Theoretical Studies of Oxidative Addition and Reductive Elimination

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of Doctor of Philosophy

California Institute of Technology
Pasadena, California

1985
(Submitted May 27, 1985)
Acknowledgment

First of all I would like thank Bill Goddard for providing me the opportunity to do research in Quantum Chemistry. We did not always agree but he allowed me to make many of my own decisions and mistakes. I do appreciate the faith he showed in me and that he trusted me enough to give me important tasks and responsibilities. I hope that I did not and will not disappoint him too often. I would also like to acknowledge my high school instructor in chemistry, Mr. Gerad A. Kass. He first kindled my interest in understanding chemistry at a fundamental level.

I would to thank my parents for providing me with the talents and for raising me the way they did. I am sure that I would not have persevered for as long as I have, if it was not for the good start they gave me.

I have appreciated the help that various Goddard group members have given me. Most of all, I would like to thank Tony Rappé, Ray Bair and Tom Upton for helping me get started in research and Mike Stiegerwald for many helpful discussions. A special thanks goes to Adria McMillan not only for her secretarial skills, but for her encouragement and for reminding me that there is life after Cal. Tech.

I would like thank Horia Metiu and Dick Messmer for their encouragement, advice and helpful discussions. They showed me that one could be a good scientist and a good person as well.

I have made a few good friends here (Steve Witt, Greg Voth, Dan Zirin, Mark Brusich, Tom Gibson, Bill Finch, The Lynches, Walther Ellis, Eric Hood, Mike Weimer, and Heidi Tanicar). They have gotten drunk with me (except Eric) and made me laugh on many occasions. I thank the Weenies for competitive softball and the Sierra Club for many relaxing excursions.
-iv-

A special thanks goes to the Blankenburgs for always being supportive and providing a retreat for me to regain equilibrium. I acknowledge Tikoes for his many loans and for being a good friend, Aunt Eleanor for good food and lots of beer, and Annette and Debbie (a future Blankenburg) for proofreading assistance.

I would like to acknowledge One West and Chippendales for many exciting Friday nights.

I finally would like thank Claudia Troesch. She was a good companion at a time when I needed a lot of support.
Chapter 1: \textit{Ab initio} calculations (Hartree-Fock, generalized valence bond, and configuration interaction), utilizing relativistic core potentials, have been used to follow the oxidative addition of H$_2$ to Pt(PH$_3$)$_2$. We find an activation barrier of 2.3 kcal/mol and an exothermicity of 15.9 kcal/mol. From examination of the geometries and wavefunctions, we find that up to the transition state the H-H bond is still intact. The role of the Pt s$^1$d$^9$ and d$^{10}$ states in oxidative addition is described, and the effects of including electronic correlation are discussed. The implications for reductive elimination of the dimethyl and hydridomethyl complexes are also discussed.

Chapter 2: \textit{Ab initio} calculations have been carried out on MR$_2$ complexes (where M = Pd or Pt and R = H or CH$_3$) to model concerted reductive coupling from MR$_2$L$_2$ complexes (where L is a substituted phosphine). The results of these calculations support the following two conclusions. (1) The differences in the driving force for reductive elimination from Pd(II) and Pt(II) complexes with the same R groups is very close (0-4 kcal/mol) to the difference in the s$^1$d$^9$–d$^{10}$ state splittings of these elements (32 kcal/mol). Thus reductive elimination is exothermic from Pd complexes (since Pd prefers d$^{10}$) and endothermic from Pt complexes (since Pt prefers s$^1$d$^9$), where the metal product is in its d$^{10}$ state. This supports the conclusion, derived from qualitative considerations of generalized valence bond wavefunctions, that Pt(II) and Pd(II) complexes have their metal atoms in a s$^1$d$^9$ configuration and the metal atoms in Pt(0) and Pd(0) complexes are in a d$^{10}$ configuration. (2) The activation barriers for
C-C coupling are approximately twice that for C-H coupling. There are essentially no barriers for processes involving H-H bonds. The origin of this trend is the directionality of the methyl sp³ orbital, which destabilizes the transition state for the case where an M-C bond is being converted to a C-C or C-H bond. Conversely, the spherical H 1s orbital can form multicenter bonds easily, allowing it to break M-H bonds while forming an H-H bond and leading to low intrinsic barriers. These results are consistent with the experimentally observed trends.

