

# Linking Molecular Switches to Platinum Electrodes Studied with DFT

Timo Jacob\*

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Mario Blanco and William A. Goddard III

Materials and Process Simulation Center, Beckman Institute (139-74), California Institute of Technology, Pasadena, California 91125

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Density functional theory (DFT) with the B3LYP exchange–correlation functional was used to study new linkages between electrodes and molecular switches (alligator-clip compounds) for molecular electronics using Pt electrodes. Starting with the commonly used molecule 3-methyl-1,2-dithiolane (MDTL), which forms a five-membered ring structure in the gas phase, we found the most stable structure of the adsorbed MDTL to be the ring-opened molecule (32.44 kcal/mol) with each S atom bound to a surface bridge position. Afterward we calculated binding energies and geometries for a variety of different compounds: S/O-based (oxathiolanes), O-based (methanol), N-based (imidazole, 1,2,3-triazole, purine, 2,4-diazapentane), and P-based molecules (methylphosphino, PCH<sub>3</sub>, 3-methyl-1,2-diphospholane before (MDPL) and after H dissociation (H<sub>diss</sub>-MDPL)). Among these alternative linkage molecules we find that only the P-based compounds lead to much higher binding energies than MDTL. The best compromise between strong surface attachment and mechanical stability provide the MDPL molecules. For the cis-ring-closed structure of MDPL a binding energy of 47.72 kcal/mol was calculated and even 54.88 kcal/mol for the ring-opened molecule. In the case of H-dissociative adsorption, which leads to H<sub>diss</sub>-MDPL, both binding energies increase to 53.74 (ring-closed) and 74.99 kcal/mol (ring-opened). Thus, MDPL provides a much more stable link to the metal surface and might increase the conductance between molecular switch and electrode. In addition, the minor differences in charge and spin-density distribution between MDTL and MDPL might indicate similar properties for the attachment of the molecular switch to either of both alligator-clip compounds.

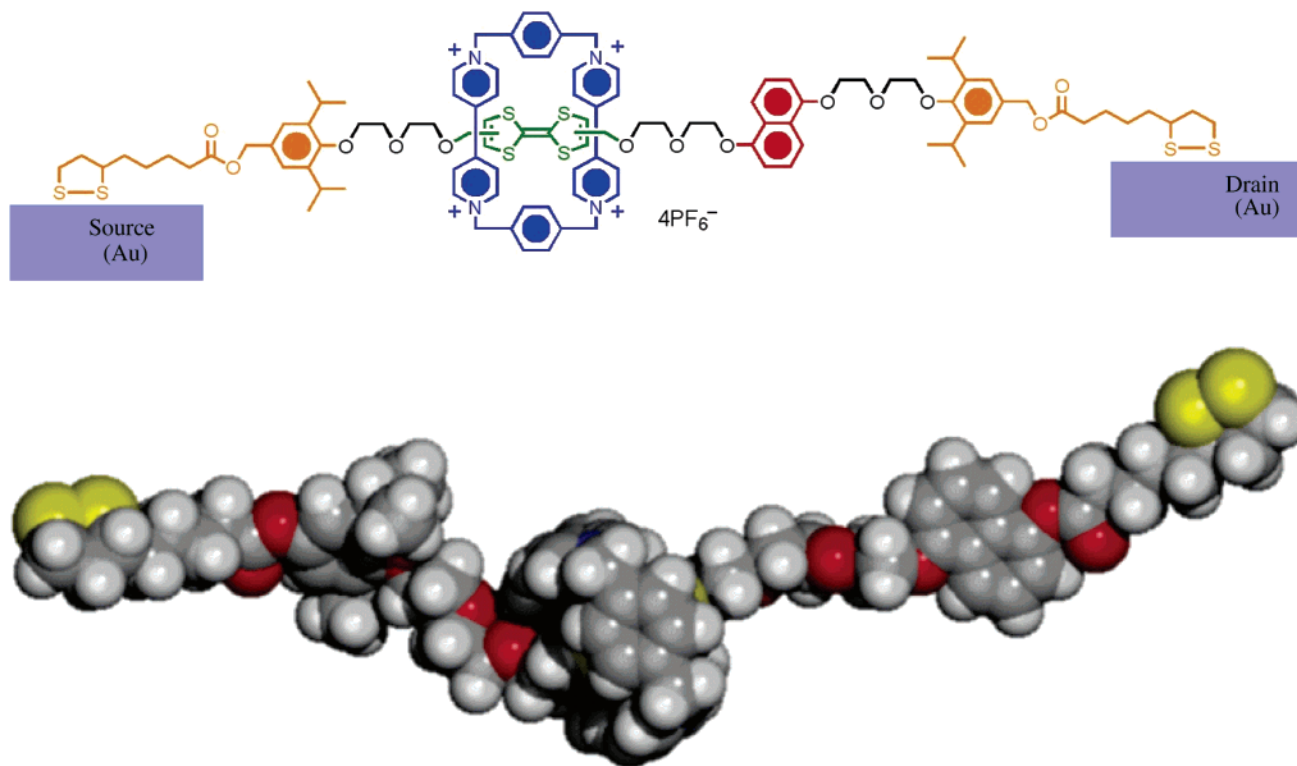
## 1. Introduction

The term “alligator-clip molecule” (linkage between electrodes and molecular switches) first appeared in the literature to designate the molecular components for adhesion of molecular scale wires to gold probes and surfaces.<sup>1</sup> Alligator-clip compounds have been applied to optimize the metal/organic interface to decrease the Schottky barrier for electron injection in light-emitting diodes (LEDs).<sup>2</sup> Compounds with electron-donating moieties and carboxylic acid alligator-clips were synthesized for the formation of SAMs (self-assembling monolayers) on aluminum oxide contacts.<sup>1,3</sup> Combinatorial synthesis of oligo(phenylene ethynylene)s with the alligator-clip 4-iodo-1-thioacetylbenzene has been employed to generate libraries for molecular electronics applications.<sup>4</sup> Oligo(phenylene ethynylene) backbones containing a terminal nitrile group alligator-clip as a means of attachment to a metal surface have also been investigated.<sup>5</sup> 4-(Thioacetyl)iodobenzene and isonitrile alligator-clips have been utilized and their cyclic voltammograms compared to the devices without them.<sup>6</sup>

After significant developments in molecular electronics (molecular switches and diodes) based on mechanically interlocked molecules such as catenanes and rotaxanes strung between metal electrodes through chemical manipulations have been demonstrated in the laboratory,<sup>7–9</sup> the effort is now shifting toward improving their current–voltage characteristics.<sup>10–12</sup>

Recent theoretical work<sup>13</sup> indicates that the changes in the HOMO and LUMO characteristics as a function of the interlocking configuration are responsible for the current–voltage characteristics. The effect of the alligator-clip molecule was not determined in these theoretical studies. The first devices featured an alligator-clip linker compound, 1,2-dithiolane, to attach one end of the molecular device to the metal surface and a less covalent linkage at the other, tetraarylmethane.<sup>14</sup> These experimental measurements on gold electrodes have shown that attaching 3-alkyl-1,2-dithiolanes (see Figure 1) to both ends dramatically increases the on–off current ratio of these devices by 2 orders of magnitude, leading to a symmetric response as a function of source to drain voltage. Low-temperature transport measurements using Pt break junctions provide information relating to such molecular properties as electronic and vibrational states, and Coulomb, exchange, and spin-magnetic field interactions.<sup>14</sup> But it is not known whether these improvements are the result of surface binding energetics or due to changes in the molecular orbitals across the entire device. On the basis of quantum mechanical (QM) studies, we concluded that the performance of the current generation of S-based alligator-clips might be improved by increasing the binding to the metal surfaces, reducing the electrical resistance. Consequently, we examined alternative P-based alligator-clips, which we find lead to stronger binding to the Pt surface than do the S-based systems. Since Ratner and co-workers found that the chemisorption process (thiol complexes on gold electrodes) mainly influences the anchoring atom and the metal surface but not the rest of the

\* To whom correspondence should be sent, e-mail: jacob@fhi-berlin.mpg.de.



**Figure 1.** Chemical structure of the molecular component ([2]rotaxane) in the Stoddart–Heath programmable molecular switch. The ring molecule CBPQT (blue in the upper picture) shuttles between the TTF (green) and the naphthyl (red) sites upon application of a large voltage gradient. The state of the switch can be probed by application of a smaller field, where the TTF location has low current but the naphthyl location has current 15 times higher.

alligator-clip molecule,<sup>15–17</sup> we expect that this will lead to improved device performance.

## 2. Theoretical Methods

To determine the binding strength of various alligator-clips to the surface, we used the B3LYP flavor of spin-unrestricted density functional theory (DFT). This density functional includes the generalized gradient approximation plus partly exact Hartree–Fock exchange.<sup>18,19</sup> The 60 core electrons (1s–4f) of each Pt atom were treated by the Hay and Wadt core–valence relativistic effective-core potential (ECP).<sup>20</sup> The remaining 18 valence electrons were treated with the LACVP\*\* basis set. All other elements were described with the 6-31G\*\* basis set, treating all electrons explicitly. In former studies these parameters were established as being suitable to describe organics on the Pt(111) surface.<sup>21,22</sup> All ab initio cluster calculations were carried out with the Jaguar program.<sup>23</sup> For the procedure that was applied to evaluate the correct ground spin state we refer to refs 21 and 22.

