimization was stopped when the forces due to displacements of an atom in the unit cell converged within 0.01 eV/Å.

In order to test the accuracy of our theoretical methods, we have studied the interatomic distances of Pt$_2$ and CPt dimers. The calculated lengths are 2.34 and 1.70 Å, which agree well with the previous data.\textsuperscript{20,21} The lattice constants of graphene sheet and diamond, which have $sp^2$ and $sp^3$ hybridization characters, were also studied. The calculated lattice constants are 2.46 Å for graphene sheet and 3.57 Å for diamond, which are in close agreement with experimental data 2.461 and 3.567 Å.\textsuperscript{22}

III. RESULTS AND DISCUSSIONS

A. Adsorption sites

By putting Pt atom on all the nonequivalent high-symmetry sites of outer and inner walls of the carbon nanotube, we carefully optimized the geometrical structures. The best adsorption configurations and some low-lying energy structures are presented in Fig. 1. As shown in Fig. 1, the Pt atom likes to sit at the bridge sites on either outer or inner walls. For the convenience to describe the adsorption sites presented in Fig. 1, we would like to classify them into three types: (a) B-type sites, with the underlying C-C bond being perpendicular to the axis of tube; (b) B-type sites, with the underlying C-C bond being parallel to the axis of tube; and (c) B-type sites, for all the other bridge sites. Figure 1 shows the configurations for the (5,5) armchair tube and the (8,0) zigzag tube. Because the adsorption sites of larger (10,10) armchair tube are similar to those of the (5,5) tube, we do not show the corresponding configurations. Figures 1(a)–1(d) are for the adsorptions on the inner wall of the (5,5) tube, the outer wall of the (5,5) tube, the inner wall of the (8,0) tube, and the outer wall of the (8,0) tube, respectively. For each figure, we present the lowest energy geometry on the left, and the low-lying energy structure on the right.

As shown in Fig. 1(a), on the inner wall of the (5,5) tube, the best adsorption site is the B site, with the isomer configuration the B$^+$ site. However, as presented in Fig. 1(b), the lowest energy site on the outer wall of the (5,5) tube is a B$^+$ site, and the low-lying one is a B-type site. Figure 1(c) shows that the lowest energy structure on the inner wall of the (8,0) tube is B$^+$ site, and the isomer is the B$^*$ site. The best adsorption site on the outer wall of the (8,0) tube is a B$^+$-type site, and the isomer is a B$^*$-type site [see Fig. 1(d)]. In our study, the armchair (10,10) tube has been found to have the similar schematic configurations for Pt adsorptions to those of the (5,5) armchair tube. When Pt adsorbed on these bridge sites, the underlying C-C bonds are drawn upward slightly, and the lengths are elongated slightly also. We put a Pt atom upon a bridge site of graphene sheet and optimized its structure. The underlying C-C bond was found to move upward, which is slightly off plane. Its length is elongated by 0.04 Å. Compared to the graphene sheet, the elongates of underlying C-C bonds of nanotubes are affected by the curvatures. The elongates for small radius (5,5) and (8,0) nanotubes are around 0.02 Å for Pt adsorbed on inner sites, while they are around 0.07 Å for Pt adsorbed on outer sites. Due to the small curvature, the elongate for (10,10) nanotube is 0.05 Å for inner site, and is 0.06 Å for outer site, which are closer to that of the C-C bond on graphene sheet.

Table I presents the binding energies for the best adsorption sites and the low-lying energy adsorption sites for the armchair (5,5) and (10,10) tubes, and the zigzag (8,0) tube. The binding energy is calculated by the formula

$$E_b = E_{Pt} + E_{tube} - E_{Pt+tube},$$

(3.1)