Chapter 3: Ab initio calculations were carried out on Pt(CH₃)₂(Cl)₂(PH₃)₂ and on various Mt(R₁)(R₂)(PH₃)₂ complexes (where Mt = Pd or Pt; R₁, R₂ = H or CH₃) in order to elucidate the differences in reductive H-C and C-C coupling from Pd(II), Pt(II), and Pt(IV) complexes. These studies explain why (1) reductive C-C coupling is facile for Pd(II), favorable for Pt(IV), and unobserved for Pt(II) systems, while (2) reductive H-C coupling is facile for Pt(II) and Pd(II) systems, and (3) oxidative addition is favorable only for addition of H₂ to Pt(0) systems.

Chapter 4: Ab initio calculations were carried out on CHₓ and NHₓ molecular fragments on small clusters of Ni atoms (Ni₁₃ and Ni₁₄), as a model for chemisorption on the Ni(100) surface. The results presented here show that these species make strong π bonds to the surface which cause methylidyne and imidogen to be the most stable CHₓ and NHₓ species on this surface. The results have also been used to estimate ΔH°₀ for various intermediates important for methanation and ammonia decomposition on Ni surfaces.
Chapter 1:

Theoretical Studies of Oxidative Addition and Reductive Elimination: \( \text{H}_2 + \text{Pt}(\text{PH}_3)_2 \rightarrow \text{Pt}[(\text{H})_2(\text{PH}_3)_2] \) ......................................................... 1

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CHAPTER 1

Theoretical Studies of Oxidative Addition and Reductive Elimination:

\[ \text{H}_2 + \text{Pt(PH}_3\text{)}_2 \rightarrow \text{Pt(H)}_2\text{(PH}_3\text{)}_2 \]

The following chapter has appeared in the *Journal of the American Chemical Society*, 1984, 106, 6928-6937.
Theoretical Studies of Oxidative Addition and Reductive Elimination: \( \text{H}_2 + \text{Pt(PPh}_3\text{)}_2 \rightarrow \text{Pt(H)}_2\text{(PPh}_3\text{)}_2 \)

John J. Low and William A. Goddard III

Contribution No. 6995 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received March 5, 1984

Abstract: Ab initio calculations (Hartree-Fock, generalized valence bond, and configuration interaction), utilizing relativistic core potentials, have been used to follow the oxidative addition of \( \text{H}_2 \) to \( \text{Pt(PPh}_3\text{)}_2 \). We find an activation barrier of 2.3 kcal/mol and an exothermicity of 15.9 kcal/mol. From examination of the geometries and wave functions, we find that up to the transition state the \( \text{H}-\text{H} \) bond is still intact. The role of the Pt t\(^{16}\) and d\(^{16}\) states in oxidative addition is described, and the effects of including electronic correlation are discussed. The implications for reductive elimination of the dimethyl and triaryl complexes are also discussed.

I. Introduction

Oxidative addition and reductive elimination are important steps in many organometallic reactions. In particular, the oxidative addition of a hydrogen molecule to a \( \text{PtL}_2 \) complex (where \( \text{L} \) is a substituted phosphine) has been observed for a number of different ligands, \( \text{L} \), e.g., \( \text{Pt(C}_2\text{H}_5\text{H)}_2 \), \( \text{Pt(F)}_2 \). \(^1\) \( \text{H}_2 \text{PtL}_2 \) complexes have been observed to undergo many types of reactions, including insertion, \(^2\) e.g.,

\[ \text{trans-H}_2\text{Pt}([\text{C}_2\text{H}_5\text{H)}_2\text{]} + \text{CS}_2 \rightarrow \text{trans-HPt}([\text{C}_2\text{H}_5\text{H)}_2\text{]} \]

dimer formation, \(^3\) e.g.,

\[ \text{trans-H}_2\text{Pt}([\text{C}_2\text{H}_5\text{H)}_2\text{]} + \text{CS}_2 \rightarrow \text{trans-HPt}([\text{C}_2\text{H}_5\text{H)}_2\text{]} \]

and oxidative addition followed by reductive elimination of \( \text{H}_2 \).

\[ \text{trans-H}_2\text{Pt}([\text{C}_2\text{H}_5\text{H)}_2\text{]} + \text{CS}_2 \rightarrow \text{trans-HPt}([\text{C}_2\text{H}_5\text{H)}_2\text{]} + \text{H}_2 \]

Such species have also been proposed as intermediates in the catalysis of the water-gas shift reaction\(^7\) and of alkene hydrogenation.