In this work, we focus on the adsorption of various compounds to Pt(111) to study trends in their behavior as potential alligator-clip molecule. Since the steady-state of a working molecular switch (as shown in Figure 1) can be described by the Landauer formalism,<sup>24</sup> which only uses information on the molecular orbitals and energy eigenvalue spectra of the leads (Pt surface + alligator clip compound), comparing the charge- and spin-density distribution should be sufficient to reproduce the trends.

## 3. Results and Discussion

In the following we will first discuss the surface models used throughout the present work. Afterward we will study the

adsorption of various compounds on the Pt(111) surface. The ground spin-states as well as structural information on each molecule in gas-phase can be found in Table 1 of the Supporting Information (SI-Table 1). Binding energies, geometries, ground spin-states, and partial charges after adsorption are summarized in Tables 1 and 2 for MTDL and MDPL, respectively. For all other compounds studied here this information can be found in SI-Tables 1 and 2.

**3.1. Surface Model.** In order to represent the surface by a finite system one has to ensure that the used cluster leads to cluster-size converged results. Thus, in previous studies<sup>21</sup> we showed that to represent the chemistry on the Pt(111) surface requires a cluster of three-layers with at least 28 atoms, and we have shown<sup>22</sup> that a 35 atom three-layer Pt cluster (hereafter Pt<sub>35</sub>) is quite suitable for adsorption studies of more complex molecules (as in the present paper). Pt<sub>35</sub> consists of 14 atoms in the first layer, 13 in the second layer, and 8 atoms in the third layer (see Figure 2). To find the correct ground state structure, we first considered several plausible initial structures and spin states of each adsorbate molecule and optimized them on the one-layer Pt<sub>12</sub> cluster. Although Pt<sub>12</sub> leads to the wrong binding energies, we used it to study several possible adsorption geometries. Starting with the most stable structure on Pt<sub>12</sub>, the final energetics was calculated by reoptimizing the geometries on the Pt<sub>35</sub> cluster. Since we were only interested in the most stable structures, the following discussion on each compound mostly refers only to the most stable system. To include the dominant surface relaxation effects the four central Pt atoms in the top layer were also allowed to freely relax under the influence of the adsorbate.

**3.2. 3-Methyl-1,2-dithiolane (MDTL).** In order to obtain a deeper insight into the connection between the Pt electrode and the molecular component, we first studied the adsorption of the

**TABLE 1: Ground Spin-State and Binding Energies for Adsorbed MDTL on Pt<sub>35</sub><sup>a</sup>**

system	spin-state	$E_{\text{bind}}$ [kcal/mol]	distances [Å]	angles [deg]	$Q(\text{ads.})$ [e]
Pt <sub>35</sub>	11				
Pt <sub>35</sub> -3-methyl-1,2-dithiolane ring-opened (Figure 4A)	11	32.44 4	C <sub>5</sub> -S <sub>1</sub> = 1.866 S <sub>2</sub> -C <sub>3</sub> = 1.883 C <sub>3</sub> -C <sub>4</sub> = 1.535 C <sub>4</sub> -C <sub>5</sub> = 1.529 C <sub>3</sub> -C <sub>6</sub> = 1.524 S <sub>1</sub> -Pt <sub>1</sub> = 2.418 S <sub>1</sub> -Pt <sub>2</sub> = 2.367 S <sub>2</sub> -Pt <sub>3</sub> = 2.437 S <sub>2</sub> -Pt <sub>4</sub> = 2.396 S <sub>2</sub> -Pt <sub>5</sub> = 2.909	S <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 109.4 C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 118.6 C <sub>4</sub> -C <sub>5</sub> -S <sub>1</sub> = 119.2 C <sub>4</sub> -C <sub>3</sub> -C <sub>6</sub> = 112.3 S <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub> = 110.1 S <sub>1</sub> -Pt <sub>1</sub> -Pt <sub>2</sub> -Pt <sub>3</sub> = 106.7 S <sub>2</sub> -Pt <sub>3</sub> -Pt <sub>4</sub> -Pt <sub>5</sub> = 81.7	+0.833
ring-closed (Figure 4B)	11	30.38 4	C <sub>5</sub> -S <sub>1</sub> = 1.862 S <sub>1</sub> -S <sub>2</sub> = 2.182 S <sub>2</sub> -C <sub>3</sub> = 1.874 C <sub>3</sub> -C <sub>4</sub> = 1.528 C <sub>4</sub> -C <sub>5</sub> = 1.527 C <sub>3</sub> -C <sub>6</sub> = 1.524 S <sub>1</sub> -Pt <sub>2</sub> = 2.367 S <sub>2</sub> -Pt <sub>3</sub> = 2.334	S <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 106.1 C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 110.7 C <sub>4</sub> -C <sub>5</sub> -S <sub>1</sub> = 107.8 C <sub>4</sub> -C <sub>3</sub> -C <sub>6</sub> = 115.6 C <sub>5</sub> -S <sub>1</sub> -S <sub>2</sub> = 94.3 S <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub> = 110.1 Pt <sub>2</sub> -S <sub>1</sub> -S <sub>2</sub> -C <sub>3</sub> = 112.9 S <sup>1</sup> -(Pt <sub>2</sub> -S <sub>1</sub> -S <sub>2</sub> -Pt <sub>3</sub> ) = 7.2	+1.101

<sup>a</sup> In addition, important distances and angles are given (for labels, see Figure 4).

commonly used alligator-clip molecule 3-methyl-1,2-dithiolane (MDTL). Optimizing the geometry of the gas-phase molecule leads to two almost degenerate five-member ring structures (C<sub>5</sub>-S<sub>1</sub>-S<sub>2</sub>-C<sub>3</sub> dihedral angle of 5.0 and 28.8°) with an energy difference of less than 0.2 kcal/mol (see Figure 3A and B). The energy to break the S-S bond in the cyclic MDTL molecule is 50.48 kcal/mol, that is 6.42 kcal/mol lower than for the same molecule in a linear conformation (C<sub>2</sub>H<sub>5</sub>-S-S-C<sub>3</sub>H<sub>7</sub>, see Figure 3C). This energy difference can be thought of as ring strain energy, which could act as a spring-loaded contribution to the surface adsorption of MDTL, an effect, which has also been found experimentally.<sup>25,26</sup>

Adsorbing MDTL on the Pt(111) surface leads to a variety of stable structures. SI-Figure 1 shows the four most stable configurations on the Pt<sub>12</sub> cluster checked for MDTL. Afterward we put the most stable ring-closed and ring-opened structure as initial configuration on Pt<sub>35</sub> and reoptimized the system. Before and after adsorption we found no change in the net spin ( $S = 11$ ) for both configurations. For the ring-opened structure (Figure 4A) we calculate a binding energy of 32.44 kcal/mol, which is 2.06 kcal/mol more stable than the ring-closed system (Figure 4B). The ring-opened structure of alkanedithiol-compounds was recently confirmed by electrochemical in situ STM studies.<sup>27</sup> In the ring-opened geometry both sulfur form short S-Pt bonds (2.367 Å to 2.437 Å) to two surface atoms, which indicate two covalent bonds between each sulfur and two Pt-atoms (on  $\mu_2$  bridge positions). This does not conform with observing no change in the net spin due to adsorption. However, according to the Mulliken population analysis (see Figure 7) every sulfur atom donates  $\approx 0.30e$  to the surface, while keeping the charge distribution of the rest of the adsorbate molecule nearly unchanged. It seems that within the adsorption the unpaired electron at each sulfur, which is created by opening the five-member ring, is transferred to the Pt cluster, suggesting that each S can be thought of as S<sup>+</sup>. In order for the moiety to bind to the surface, a lone electron pair at each sulfur has to spin-unpair, finally resulting in two covalent bonds between each sulfur and the surface. This would explain that no change in the net spin was observed. Despite of this, forming two covalent bonds results in an increase of the net spin density located on each sulfur atom (Figure 8). Interestingly, the increase in spin density on S<sub>1</sub> (0.23) is around twice the value calculated for S<sub>2</sub>

(0.11). The lower value for S<sub>2</sub> seems to be a consequence of the additional methyl group substituted to the carbon atom bound to S<sub>2</sub>.