where $E_{Pt}$ and $E_{tube}$ are the total energies for a free standing Pt atom and a bare carbon nanotube, respectively, the $E_{Pt+tube}$ is the total energy for the configuration with one Pt atom adsorbed on a tube. For the small radius (8,0)
and (5,5) tubes, one can see that the average binding energies are around 0.9 eV on the inner walls, and around 2.4 eV on the outer walls. The energy difference reaches 1.5 eV. However, the energy difference for the larger (10,10) tube decreases much, which is only 0.6 eV. The binding energy on the inner wall is $\sim$1.4 eV, and on the outer wall is $\sim$2.0 eV. Comparing the binding energies on the small radius tubes with those on the larger tube, we could conclude that the curvature of the tube has an obvious effect on the interaction between the Pt and tube. Considering the graphene sheet, besides the three electrons bonded in three strong $\sigma$ bonds for each C atom that consist of the well-known $sp^2$ hybridization configuration, the C atom has another one valence electron in $\pi$ orbital, which develops the conjugate $\pi$ covalent bonds with the neighboring C atoms. The charge density of the conjugate $\pi$ bond is distributed equally above and under the graphene plane. We calculated the binding energy of Pt adsorbed on the bridge site of graphene, which is only $\sim$1.73 eV. Compared to the binding energies of 4.6 eV for Pt$_2$ dimer and 8.6 eV for CPt dimer, we could say that the interaction between Pt atom and graphene sheet is weak, which agrees well with the experimental observations. Zhang et al. studied the adsorption of several metal atoms on the sidewall of carbon nanotube, and found that many types of metals (e.g., Au, Al, Pd, Pt, and Fe) interact weakly with the sidewall of the tube. When coiling the graphene sheet into a nanotube, the strain due to the curvature of the nanotube will induce charge redistribution of conjugate $\pi$ bonds. When the space is squeezed, the charge density on the inner wall will increase, which actually increases also repulsion between electrons, and finally adjusts charge distribution on both sides of the wall. The charge on the inner wall will be reduced and that on the outer wall will be increased, which then facilitates the bonding of Pt to the outer wall of the nanotube. The curvature of the small radius nanotube is larger, and more charge on the outer wall could be gained, which makes the bonding of Pt to its outer wall stronger. The binding energies of Pt on outer walls of small radius (8,0) and (5,5) tubes are higher than that on graphene by $\sim$0.7 eV, however, on the inner walls are lower by $\sim$0.8 eV. For the curvature of (10,10) nanotube is small, the strain in conjugate $\pi$ bonds is reduced much compared to those of small radius nanotubes. The binding energies on the outer wall as well as on the inner wall are close to that on the graphene sheet.

Even in a similar situation, one can see that the curvature has an effect on binding energy as well. On the outer wall of the (5,5) tube, the binding energy of the B site is 0.26 eV lower than that of the B$^-$ site, however, on inner wall the B site is 0.11 eV higher in binding energy than B$^-$ site. The larger (10,10) tube has the same energy sequence, the B$^+$ site is more stable than the B site on the outer wall, while the B site on the inner wall has a higher binding energy. The difference in binding energies for B and B$^-$ sites of (10,10) nanotube decrease, which could be attributed to the small curvature of nanotube. It is 0.15 eV on the outer wall, and 0.07 eV on the inner wall. As shown in Fig. 1, the bending of the underlying C-C bond of the B site is more severe than that of the B$^-$ site for armchair tube. For the zigzag (8,0) nanotube, one can note that the underlying C-C bond of the

![FIG. 2. (Color online) The initial and final states for Pt approaching the (10,10) tube along the paths which are perpendicular to the wall of the tube. (a) Path B, approaching toward the center of the corresponding C-C bond; and (b) Path H, approaching toward the center of the corresponding hexagon. The big balls are for Pt atoms, and the small balls are for C atoms.](image)

B$^+$ site actually has no bending. The B$^*$ site of the (8,0) nanotube, which has a bended underlying C-C bond, is higher in binding energy on the inner wall, while it is lower on the outer wall. Based on the energies presented in Table I and the bendings of the underlying C-C bonds illustrated in Fig. 1, we could conclude that, for the same nanotube, on the outer wall the more severe bending of the underlying C-C bond the lower binding energy; however, it is higher in binding energy on the inner wall. Such phenomena might be understood by the fact that the bending has contrary effects on the distances between Pt and its nearest C atoms for both sidewalls of the nanotube. On the outer wall, the bending elongates the distance, while on the inner wall the distance will be shortened. The elongate of the distance on the outer wall minimizes the attraction strength between the Pt and C atoms.