As a first step in gaining a better understanding of the formation of covalent bonds through reductive elimination and the scission of bonds via oxidative addition, we have examined the process

\[ \begin{align*}
\text{Pt} & + \text{H}_2 \rightarrow \text{Pt} + \text{H}_2 \\
\text{Pt} & + \text{H}_2 \\
\end{align*} \]

Of particular interest in analyzing these results will be to explain why (i) the addition of hydrogen to \( \text{PtL}_2 \) occurs at room temperature, but reductive elimination is quite slow; \(^2\) (ii) the reductive elimination of methane from \( \text{(H)(CH}_3\text{)}_2\text{Pt(H)} \), proceeds at room temperature; \(^1\) (iii) the \( \text{PtL}_2 \) dihydridyl complexes tend to be stable with respect to forming carbon-carbon bonds through reductive elimination. Thus, dihydridyl complexes will disproportionate through \( \beta \)-hydride elimination

\[ \begin{align*}
\text{Pt} & + \text{H}_2 \rightarrow \text{Pt} + \text{H}_2 \\
\text{Pt} & + \text{H}_2 \\
\end{align*} \]

rather than reductively eliminate when they thermally decompose. \(^2\) Only for \( \text{PtL}_2 \) dihydridyl complexes, where \( \beta \)-elimination is impossible, have carbon-carbon bonds been formed through reductive elimination at high temperatures. \(^2\) On the other hand, \( \text{PtL}_2 \) dihydridyl complexes are quite unstable with respect to reductive elimination to yield \( \text{C-C} \) coupling. \(^2\)

In this paper we develop a relatively simple model of reaction 1 by examining the energetics, geometries, and wave functions along the reaction coordinate. These results indicate that oxidative addition of \( \text{H}_2 \) to \( \text{PtL}_2 \) depends crucially on the relative positions of the 5d\(^{10}\) and 6s\(^{16}\)\/5d\(^{16}\) states of the platinum atom. The resulting energetics explain the observed differences regarding oxidative

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Oxidative Addition and Reductive Elimination

![Diagram of Pt-H bond pairs](image)

Figure 1. GVB orbitals for the Pt-H bonds of H₂P₆(PH₃)₂ at equilibrium. Hybridization for each singly occupied GVB orbital is shown on each plot. Each contour represents a change of 0.05 in amplitude. Solid lines represent positive amplitude. Dashed lines represent negative amplitude. Asterisks represent the position of atoms.

Summary of Results

The details of the calculations are described in section IV. Here we will emphasize the main lessons from the theoretical studies.

In the ground state of the reactants,

\[ \text{PH}_3 + \text{Pt} \rightarrow \text{H} \]

the lone pairs of the phosphines make strong Lewis base bonds to the Pt atom, stabilizing the (d⁶) configuration and leading to a linear complex. The oxidative addition product is square-planar,

\[ \text{H}_2 \text{Pt-Pt-H}_2 \]

with an H-Pt-P angle of 79.4° and a P-P angle of 99.8°. Despite the terminology "oxidative addition", we find that there is essentially no charge transfer from the Pt to the H. Instead, we find that the Pt in II corresponds to a (6s)²(5d)⁶ configuration of Pt, allowing the formation of two covalent bonds to the H atoms. The generalized valence bond (GVB) orbitals for these bond pairs are shown in Figure 1 where each bond involves one electron in an H-1s-like orbital and one electron in a 6s-5δ hybrid (60% δ) pointing at the H. The net exothermicity of reaction 1 is calculated to be 16 kcal/mol, so that one can consider the two Pt-H bonds of II to be worth 60 kcal/mol each. If the geometry of the Pt(PH₃)₆ fragment were kept fixed, then the average Pt-H bond energy would be 72 kcal/mol. The next question is how do the orbitals change as the system goes from I to II? This process is orbital symmetry allowed and indeed we find in Figure 2 that the reaction has only a 2.3 kcal/mol barrier. In examining the potential curve in Figure 2, three distinct phases in the process of oxidative addition are discerned.