A comparison of the bond angles of MDTL in gas-phase and after adsorption shows a significant increase of the C<sub>3</sub>-C<sub>4</sub>-C<sub>5</sub> and C<sub>4</sub>-C<sub>5</sub>-S<sub>1</sub> angles by about 10°, but nearly no change for all other valence angles. Thus, the steric interaction and stress within the carbon-framework seems to restrict the S<sub>1</sub>-S<sub>2</sub> distance in such a way that only two surface bridge sites can fulfill these steric requirements. In addition, the increase of these angles confirms the already mentioned spring-loaded contribution to the surface adsorption. Indeed, all angles of the chemisorbed species are close to the structure of the triplet state formed by breaking the S-S bond (e.g., C<sub>3</sub>-C<sub>4</sub>-C<sub>5</sub> and C<sub>4</sub>-C<sub>5</sub>-S<sub>1</sub> are 115–116°). Taking into account the energy to break the molecular MDTL ring-structure (50.48 kcal/mol), the covalent surface bond (contribution to the adsorption energy) is approximately 41.5 kcal/mol per sulfur atom.

Adsorbing to the surface without breaking the five-membered ring structure leads to a binding energy of 30.38 kcal/mol. Compared to the free molecule in gas-phase the S-S bond distance increases only by 0.033 Å, which indicates that the covalent S-S bond is still intact. Although each S has only two unpaired electrons, besides the S-S and the S-C bond it forms another covalent bond to one Pt surface atom (2.334 and 2.367 Å), leading to a  $\mu_2$  bridge binding. Similar to the already discussed behavior for the ring-opened MDTL in the ring-closed system each S atom donates 0.41e to the cluster, allowing again each sulfur to form three covalent bonds in total. Since the S-S length increases only insignificantly due to adsorption all other MDTL distances and angles also show only minor changes.

**3.3. S/O-Based Compounds.** Since our goal was to find a compound that has better surface binding properties than MDTL, we started to study the effect of replacing a single sulfur atom with its homologous element oxygen. This leads to either 3-methyl-1,2-oxathiolane or 3-methyl-2,1-oxathiolane (see SI-Figure 2). After performing the same procedure to determine the most stable adsorption structure as for MDTL (see section 3.2.), we found comparable surface geometries (SI-Figure 3, parts A and B). Both molecules are ring-opened and each sulfur and oxygen binds to two Pt atoms ( $\mu_2$  bridge sites). All distances and angles within the carbon framework deviate from the values of adsorbed ring-opened MDTL by <0.02 Å, and <2° respec-

**TABLE 2: Ground Spin-State and Binding Energies for Adsorbed MDPL (before and after H Dissociation) on Pt<sub>35</sub><sup>a</sup>**

system	spin-state	$E_{\text{bind}}$ [kcal/mol]	distances [ $\text{\AA}$ ]	angles [deg]	$Q(\text{ads.})$ [e]
Pt <sub>35</sub>	11				
Pt <sub>35</sub> -3-methyl-1,2-diphospholane ring-opened (Figure 5A)	11	54.88 4	C <sub>5</sub> -P <sub>1</sub> = 1.864 P <sub>2</sub> -C <sub>3</sub> = 1.894 C <sub>3</sub> -C <sub>4</sub> = 1.535 C <sub>4</sub> -C <sub>5</sub> = 1.549 C <sub>3</sub> -C <sub>6</sub> = 1.531 P <sub>1</sub> -Pt <sub>1/2</sub> = 2.261 P <sub>2</sub> -Pt <sub>3/4</sub> = 2.301 P <sub>2</sub> -Pt <sub>5</sub> = 3.016	P <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 113.3 C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 115.1 C <sub>4</sub> -C <sub>5</sub> -P <sub>1</sub> = 114.7 C <sub>4</sub> -C <sub>3</sub> -C <sub>6</sub> = 111.6 P <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub> = 112.3 P <sub>1</sub> -Pt <sub>1</sub> -Pt <sub>2</sub> -Pt <sub>3</sub> = 103.6 P <sub>2</sub> -Pt <sub>3</sub> -Pt <sub>4</sub> -Pt <sub>5</sub> = 88.9	+1.199
cis-ring-closed (Figure 5B)	11	47.71 8	C <sub>5</sub> -P <sub>1</sub> = 1.866 P <sub>1</sub> -P <sub>2</sub> = 2.193 P <sub>2</sub> -C <sub>3</sub> = 1.873 C <sub>3</sub> -C <sub>4</sub> = 1.545 C <sub>4</sub> -C <sub>5</sub> = 1.542 C <sub>3</sub> -C <sub>6</sub> = 1.529 P <sub>1</sub> -Pt <sub>2</sub> = 2.251 P <sub>2</sub> -Pt <sub>3</sub> = 2.248 C <sub>3/4/5/6</sub> -H = 1.094 P <sub>1/2</sub> -H = 1.411	C <sub>5</sub> -P <sub>1</sub> -P <sub>2</sub> = 95.4 P <sub>1</sub> -P <sub>2</sub> -C <sub>3</sub> = 96.0 P <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 106.7 C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 112.2 C <sub>4</sub> -C <sub>5</sub> -P <sub>1</sub> = 107.9 C <sub>4</sub> -C <sub>3</sub> -C <sub>6</sub> = 114.4 P <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub> = 112.0 Pt <sub>2/3</sub> -P <sub>1/2</sub> -H = 120.5 C <sub>3</sub> -P <sub>2</sub> -P <sub>1</sub> -C <sub>5</sub> = 1.0 S <sup>  </sup> -(C <sub>3</sub> -P <sub>2</sub> -P <sub>1</sub> -C <sub>5</sub> ) = 36.2	+1.214
trans-ring-closed (Figure 5C)	11	39.27 2	C <sub>5</sub> -P <sub>1</sub> = 1.895 P <sub>1</sub> -P <sub>2</sub> = 2.228 P <sub>2</sub> -C <sub>3</sub> = 1.871 C <sub>3</sub> -C <sub>4</sub> = 1.537 C <sub>4</sub> -C <sub>5</sub> = 1.536 C <sub>3</sub> -C <sub>6</sub> = 1.529 P <sub>2</sub> -Pt <sub>2</sub> = 2.252 P <sub>1</sub> -H = 1.439 P <sub>2</sub> -H = 1.418 Pt <sub>3</sub> -H = 2.272	C <sub>5</sub> -P <sub>1</sub> -P <sub>2</sub> = 89.8 P <sub>1</sub> -P <sub>2</sub> -C <sub>3</sub> = 98.8 P <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 106.3 C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 110.8 C <sub>4</sub> -C <sub>5</sub> -P <sub>1</sub> = 108.5 C <sub>4</sub> -C <sub>3</sub> -C <sub>6</sub> = 114.9 P <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub> = 112.3 Pt <sub>2</sub> -P <sub>2</sub> -P <sub>1</sub> /C <sub>3</sub> = 117.9 C <sub>3</sub> -P <sub>2</sub> -P <sub>1</sub> -C <sub>5</sub> = 10.1	+0.936
Pt <sub>35</sub> -3-methyl-1,2-diphospholane (H dissociated) ring-opened (Figure 6A)	10	74.98 8	C <sub>5</sub> -P <sub>1</sub> = 1.877 P <sub>1</sub> -P <sub>2</sub> = 3.600 P <sub>2</sub> -C <sub>3</sub> = 1.855 C <sub>3</sub> -C <sub>4</sub> = 1.550 C <sub>4</sub> -C <sub>5</sub> = 1.545 C <sub>3</sub> -C <sub>6</sub> = 1.538 P <sub>1</sub> -Pt <sub>7/8</sub> = 2.261 P <sub>1</sub> -Pt <sub>6</sub> = 2.311 P <sub>2</sub> -Pt <sub>2/3</sub> = 2.227 P <sub>2</sub> -Pt <sub>6</sub> = 2.238	P <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 111.6 C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 116.8 C <sub>4</sub> -C <sub>5</sub> -P <sub>1</sub> = 117.0 C <sub>4</sub> -C <sub>3</sub> -C <sub>6</sub> = 112.2 P <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub> = 109.4 Pt <sub>6</sub> -P <sub>1</sub> -C <sub>5</sub> = 109.3 Pt <sub>6</sub> -P <sub>2</sub> -C <sub>3</sub> = 116.1 C <sub>3</sub> -P <sub>2</sub> -P <sub>1</sub> -C <sub>5</sub> = 0.1 S <sup>⊥</sup> -(C <sub>3</sub> -P <sub>2</sub> -P <sub>1</sub> -C <sub>5</sub> ) = 0.4	+1.022
ring-closed (Figure 6B)	10	53.73 8	C <sub>5</sub> -P <sub>1</sub> = 1.898 P <sub>1</sub> -P <sub>2</sub> = 2.235 P <sub>2</sub> -C <sub>3</sub> = 1.895 C <sub>3</sub> -C <sub>4</sub> = 1.532 C <sub>4</sub> -C <sub>5</sub> = 1.538 C <sub>3</sub> -C <sub>6</sub> = 1.524 P <sub>1</sub> -Pt <sub>3</sub> = 2.339 P <sub>2</sub> -Pt <sub>2</sub> = 2.324	C <sub>5</sub> -P <sub>1</sub> -P <sub>2</sub> = 93.9 P <sub>1</sub> -P <sub>2</sub> -C <sub>3</sub> = 93.9 P <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 106.8 C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 109.2 C <sub>4</sub> -C <sub>5</sub> -P <sub>1</sub> = 109.6 C <sub>4</sub> -C <sub>3</sub> -C <sub>6</sub> = 117.3 P <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub> = 111.5 C <sub>3</sub> -P <sub>2</sub> -P <sub>1</sub> -C <sub>5</sub> = 7.2 S <sup>  </sup> -(C <sub>3</sub> -P <sub>2</sub> -P <sub>1</sub> -C <sub>5</sub> ) = 15.0	+0.869

<sup>a</sup> In addition, important distances and angles are given (for labels, see Figures 5 and 6).