### B. Energy barrier

Judged by the experimental transmission electron microscopy pictures, Pt could sit dispersively on the outer wall of either carbon nanotubes or carbon nanohorns. The dispersive distribution of Pt on nanotubes or nanohorns could increase the effective surface for the catalytic reaction and then minimize the required amount of Pt materials. However, Yuge et al. reported their experimental study on the adsorption of Pt on a carbon nanohorn and found that almost all the Pt particles appear to be adsorbed on the inner wall when the Pt content is 20% of the mixture, which lowers the mass activity of the methanol oxidation compared to that of Pt deposited on outer wall. This in fact proposes one question: could the Pt metal enter inside through the wall of the nanotube or nanohorn?

Because of the large difference in binding energies on outer wall and inner wall of a small radius carbon nanotube, the Pt atom should not like to sit inside (8,0) and (5,5) tubes. The (10,10) tube has a larger radius and the binding energies on both sidewalls are close to that on graphene. This indicates that the Pt atom may pierce the wall and sit on the inner wall. In Fig. 2, we present the result of the study by pushing...
the Pt atom toward the wall of the nanotube step by step. For each configuration in Fig. 2, the left is the side view picture, and the right gives the top view picture. The atoms on the back wall of the nanotube are fixed to limit the movement of the tube when Pt approaches it. The Pt atom is limited to move only along the line being perpendicular to the wall. We first optimized the structures by putting a Pt atom on the B site and on the site above the center of the hexagon, which were selected as the initial states. Based on the optimized structure, we then pushed the Pt toward tube by a small distance, and then fully relaxed the atoms. Two paths are selected. One is the vertical path that goes through the center of the C-C bond [path B, see Fig. 2(a)], and the other one is along the vertical line that goes through the center of the hexagon [path H, see Fig. 2(b)]. As shown in Fig. 2, from the initial state to the studied final state, the Pt atom is not found to pierce into the tube even when the tube is pressed to be flat. The total energy increases by more than 9 eV for the final state compared to the initial state, which suggests that it is very hard for Pt entering inside through the wall in the step by step processing. In the final state of path H, the nanotube is distorted besides being pressed to be flat. The center of the hexagon deviates from the vertical line of path H, as shown in Fig. 2(b). This agrees with our study on the adsorption sites, which suggests that the hexagon center site should not be an equilibrium adsorption site. When putting the Pt above the center of the hexagon, and optimizing the geometrical structure by fully relaxing all the atoms, the Pt is found finnally to move away from the site atop the center of the hexagon.

In order to figure out the smaller energy barrier for the Pt diffusing from the outside to the inside, we have also employed the dimer method based on the first-principles calculations. The dimer method was developed by Henkelman and Jónsson\textsuperscript{22} to search the saddle point (although not the entire minimum energy path), by defining a dimer with two neighboring images on the potential surface. If the images are away from the saddle point, the dimer will be moved uphill on the potential energy surface. Along the way, the dimer is rotated in order to find the lowest curvature mode of the potential energy at the point where the dimer is located. This method can give a good estimation of energy barrier, which was confirmed in the previous literatures.\textsuperscript{23,24} Limited by the computer resource, we used the $l^\prime$ point in the summation of electronic property in $k$-space for the energy barrier study by the dimer method. We ran the dimer method many times starting from different initial configurations and found two lower energy saddle points, which are presented in Fig. 3. Figure 3(a) is for the saddle point P, for the path of the Pt atom penetrating the wall of the tube through the center of the hexagonal ring. Figure 3(b) gives the saddle point S for the path of the Pt atom entering the tube by substituting one C atom. The energy barriers found by the dimer method are 8.5 eV for saddle point S and $\sim 7.9$ eV for saddle point P. The atomic radius is 1.35 Å for the Pt atom and 0.70 Å for the C atom, and the sum is 2.05 Å. Though the C-Pt dimer length is calculated to be 1.7 Å, the distance between Pt and its nearest C is $\sim 2.08$ Å for Pt adsorbed on the outer wall of the tube. The longest distance between two vertexes of the hexagon is $\sim 2.8$ Å, which is too small to provide enough room for Pt passing through. When passing through the wall of the tube, Pt would make a big hole on the wall. As shown in Fig. 3, one can see that some of the C-C bonds are broken. On experiment, the tubes in fact usually are twisted, which may introduce some defects such as the pentagons and heptagons. The longest distances between vertexes are $\sim 2.3$ Å for the pentagon and $\sim 3.2$ Å for the heptagon, which indicate that the pentagon and heptagon defects do not have enough room for the Pt atom passing through. Considering the experimental observations that the many Pt particles sit on the inner wall of the carbon nanohorn, we would like to say that a Pt atom may enter into the carbon nanohorn through its open mouth or the big hole in its wall which may be introduced when preparing the nanohorn materials.