(i) Lewis Base/Lewis Acid Bonding of H₂ to Pt(PH₃)₆ (D → C in Figure 2). Since the platinum atom is in a d⁶ state, the Pt 6s orbital is empty and can serve as an electron acceptor. As the hydrogen molecule approaches the diphosphine complex, the H₂ electrons utilize the Pt 6s orbital, making a Lewis acid/Lewis base bond. As this occurs, the phosphine ligands bend back (a) to lower steric interactions between the hydrogen molecule and the phosphine ligands and (b) to increase the overlap between the Pt 6s orbital and the H-H bonding orbital. The overlap between the Pt 6s and H-H bonding orbitals increases because the Pt 6s orbital polarizes away from the phosphines (hybridizes with the 6p orbital) to get orthogonal to the phosphine lone-pair orbitals. By the transition state, the P-Pt-P bond angle has decreased from 180° to 153°, but the H-H bond length remains essentially constant (changing by only 0.005 Å). The overall energy increase is 2.3 kcal/mol, whereas to bend the P-Pt-P angle the same amount in the diphosphine complex would cost 9 kcal/mol. Therefore, we can consider the H₂-Pt-Lewis base/Lewis acid interaction to be worth 7 kcal/mol at the transition state.

(ii) Electronic Promotion of the Platinum Atom (C → B in Figure 2). Once the H₂ molecule has passed the transition state (point B in Figure 2), the platinum atom begins to build in some d⁶ character. As the phosphines bend back from 153° to 113°, this becomes more favorable because the splitting between the d⁵(3d) ground state and the lowest s⁶d⁶(4d) state decreases as the P-Pt-P angle decreases. Thus, as the P-Pt-P angle decreases from 180° to 140° and then to 90°, this splitting decreases from 107 kcal/mol to 63 kcal/mol, and then to 20 kcal/mol. The mixing of the d⁵s and the d⁶ states occurs mainly through the delocalization of the H₂ electrons into the Pt 6s orbital and the back-donation of the Pt 6d₄, electrons into the H-H antibonding

\[ \text{H} \rightarrow \text{H}_2 \rightarrow \text{Pt} \rightarrow \text{H}_2 \rightarrow \text{Pt} \]

Figure 2. Potential energy curve along the reaction coordinate.

Table I. Pt Atom State Splittings (in kcal/mol)

<table>
<thead>
<tr>
<th>State</th>
<th>GVB-3</th>
<th>RCI</th>
<th>GVB/C-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>s^3(d^9p^6)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>s^3(d^9)</td>
<td>11.0</td>
<td>31.4</td>
<td>27.0</td>
</tr>
<tr>
<td>s^3(d^9p^6)</td>
<td>14.7</td>
<td>8.4</td>
<td>11.2</td>
</tr>
</tbody>
</table>

*See Calculational Details section. The total energies of the 3d state are ~27,506.19 hartrees at the HF level, ~27,519.18 at the GVB-3 level, and ~27,531.29 hartrees at the RCI(3/10) level (using the relativistic effective core potential of ref. 37). The energies in this column are actually the average of experimentally observed j states derived from each Russell-Saunders term.

orbital as methane reductively eliminates. This should lead to an activation barrier for reductive elimination of methane from hydridomethyloctahedron(II) complexes that is intermediate between those for breaking H-H and forming C=C bonds, in agreement with the observed reactivities of hydridomethyl complexes.