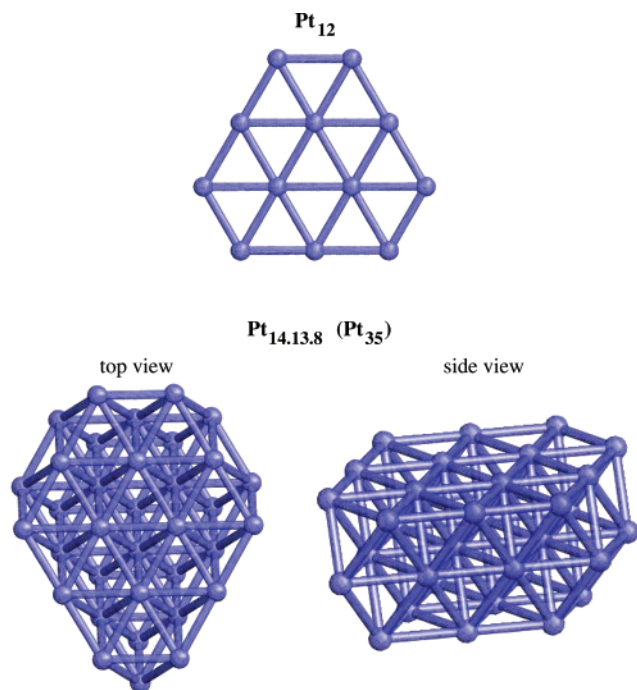
tively. The same holds true for the S-Pt distances. Since for both adsorbates the O-C distance is  $\approx 1.42 \text{ \AA}$ , which indicates a single covalent bond, there remains an unpaired electron at each oxygen. However, the oxygens gain  $\approx 0.48e$  mainly from the cluster, which spin-pair to the remaining oxygen valence electron. Thus, the surface attachment can be thought of two Pt-O donor-acceptor bonds with oxygen lone pair orbitals. This also explains the lower binding energies calculated for both oxathiolanes compared to ring-opened MDTL:  $\Delta E = 20.47 \text{ kcal/mol}$  for 3-methyl-1,2-oxathiolane and  $\Delta E = 21.00 \text{ kcal/mol}$  for 3-methyl-2,1-oxathiolane.

The question arises whether the weak surface binding of both oxathiolanes is a result of forming donor-acceptor Pt-O bonds rather than covalent bonds. Therefore, we calculated the adsorption of methanol on Pt(111) (see SI-Figure 3C). Since both unpaired valence electrons of O are used to bind H and the methyl group, we expect the same type of Pt-O bond as for the oxathiolanes. Indeed, the oxygen has the same net charge of  $-0.46e$ , which now mainly comes from the hydrogen and the methyl-group, but not from the Pt cluster. In addition, the

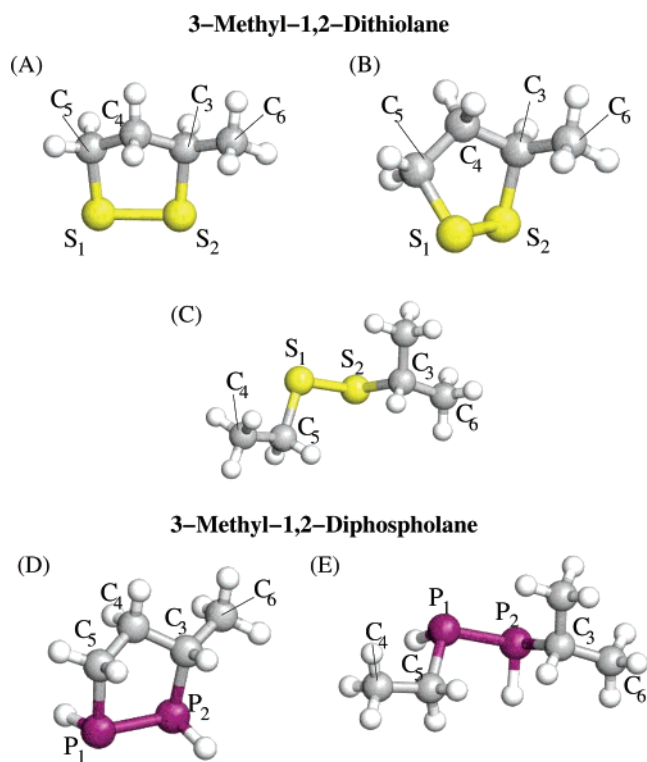
Pt-O bond distance of  $1.44 \text{ \AA}$  is comparable to both oxathiolanes ( $1.42 \text{ \AA}$ ). This results in an on top binding of methanol, using the remaining oxygen lone pair orbital. However, now the binding energy is  $11.72 \text{ kcal/mol}$  that is close to the value obtained for 3-methyl-1,2-oxathiolane. This value is in good agreement with experimental values<sup>28,29</sup> of  $9.2-11.5 \text{ kcal/mol}$  and other DFT calculations employing Pt clusters<sup>30</sup> ( $15.0 \text{ kcal/mol}$ ) or periodic systems<sup>31</sup> ( $8.8 \text{ kcal/mol}$ ).

We conclude, that oxygen is the reason for the weaker surface attachment of both oxathiolanes. On one hand, O is highly electronegative and gains  $\approx 0.46e$ , which also disturbs the charge distribution of the remaining adsorbates and weakens the Pt-S bonds. On the other hand, the carbon-framework causes a tilting of the three oxygen bonds (two Pt-O and one O-C bonds), resulting in angles different from  $90^\circ$  (directions of the oxygen p-orbitals). This strain also weakens the Pt-O bonds (compared to methanol).

**3.4. N-Based Compounds.** Since O-based compounds led to lower binding energies compared to MDTL, we studied the role of moving to the left in the periodic table. Thus, we started

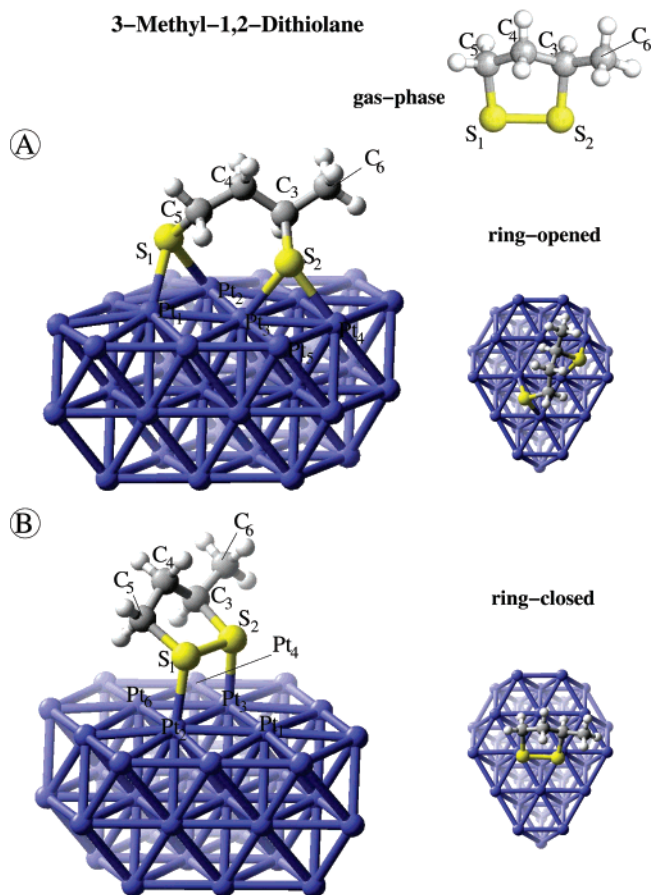


**Figure 2.** Clusters that were used to model the Pt(111) surface.



**Figure 3.** Different structures for the 3-methyl-1,2-dithiolane and 3-methyl-1,2-diphospholane gas-phase molecules. Structures A and D are the most stable ones.

with N-based compounds (see SI-Figures 2 and 4), which seemed to have promising effects and further applications. For example, in the nonrelated field of fuel cell research it was found that imidazole poisons the Pt surface at the electrodes.<sup>32</sup> In order to bind to the surface, imidazole uses the lone pair orbital on N<sub>3</sub> and attaches on top of a Pt atom with a distance of 2.117 Å and a binding energy of 26.50 kcal/mol, which explains the poisoning effect mentioned before. Both the binding energy and bond distance are in good agreement with periodic DFT-calculations of 0.25ML imidazole adsorbed on Pt(111)<sup>33</sup> obtain-