C. Electronic properties

The electronegativities are 2.2 for Pt and 2.5 for C.\textsuperscript{22} It is not easy to judge by the electronegativity which atom could get charge. We have, for example, studied the charge transfer for the Pt on the (5,5) tube. The total charge of Pt adsorbed on the (5,5) tube was calculated first, and then we calculated the charge of Pt and the (5,5) tube, respectively, by keeping atomic positions as those of Pt adsorbed on the tube. Then we estimated the charge transfer by extracting the charge of the Pt and (5,5) tube from that of the tube with Pt adsorbed on. The results show that some charge is accumulated between Pt and C, which may come from Pt and C atoms. However, by this charge transfer analysis we could not say which atom get electrons from the other one, which indicates that the bonding nature of the C-Pt bond should not be ionic. In Fig. 4, we studied the charge density of the Pt adsorbed on the (5,5) tube and graphene sheet, respectively. The isosurfaces of charge density with the value of 0.5 e/Å$^3$ are plotted. In Fig. 4, the left one is for the (5,5) tube, and the right one is for graphene. There is some charge accumulated between the metal atom and tube (or graphene), which suggest that the covalent-like Pt-C bonds are developed. The well-known electron localization function (ELF)\textsuperscript{26,27} was applied to study the localization of the electrons of Pt on (5,5) as well. The ELF is introduced in quantum chemistry to measure the parallel spin correlation by defining conditional probability of finding an electron in the neighborhood of
the nature of the interaction between Pt and C atoms may be close to the van der Waals interaction and outer wall of the tube, and to 1.73 eV for Pt on graphene; the binding energy reaches to above 2.0 eV for Pt on the tube.

The ELF analysis of the studied nanotubes. The ELF analysis, the charge density study, and the binding energy for Pt adsorbed on the (5,5) tube (which is above 2.0 eV, see Table I), we could conclude that C-Pt bonds should be weak covalentlike bonds.

The coating of Au and Al metal atoms on carbon nanotubes was studied with experiment. These metal atoms were reported to condense on the suspended nanotube to form isolated discrete particles. The interaction was presumed to be weak van der Walls in nature. Zhang et al. studied the coating of Pt atoms on the wall of the carbon nanotube, and found that Pt formed small discrete particles also, which suggested the weak interaction between Pt and nanotube. In the optimized configurations of the Pt adsorbed on carbon nanotube and graphene sheet, the distances between the Pt atom and its nearest C atoms are ~2.08 Å for Pt on the outer wall of the (5,5) tube, and ~2.11 Å for it on graphene, which are close to the van der Waals interaction distance. Judged from the distance, one may also image that the nature of the interaction between Pt and C atoms may be van der Waals. However, considering the facts: (a) the calculated binding energy reaches to above 2.0 eV for Pt on the outer wall of the tube, and to 1.73 eV for Pt on graphene; and (b) as shown in Fig. 4, some charge accumulation between C and Pt atoms could be observed in our charge density analysis, we would not like to attribute the nature of interaction between Pt and C atoms to van der Waals.