We find that oxidative addition of H_2 to Pt(PH_3)_2 proceeds with a small activation barrier (2.3 kcal/mol) and the overall reaction is sufficiently exothermic that the products should be stable with respect to reductive elimination. This is in agreement with the results of Ponsens and Trogler. They have prepared the dihydrides of the sterically unhindered Pt(PMe_3)_2 and Pt(PPh_3)_2 and found these complexes to be stable under 0.5 atm of H_2 and to decompose slowly under vacuum. The singular difference between Pd and Pt is that the Pd atom prefers the d^9 configuration by 22 kcal/mol, while Pt prefers the d^9 configuration by 11.0 kcal/mol. Thus Pd has a total bias of about 33 kcal/mol in favor of the d^9 configuration. Since the reductive eliminations considered here involve mostly changing from s^d to d^9, this means that the increased splitting should make the Pd(II) complexes considerably (about 34 kcal/mol) less stable than their Pd counterparts. This is in agreement with observed reductive elimination of ethane from Pd(C_2H)Cl_2 complexes (where L = PPh_3 and PPh_3) and the fact that hydrogen will not oxidatively add to a Pd diphosphine complex but does add for the corresponding platinum complex.

III. Results

A. Platinum Atom. The changes occurring during oxidative addition are partly determined by the electronic structure of the Pt atom. As with Ni and Pd, the platinum atom has three low-lying states, s^3(d^9p^6), s^3(d^9), and s^3(d^9p^6). We find that the Pt complexes tend to have the character of one or another of these atomic states and that the chemistry is dominated by this atomic character. In Table I, we summarize the relative energies of these states for various levels of calculations and experimental results.

Clearly, Hartree-Fock (HF) calculations are strongly biased against the d^9 state. In the jargon of theorists, electron correlation is far more important if the two electrons are in a 5d orbital than if the electrons are in different orbitals (5d or 6s). A simple way to account for the major electron correlation error implicit in the HF or molecular orbital (MO) description is the use of the GVB wave function, which allows each electron to have a differently shaped orbital and allows the orbitals for singly-coupled electrons to overlap. Thus, in GVB each doubly occupied valence orbital of the HF wave function is described by a pair of overlapping GVB orbitals. For an atom with a doubly occupied d orbital in the HF wave function, the GVB wave function has two contributions to one tight d orbital (near the nucleus) and one diffuse d orbital (farther from the nucleus). We have chosen to describe the doubly occupied orbital of the 5f state by tight and diffuse orbitals in order to be consistent with the correlation included in the GVB pairs describing d electrons.


Figure 3. Potential energy curves for the low-lying states of Pt(\(\text{PH}_3\)) as a function of P-Pt-P angle.

In many systems, electron correlation plays an important chemical role only for certain orbitals. In the platinum atom most of the electronic correlation important for state splittings occurs in the Pt 5d and 6s orbitals. Thus, if all ten d electrons in the Pt (5d\(^{10}\)) state are correlated in the GVB wave function, we denote this wave function as GVB(5/10) [here the 5 is the number of singlet-coupled electron pairs, while the 10 is the number of orbitals used to describe the five pairs]. If only one pair of electrons were to be correlated (i.e., for the bonding pair of electrons in Pt-H), we would use a GVB(1/2) wave function. When there is more than one pair to correlate, there are additional options in describing the wave function. The simplest description is for each pair to have singlet spin coupling as a simple valence bond (VB) wave function. This is denoted as GVB-P. However, for a system with five pairs of electrons (ten VB orbitals), there are 42 VB structures or spin couplings that should all be included in calculating the final wave function. In addition, there are interpair correlation effects, wherein if the two electrons in the \(d_{xy}\) orbitals are at some instant closer to the nucleus, the two electrons in the \(d_{xy}\) orbital will at that instant tend to be farther from the nucleus. These spin coupling and interpair correlation effects are included by carrying out a configuration interaction (CI) calculation in which the two electrons in each pair of orbitals are simultaneously allowed all possible occupations of those two orbitals, leading to what is termed a GVB–RCI wave function. Thus, for a GVB–PPP(5/10) wave function, there are \(3^2 = 243\) configurations in the GVB–RCI wave function.

The most complete wave function that can be described with just the GVB orbitals is to carry out a full CI with use of all possible occupations of those orbitals. This is termed GVB–CI, and for a GVB–PPP(5/10) wave function, this leads to 8953 configurations. Since the GVB–RCI and GVB–CI are based on GVB orbitals, we can interpret these CI wave functions in terms of simple VB concepts. As is evident from the results in Table I, the GVB–RCl wave function gives results that are as consistent as the GVB–CI results but with significantly fewer configurations.