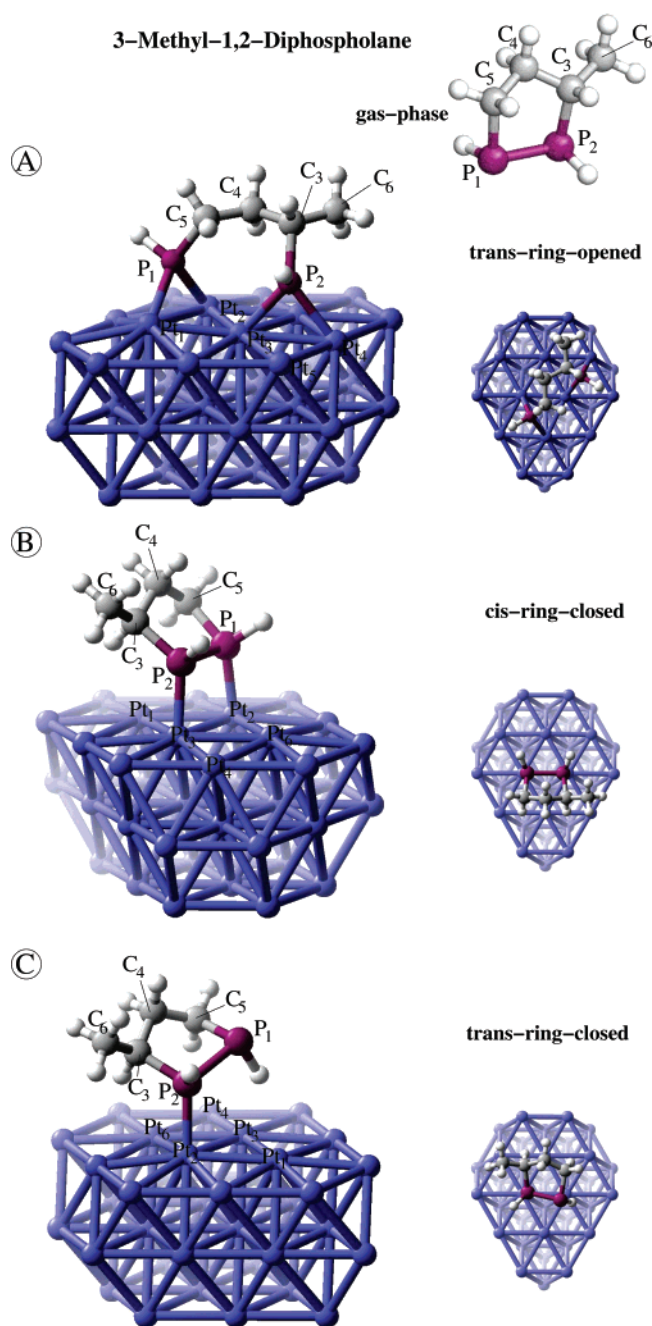


**Figure 4.** Structures of the commonly used alligator-clip molecule MDTL in gas-phase and adsorbed on the Pt(111) surface.

ing 21.1 kcal/mol and  $d(\text{N}_3\text{-Pt}) = 2.10$  Å. As a result of the lone pair binding imidazole donates a charge of 0.342e to the cluster, which mainly comes from N<sub>3</sub>. Since there is no spin pairing that involves electrons from the cluster, this corresponds with observing no spin change due to adsorption (pure Pt<sub>35</sub> also has  $S = 11$ ). Moreover, N<sub>3</sub> and N<sub>1</sub> still keep their different electronic character (see above), as indicated by only slight N–C distance changes ( $<0.007$  Å). The orientation of the adsorbate is perpendicular to the surface with C<sub>2</sub> and C<sub>4</sub> being above  $\mu_3$  3-fold surface sites. The H atoms bound to C<sub>2</sub> and C<sub>4</sub> provide further stabilization of the adsorbate position.

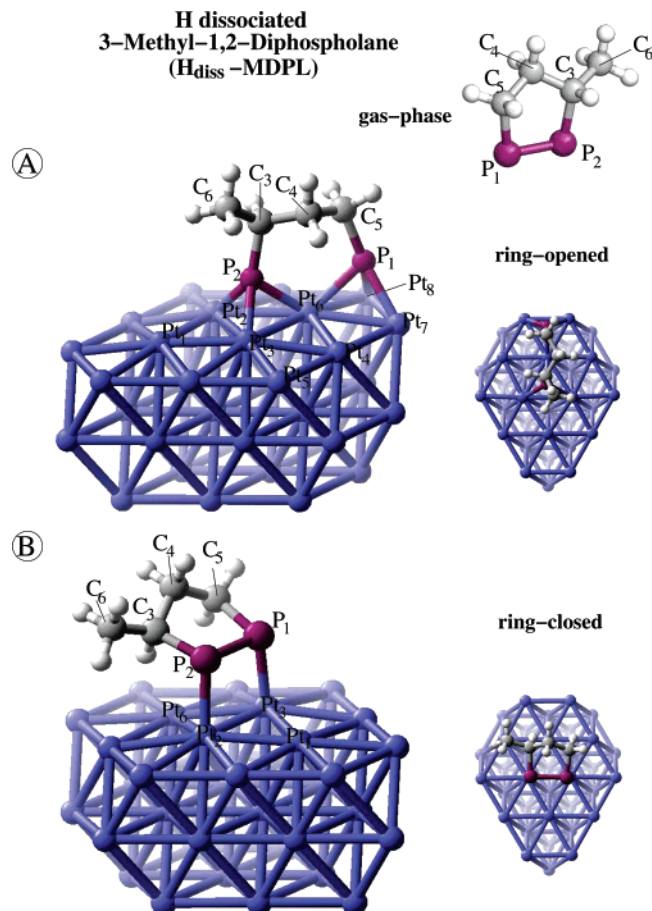
Because of an electronic structure similar to imidazole the binding of 1,2,3-triazole to Pt<sub>35</sub> (SI-Figure 4B) is also realized by the lone pair orbital on N<sub>2</sub> connecting on top of a Pt atom with a binding energy of 17.76 kcal/mol. The 67% lower binding energy compared to imidazole directly corresponds to the 69% less charge transfer from the adsorbate to the Pt cluster, which is a result of the surrounding of N<sub>2</sub>. While in the case of imidazole the surface bound nitrogen is surrounded by two C atoms, in 1,2,3-triazole N<sub>2</sub> is bound to two N atoms, which have a higher electronegativity than carbon. Again, the orientation of the adsorbate is perpendicular to the surface plane with N<sub>1</sub> and N<sub>3</sub> above  $\mu_3$  3-fold sites. Since only N<sub>3</sub> has a hydrogen facing toward the surface, 1,2,3-triazole is rotated by  $\approx 60^\circ$  in order to have this H atom above a  $\mu_3$ -hcp site (rather than a  $\mu_3$ -fcc site).

After imidazole and 1,2,3-triazole, which both form a single bond to the surface, we studied the possibility of having two N–Pt surface bonds in a ring-compound (purine, SI-Figure 4C) and without ring structure (2,4-diazapentane, SI-Figure 4D). Purine consists of a five- and a six-membered ring, which both



**Figure 5.** Structures of the new proposed alligator-clip molecule MDPL in the gas-phase and adsorbed on the Pt(111) surface.

share two C atoms ( $C_4$  and  $C_8$ ). Again, only  $N_7$  is hydrogenated and therefore uses the lone pair orbital for the delocalized  $\pi$  bond, which expands over both rings. Since  $N_3$  and  $N_5$  have lone pair orbitals facing away from their rings, both bind on top of neighboring Pt surface atoms. This leads to purine being located above a Pt–Pt bridge. However, instead of binding twice as strong as imidazole, which would be consistent with having two independent N–Pt bonds, the binding energy is only 24.74 kcal/mol. Since the separation between  $N_3$  and  $N_5$  is 2.431 Å, but the initial surface Pt–Pt distance is 2.775 Å, the adsorbate initiates a surface relaxation while adsorbing. As a result the Pt–Pt distance decreases by 0.07 Å and the N–Pt bonds are 0.06 and 0.09 Å longer compared to Pt<sub>35</sub>-imidazole, leading to a lowering of the purine binding energy. In addition, both  $N_3$  and  $N_5$  donate charge to the cluster (0.433e), which is mainly located at both adjacent Pt atoms and therefore lowers the bond strength, too.



**Figure 6.** Structures of the new proposed alligator-clip molecule MDPL in the gas-phase and adsorbed on the Pt(111) surface after dissociation of the H atoms from both P.

Opening of both purine rings leads to 2,4-diazapentane, which has two N atoms and three CH<sub>2</sub> groups. As for purine, both N atoms use their lone pair orbitals to bind on top of adjacent Pt surface atoms, leading to an adsorption structure comparable to purine. Since the binding energy of 1,2-diazapentane (24.74 kcal/mol) is only 0.01 kcal/mol lower than the value calculated for purine, the absence of both rings seems to have minor influence on the surface binding. However, 1,2-diazapentane donates a charge of 0.547e to the Pt cluster (0.114e more than purine), which seems to cause an unpairing of two spin paired Pt d-electrons and therefore leads to an increase of the ground spin-state by  $\Delta S = 1$  to  $S = 12$ .