The band structures and the projected density of states (PDOS) on Pt atoms for Pt-deposited (5,5) and (8,0) nanotubes are shown in Fig. 5. The band structures of the free standing (5,5) and (8,0) nanotubes become complex, which are due to the bonding of Pt atoms to nanotubes and the destruction of the high symmetries as well. The band structures show that the adsorption of Pt atoms do not change the conductive properties of the studied nanotubes. The (5,5) is a metallic nanotube, and the (8,0) is a semiconductive nanotube. The PDOS and the band structures seem to support the conclusion of the binding nature analysis which suggests the weak covalentlike bonding between Pt and its nearby C atoms.

The weak interaction between the metal atom and its nearby C atoms was proposed to be one of the reasons for the formation of the discrete metal particles on the wall of the nanotube. The classical nucleation theory was successfully used to explain the condensation of various metal atoms on the wall of the nanotube. The binding energy plays a crucial role. The weak binding strength hints that the diffusion barrier could be low. We could say that the smaller the binding energy, the lower the diffusion barrier, and then the faster the metal atoms diffuse on the wall of the nanotube.

Another electron with the same spin, and is defined as

\[
\text{ELF} = \frac{1}{1 + [D/D_b]^2},
\]

\[
D = \frac{1}{2} \sum_i |\Delta \Phi_i|^2 - \frac{1}{8} \frac{|\Delta \phi|^2}{\rho},
\]

\[
D_b = \frac{3}{10} (3 \pi^2)^{2/3} \rho^{3/5},
\]

where \( \Phi_i \) is the Kohn-Sham orbital, and \( \rho \) is the local density. The ELF analysis of the (5,5) tube with Pt adsorbed on shows that the localization of electrons between C and Pt is not strong. Combining the ELF analysis, the charge density analysis, and the binding energy for Pt adsorbed on the (5,5) tube (which is above 2.0 eV, see Table I), we could conclude that C-Pt bonds should be weak covalentlike bonds.

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diffusion could enhance the probability of the metal atom or even cluster to meet the other ones. The weak binding between the metal atom and its nearby C atoms may be weaker than that between metal atoms. The metal atoms could then merge into isolated particles once they meet each other. Our results on the weak binding could support this explanation. Pt is weakly bonded on the wall of the tube and could move rapidly on the wall to meet other metal atoms. In our study, we have also simulated the adsorption of four Pt atoms on the outer wall of the carbon nanotube. These four Pt atoms are found to form a tetrahedron structure, which is a three-dimensional structure and adheres to the wall of the nanotube. The structure of a rhombus ring coating on the wall was found to be about 0.7 eV higher in total energy. This indicates that the formation of the three-dimensional structure of Pt cluster is preferable and the binding strength between Pt atoms should be comparable to the one between the Pt atom and its nearby C atoms, which should be one crucial factor for the formation of Pt particles on the wall of the carbon nanotube.

IV. CONCLUSIONS

We have performed the first-principles method on the study of the interaction between a single Pt atom and a carbon nanotube in detail. Some results of graphene are also included for a comparative study. The best adsorption site of Pt on a carbon nanotube is the bridge-type site, and the outer one is preferable. The curvature does affect the adsorption. For the studied small radius carbon nanotubes, the binding on the outer site is stronger by about 1.5 eV than that on the inner one. However, for the larger (10,10) tube the binding energy difference decrease much, which is only about 0.6 eV. Compared to the binding energy of Pt on graphene (~1.73 eV), the binding on the outer wall due to the curvature becomes stronger while it becomes weaker on the inner wall. The energy barrier for Pt diffusing into the (10,10) nanotube through the wall of the tube is predicted to be above 6 eV [based on the dimer method studies on the (10,10) tube], which suggests that it is in fact very hard for Pt entering into the nanotube through the wall. The charge density analysis and the binding strength indicate that Pt-C bonding should be weak covalentlike binding in nature.

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