**3.5. P-Based Compounds.** Replacing S with O leads to lower binding energies. Therefore, we moved down in the periodic table and tested compounds which include phosphorus instead of N. As with the N-based systems we investigated molecules with one or two P atoms.

**3.5.1. PHCH<sub>3</sub> and PCH<sub>3</sub>.** First we studied methylphosphino (PHCH<sub>3</sub>), which is comparable to methanol with the oxygen replaced by a P atom (SI-Figure 5A). Compared to methanol the P atom of PHCH<sub>3</sub> has an additional unpaired electron, which spin-pairs to a Pt d-electron, resulting in on top binding of methylphosphino. As a result of this covalent bond the binding energy (44.69 kcal/mol) and charge transfer (0.429e) of methylphosphino are much higher than calculated for methanol (11.72 kcal/mol and 0.284e). However, both still show comparable binding geometries.

Dissociating the H atom, which is bound to phosphorus, leads to PCH<sub>3</sub>. Since the P atom has an additional unpaired electron, which wants to spin pair with a cluster d-electron, the adsorbate

twists around and reorients to a structure perpendicular to the surface (see SI-Figure 5B). However, instead of binding at a surface bridge position, phosphorus shows an  $sp^3$  hybridization with tetragonal bonds to carbon and three Pt surface atoms, leading to a 3-fold adsorption site ( $\mu_3$ -fcc). In previous studies<sup>22</sup> we found a similar geometry for  $Pt_{35}$ -CCH<sub>3</sub>, which has a molecular  $^2\Pi$  ground state, but adsorbs after excitation to the  $^4\Sigma^-$  state. In the case of PCH<sub>3</sub>, which has an extra p-electron compared to carbon, the adsorbate (mainly the P atom) donates a charge of 0.598e to the cluster. Thus, PCH<sub>3</sub> more likely adsorbs as  $P^+CH_3$ , leading to the same binding characteristics as CCH<sub>3</sub> ( $^4\Sigma^-$  state). This finally allows the adsorbate to form almost equivalent bonds to three Pt surface atoms (2.237, 2.237, 2.219 Å), and leads to a strong surface bond of 92.93 kcal/mol.

**3.5.2. 3-Methyl-1,2-diphospholane (MDPL).** Because both PHCH<sub>3</sub> and PCH<sub>3</sub> have higher binding energies than MDTL, we studied 3-methyl-1,2-diphospholane (MDPL), which has a structure comparable to MDTL, but with PH groups instead of sulfur atoms (see Figure 5).

Gas-phase MDPL can have a cis and a trans configuration. Between both orientations the trans-MDPL (Figure 3D) is 2.30 kcal/mol more stable. Moreover, similar to MDTL trans-MDPL has two stable conformations with  $C_5-P_1-P_2-C_3$  dihedral angles of 3.5 and 22.3°, but now the twisted one is 2.10 kcal/mol less stable. Breaking the P–P bond of ring-closed MDPL requires the same amount of energy (53.19 kcal/mol) as breaking the P–P bond of the linear  $C_2H_5-HP-PH-C_3H_7$  molecule (Figure 3E). Thus, different from ring-closed MDPL there is no internal strain energy released while opening the ring (no spring-loading).

Adsorbing on  $Pt_{35}$ , we find that MDPL prefers the ring-opened structure (BE = 54.88 kcal/mol) rather than the cis-ring-closed structure (BE = 47.72 kcal/mol) rather than the trans-ring-closed structure (BE = 39.27 kcal/mol). Consequently ring-opened MDPL has a 22.44 kcal/mol stronger surface attachment than MDTL, but it also binds to two Pt–Pt bridge sites (P–Pt = 2.26–2.30 Å). Including the ring opening energy [DH(P–P) = 53.19 kcal/mol], we can consider that each covalent bond of P to Pt(111) is 54.0 kcal/mol (41.5 kcal/mol for MDTL).

For ring-opened MDPL the  $C_3-C_4-C_5$  and the  $C_4-C_5-P_1$  angles are stretched by only  $\approx 5^\circ$ , which should be compared to  $\approx 10^\circ$  in the case of MDTL. This may explain in part the higher binding energy of the diphospholane vs the dithiolane compound, and the absent spring-loading effect. For both compounds the bridge binding seems to be caused by steric effects, because only two bridge sites can accomplish the P–P distance requirements, respectively S–S. The directed bonds of each C atom in the carbon framework strongly determine the angles within the adsorbate.

The charge analysis using Mulliken populations (Figure 7) shows that in ring-opened MDPL both phosphorus have an even greater decrease than sulfur in MDTL ( $P_1$ , 0.47e;  $P_2$ , 0.41e vs  $S_1$ , 0.33e;  $S_2$ , 0.26e). Interestingly, the behavior in the spin density distribution (Figure 8) is different. While showing the same trends the spin density located on the P atoms of MDPL is 0.07–0.15 lower compared to both S atoms of MDTL. Caused by the additional methyl group again we find that the increase in spin density on  $P_1$  (0.09) is around twice the value calculated for  $P_2$  (0.04). Both the charge and spin density distribution indicate that similar to MDTL both P can also be thought of as  $P^+$ , allowing each P to form two covalent bonds to the surface while not changing the ground spin state of the  $Pt_{35}$ -cluster. In addition, the charge and spin density distribution within the

carbon framework remains nearly unchanged during chemisorption of the compound to the surface. This is in agreement with the already mentioned results by Ratner and co-workers,<sup>15–17</sup> who showed that the chemisorption influences the anchoring atoms while keeping the rest of the adsorbate almost unaffected. Thus, we expect both alligator-clip compounds to have similar properties regarding the attachment of the molecular switch.

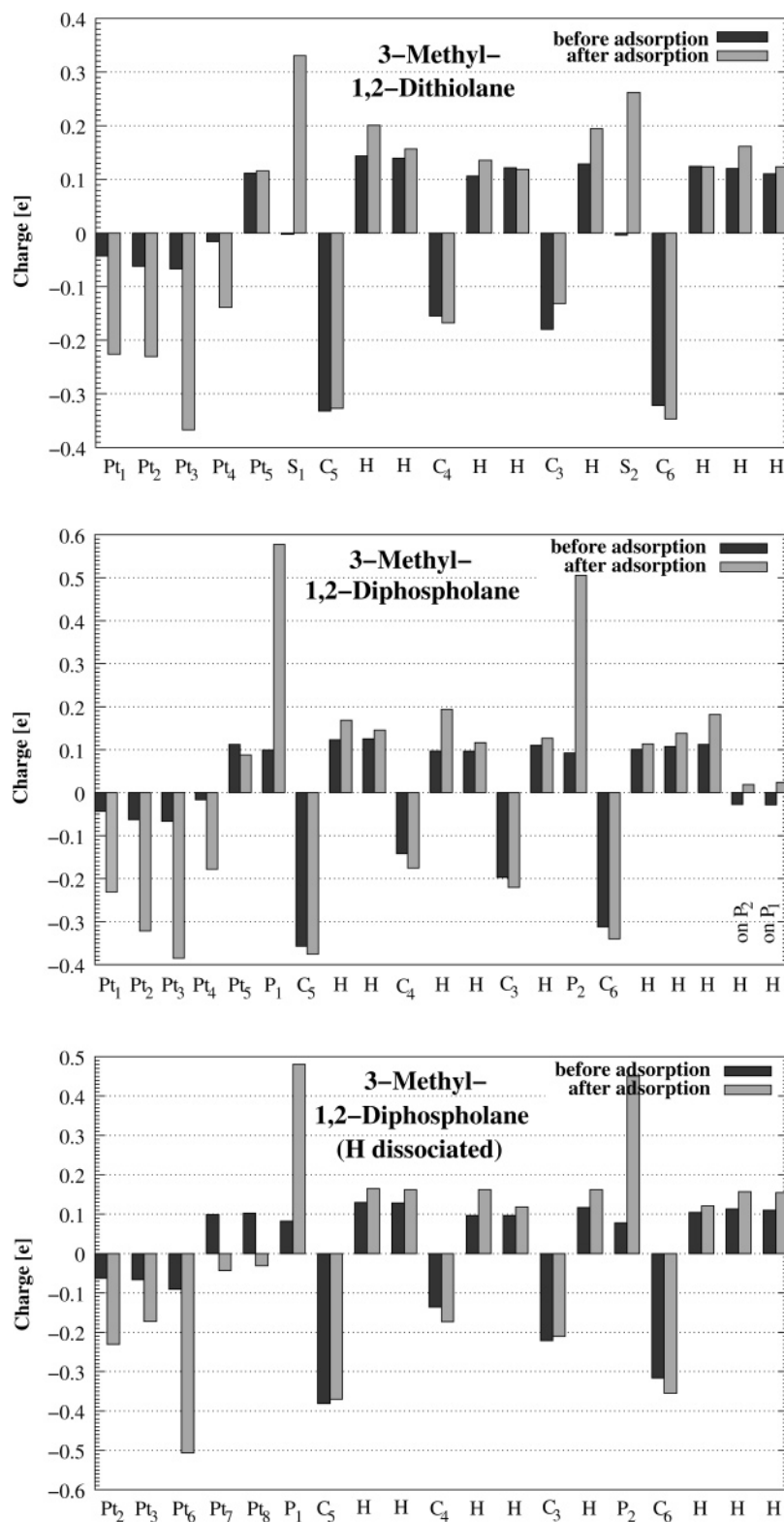
Between both ring-closed MDPL structures the cis-conformation is 8.45 kcal/mol more stable. Since the P–P bond is still intact, the  $sp^3$ -hybridization allows each P atom to form only one P–Pt bond, leading to a bridge type binding of the adsorbate (P–Pt = 2.248, 2.251 Å). However this involves a relatively large charge transfer of 1.214e from the adsorbate to the cluster, whereas each P atoms participates with  $\approx 0.45e$  and the entire carbon framework donates only  $\approx 0.31e$ . Consequently, all internal distances and angles within the adsorbate (cis-ring-closed MDPL) show only small deviations from the free molecule. In addition, this again suggests that both P can be thought of as  $P^+$ . Further stabilization of the binding site is achieved by tilting the carbon framework toward the adjacent  $\mu_3$  3-fold site by 53.8° (angle between the surface normal  $S^\perp$  and the  $C_3-P_2-P_1-C_5$  plane).

In the trans-ring-closed configuration (BE = 39.27 kcal/mol) only  $P_2$  is covalently bound to the surface ( $P_2-Pt_2 = 2.252$  Å), with 0.434e transferred to the cluster. The H atom at  $P_1$  faces toward the surface to form a donor–acceptor bond nearly on top of  $Pt_3$  (2.272 Å). The net result is that chemisorption decreases the charge of this H atom by 0.11e while  $Pt_3$  gains  $\approx 0.34e$  and  $P_1$  loses 0.20e. Comparing the internal distances and angles of adsorbed ring-closed MDPL with the free molecule shows little change. However, the  $C_3-P_1-P_2-C_5$  dihedral angle opens to 10.1°. Certainly, this is caused by the interaction of the hydrogen atoms with the surface.

**3.5.3. H-Dissociated MDPL.** Dissociation of the H atoms bound to both phosphorus leads to H-dissociated 3-methyl-1,2-diphospholane ( $H_{diss}$ -MDPL). The gas-phase molecule has the same ring-structure as MDPL. However,  $H_{diss}$ -MDPL exists only with a  $C_5-P_1-P_2-C_3$  dihedral angle of  $\approx 0^\circ$ . Compared to MDPL with H atoms a double bond is formed after H dissociation (distance decreases from 2.275 to 2.046 Å). Therefore, the energy required to open the five-membered ring increases to 76.69 kcal/mol that is 23.50 kcal/mol more than calculated for MDPL. Similar to MDPL, there is no strain energy released while breaking up the ring of  $H_{diss}$ -MDPL.

After adsorption on the surface different structures are possible, which again can be separated into ring-closed and ring-opened systems. For the most stable surface arrangement of ring-opened  $H_{diss}$ -MDPL (Figure 6A), we calculate a binding energy of 74.99 kcal/mol, which is 20.10 kcal/mol higher than MDPL. Caused by the extra unpaired electron on each P, the molecule rearranges on the surface such that both P can occupy 3-fold surface sites. In order to achieve the correct amount of valence electrons, each P atom donates a charge of  $\approx 0.48e$  to the cluster. Thus, as for all P-based compounds phosphorus can be thought of as  $P^+$ . Caused by steric interactions within the carbon framework we find two short and one longer P–Pt bonds (Table 2). In addition, the hybridization of both P atoms causes an orientation of the adsorbate, which is almost perpendicular to the surface plane [ $S^\perp-(C_3-P_2-P_1-C_5) = 0.4^\circ$ ].

To analyze the energetics, we start with the ring-closed  $H_{diss}$ -MDPL molecule. The energy to break the P=P bond and open the ring is 76.69 kcal/mol, leading to a  $P_1-P_2$  distance of 5.662 Å. Afterward we have to decrease the  $P_1-P_2$  distance to 3.600 Å and tilt the molecule to have a  $C_3-P_2-P_1-C_5$  dihedral angle

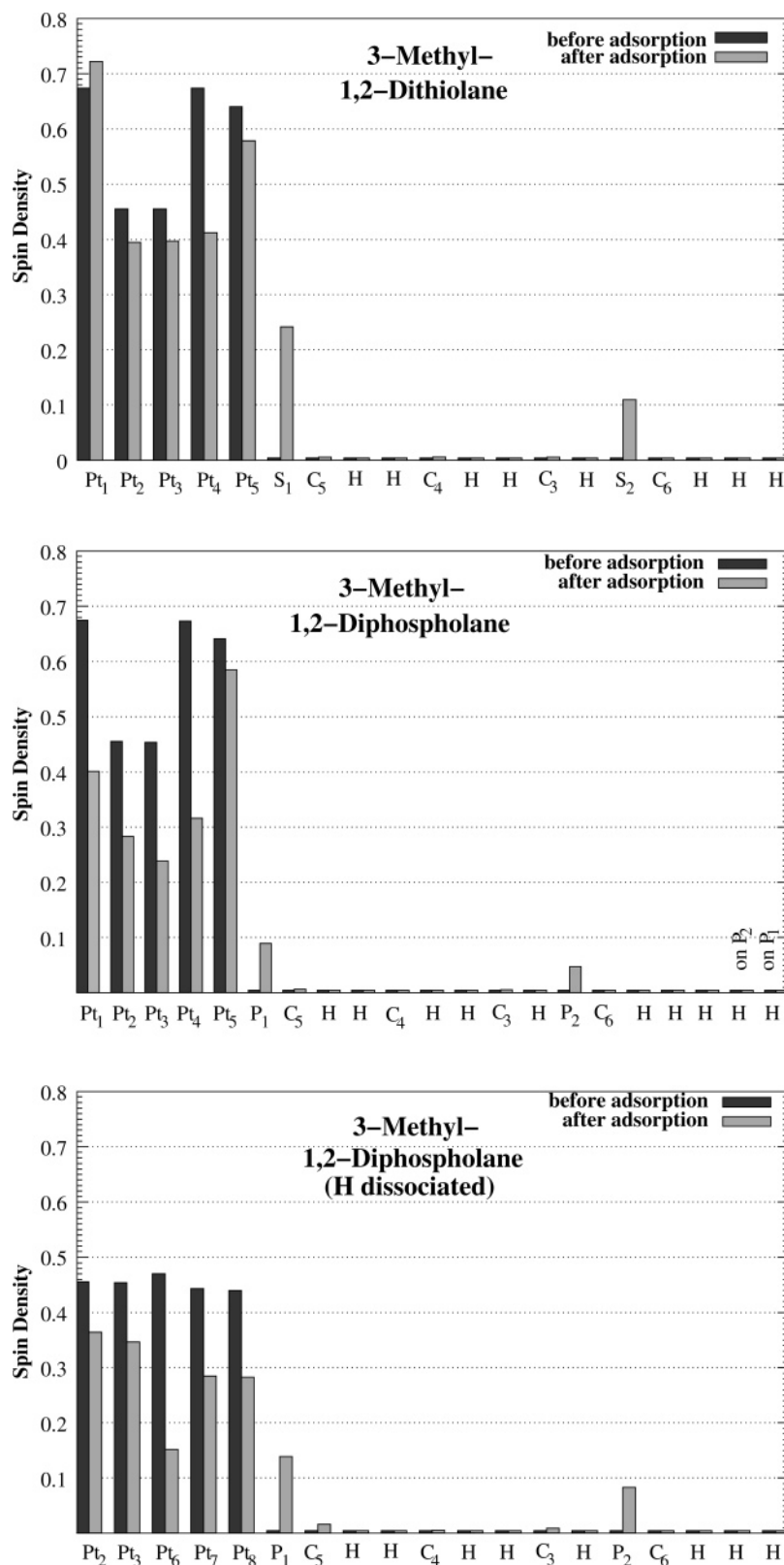


**Figure 7.** Mulliken partial charges for ring-opened MDTL, ring-opened MDPL, and ring-opened  $H_{\text{diss}}$ -MDPL before and after adsorption on the  $Pt_{35}$  cluster (for labels, see Figures 4A, 5A, and 6A). Special attention should be given to the indices of the Pt atoms.

of  $0.1^\circ$ . This requires 5.93 kcal/mol. Including these numbers and the calculated binding energy of 74.99 kcal/mol, which is with respect to ring-closed  $H_{\text{diss}}$ -MDPL, we obtain a bond strength of each P atom to the surface of 78.81 kcal/mol. This should be compared to the binding energy of  $PCH_3$  of 92.93 kcal/mol. The difference of 14.12 kcal/mol is a consequence of both P atoms adsorbing at close surface sites, and not being able to form three equivalent P–Pt bonds.

The other (less stable) structure is ring-closed  $H_{\text{diss}}$ -MDPL (Figure 6B), which shows a similar structure as ring-closed MDPL. However, the  $P_1$ – $P_2$  and P–Pt bond distances, and also the reduction in ground spin state by  $\Delta S = 1$  due to adsorption, indicate a different type of surface bond. The extra unpaired valence electron of each P atom prevents the  $sp^3$ -hybridization, leading to a single covalent bond between the P atoms after adsorption (2.235 Å). Consequently, the molecule binds to the





**Figure 8.** Spin density distribution for ring-opened MDTL, ring-opened MDPL, and ring-opened  $H_{\text{diss}}$ -MDPL before and after adsorption on the  $Pt_{35}$  cluster (for labels, see Figures 4A, 5A, and 6A). Special attention should be given to the indices of the Pt atoms.

surface by using the doubly occupied lone pair orbital of each P atom, resulting in a P–Pt bond length, which is 0.08–0.09 Å larger than obtained for cis-ring-closed MDPL. Moreover, there is 0.345e less charge transfer from the adsorbate to the  $Pt_{35}$  cluster. As expected the binding energy of 53.74 kcal/mol is comparable to cis-ring-closed MDPL.

As MDPL the charge distribution of the carbon framework of  $H_{\text{diss}}$ -MDPL is comparable to MDTL (Figure 7). For the spin density distribution (Figure 8) the missing H atoms cause a slight increase at both P atoms, which result in a behavior even more comparable to MDTL. Thus, although a much better surface attachment is achieved, for  $H_{\text{diss}}$ -MDPL we also expect the same

good behavior (as MDTL) for the mechanical and electronic coupling of the remaining molecular switch to the alligator-clip.

#### 4. Summary

Following the experimental studies by Tour et al.,<sup>1,2</sup> who investigated the nanodevice conductivity of identical arrays of molecular wires, but with different alligator-clip molecules (from S- to Se- to Te-based), we performed DFT calculations on the binding of alternative alligator-clips to a Pt(111) surface. Starting with the commonly used alligator-clip molecule 3-methyl-1,2-dithiolane, we calculated a variety of possible adsorption structures to find the most stable configuration (BE = 32.44 kcal/mol). Afterward different S/O-based, O-based, N-based, and P-based molecules were studied as potential alternatives. We find that moving up in the periodic table leads to lower binding energies, while moving to the left has the opposite effect. Consequently, within the range of studied systems P-based adsorbates should form strong surface bonds. As expected, PHCH<sub>3</sub> and PCH<sub>3</sub> showed a drastically increase in binding energy, but due to only a single surface bond, this would result in a mechanically less stable surface attachment.

Therefore, a promising candidate for attaching rotaxanes and related molecules to metal surfaces is 3-methyl-1,2-diphospholane, which forms a 22.44 kcal/mol stronger connection to the Pt(111) surface than MDTL does. Since changing the atoms that are directly bonded to the surface from S to P leads to only minor effects on the charge and spin-density distribution of the remainder of the alligator-clip molecule, we expect the properties for the molecular switch to be nearly unaffected. However, MDPL provides a more stable link between metal surface and molecular switches and diodes, reducing the risk of an open circuit.

Dissociation of the H atoms, which are bound to both P atoms of MDPL, would further increase the connection to the Pt electrode by 20.10 kcal/mol (compared to MDPL). However, in order to understand the probability of dissociative adsorption of MDPL ( $H_{\text{diss}}\text{-MDPL}$ ), which requires knowledge about the barriers for H-dissociation, additional studies are necessary.

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**Supporting Information Available:** Figure 1, structures of the calculated configurations for 3-methyl-1,2-dithiolane on a Pt<sub>12</sub> cluster; Figure 2, different compounds studied as alternative alligator-clip molecules; Figure 3, optimized structures (on the Pt<sub>35</sub> cluster) for some of the studied compounds; Figure 4, optimized structures (on the Pt<sub>35</sub> cluster) for all studied N-based compounds; Figure 5, optimized structures (on the Pt<sub>35</sub> cluster) for all studied P-based compounds; Table 1, ground spin-state and total energies for the different compounds in the gas phase; and Table 2, ground spin-state and binding energies for all

compounds except MDTL and MDPL. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### References and Notes

- (1) Tour, J. M.; Reinerth, W. A.; Jones, L.; Burgin, T. P.; Zhou, C. W.; Muller, C. J.; Deshpande, M. R.; Reed, M. A. *Mol. Electron.: Sci. Technol., Ann. N.Y. Acad. Sci.* **1998**, *852*, 197.
- (2) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y. X.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C. W.; Chen, J.; Wang, W. Y.; Campbell, I. *Chem.-Eur. J.* **2001**, *7*, 5118.
- (3) Tao, Y.-T.; Hietpas, G. D.; Allara, D. L. *J. Am. Chem. Soc.* **1996**, *118*, 6724.
- (4) Hwang, J. J.; Tour, J. M. *Tetrahedron* **2002**, *58*, 10387.
- (5) Dirk, S. M.; Tour, J. M. *Tetrahedron* **2003**, *59*, 287.
- (6) Price, D. W.; Dirk, S. M.; Maya, F.; Tour, J. M. *Tetrahedron* **2003**, *59*, 2497.
- (7) (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (b) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009. (c) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021.
- (8) (a) Stupp, S. I.; Braun, P. V. *Science* **1997**, *277*, 1242. (b) Nishinga, T.; Tanatani, A.; Oh, K.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 5934. (c) Percec, V.; Cho, W.-D.; Moeller, M.; Prokhorva, S. A.; Ungar, G.; Yearly, D. J. P. *J. Am. Chem. Soc.* **2000**, *122*, 4249. (d) Yearly, D. J. P.; Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G. *J. Am. Chem. Soc.* **2000**, *122*, 1684.
- (9) (a) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725. (b) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 1643. (c) Tseng, H. R.; Vignon, S. A.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2003**, *42* (13), 1491.
- (10) Luo, Y.; Collier, P.; Jeppesen, J. O.; Nielsen, K. A.; Delonno, E.; Ho, G.; Perkins, J.; Tseng, H. R.; Yamamoto, T.; Stoddart, J. F.; Heath, J. R. *Chem. Phys. Chem.* **2002**, *3*, 519.
- (11) Collier, C. P.; Jeppesen, J. O.; Luo, Y.; Perkins, J.; Wong, E. W.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 12632.
- (12) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433.
- (13) Deng, W.; Muller, R. P.; Goddard, W. A., III. *J. Am. Chem. Soc.* submitted.
- (14) Yu, H.; Luo, Y.; Beverly, K.; Stoddart, J. F.; Tseng, H. R.; Heath, J. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 5706.
- (15) Basch, H.; Ratner, M. A. *J. Chem. Phys.* **2003**, *119*, 11926.
- (16) Xue, Y. Q.; Datta, S.; Ratner, M. A. *Chem. Phys.* **2002**, *281* (2-3), 151.
- (17) Xue, Y. Q.; Datta, S.; Ratner, M. A. *J. Chem. Phys.* **2001**, *115*, 4292.
- (18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (20) Hay, P. J.; Wadt, W. R. *J. Phys. Chem.* **1985**, *82*, 299.
- (21) Jacob, T.; Muller, R. P.; Goddard, W. A., III. *J. Phys. Chem. B* **2003**, *107*, 9465.
- (22) Jacob, T.; Goddard, W. A., III. *J. Phys. Chem. B* **2005**, *109*, 297.
- (23) *Jaguar 5.0*; Schrödinger, Inc.: Portland, OR, 2002.
- (24) Kim, Y. H.; Jang, S. S.; Jang, Y. H.; Goddard, W. A., III. *Phys. Rev. Lett.* **2005**, *94*, 156801.
- (25) Meyer, B. *Chem. Rev.* **1976**, *76*, 367.
- (26) Dixon, D. A.; Zeroka, D.; Wendoloski, J. J.; Wasserman, Z. R. *J. Phys. Chem.* **1985**, *89*, 5334.
- (27) Yang, Y.-C.; Lee, Y.-L.; Yang, L.-Y. O.; Yau, S.-L. *Langmuir* **2006**, *22*, 5189.
- (28) Sexton, B. A. *Surf. Sci.* **1981**, *102*, 271.
- (29) Greeley, J.; Mavrikakis, M. *J. Am. Chem. Soc.* **2002**, *124*, 7193.
- (30) Ishikawa, Y.; Liao, M. S.; Cabrera, C. R. *Surf. Sci.* **2000**, *463*, 66.
- (31) Mattsson, T. R.; Paddison, S. J. *Surf. Sci.* **2003**, *544*, L697.
- (32) Yang, C.; Costamagna, P.; Srinivasan, S.; Benziger, J.; Bocarsly, A. B. *J. Power Sources* **2001**, *103*, 1.
- (33) Deng, W.-Q.; Molinero, V.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2004**, *126*, 15644.