For the purposes of this paper, the GVB–RCl provides the best combination of accuracy and simplicity.

B. Pt(\(\text{PH}_3\))\(_3\). When two phosphines are added to a platinum atom, the major effect is to raise the energy of the platinum 6s orbital relative to the Pt 5d orbitals. This occurs because the phosphine lone pair makes a Lewis acid–base bond by overlapping with (donating into) the Pt 6s orbital. The net result is that the ground state of Pt(\(\text{PH}_3\))\(_3\) is a singlet \(^1\text{A}_1\) state derived from the \(5\text{d}^{10}\) state of the platinum atom. In this state, the phosphines minimize their steric repulsions by increasing the P–P–Pt bond angle to 180°. The low-lying triplet states of Pt(\(\text{PH}_3\))\(_3\) are both

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Table I. State Splittings for the \(d^{10}\) and \(d^{10}\) States of Pt(\(\text{PH}_3\))\(_3\)

<table>
<thead>
<tr>
<th>State</th>
<th>(\text{PH}_3)-Pt–(\text{PH}_3) angle, \text{deg}</th>
<th>HF</th>
<th>GVB(5/10)</th>
<th>RCI(5/10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{A}_1)</td>
<td>180.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(^3\text{A}_1)</td>
<td>180.0</td>
<td>81.9</td>
<td>89.2</td>
<td>105.6</td>
</tr>
<tr>
<td>(^3\text{A}_2)</td>
<td>180.0</td>
<td>65.7</td>
<td>53.3</td>
<td>106.9</td>
</tr>
<tr>
<td>(^3\text{B}_1)</td>
<td>99.09</td>
<td>28.5</td>
<td>35.2</td>
<td>51.5</td>
</tr>
<tr>
<td>(^3\text{B}_2)</td>
<td>99.09</td>
<td>22.8</td>
<td>22.1</td>
<td>24.6</td>
</tr>
<tr>
<td>(^3\text{A}_1)</td>
<td>99.09</td>
<td>72.9</td>
<td>74.0</td>
<td>75.3</td>
</tr>
</tbody>
</table>

*The total energies for the \(^1\text{A}_1\) states are \(-712.170592\) hartree at the HF level, \(-712.119127\) hartree at the GVB–PPP(5/10) level, and \(-712.260738\) hartree at the RCI(5/10) level. \(99.09^\circ\) is the optimum bond angle for the \(^1\text{B}_2\) state.

---


Table III. Summary of Results for Pt-H

<table>
<thead>
<tr>
<th></th>
<th>R. Å</th>
<th>D_h (kcal/mol)</th>
<th>total energy (hartrees)</th>
<th>( \omega ) (cm(^{-1}))</th>
<th>dipole moment (Debye)</th>
<th>Mulliken pop. on Pt</th>
<th>Mulliken pop. on H</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>1.516</td>
<td>37.3</td>
<td>-28.065612</td>
<td>2027</td>
<td>2.52</td>
<td>10.07</td>
<td>0.93</td>
</tr>
<tr>
<td>GVB-PP(1/2)</td>
<td>1.526</td>
<td>51.6</td>
<td>-28.088370</td>
<td>1948</td>
<td>1.89</td>
<td>10.10</td>
<td>0.90</td>
</tr>
<tr>
<td>GVB-PP(5/10)</td>
<td>1.549</td>
<td>51.6</td>
<td>-28.090619</td>
<td>1990</td>
<td>1.89</td>
<td>10.10</td>
<td>0.90</td>
</tr>
<tr>
<td>RCI(5/10)</td>
<td>1.544</td>
<td>48.9</td>
<td>-28.128813</td>
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<td>1.86</td>
<td>10.11</td>
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<tr>
<td>GVB-Cl(5/10)</td>
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<td>1909</td>
<td>1.90</td>
<td>10.10</td>
<td>0.90</td>
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<tr>
<td>DC-Cl</td>
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<td>60.6</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>experiment</td>
<td>1.528</td>
<td>&lt;79.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Huber, K. P.; Herzberg, G. " Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules," Van Nostrand-Reinhold Co.: New York, 1979. *Frequencies were obtained from the curvature at \( R_2 \) which was obtained from a cubic spline fit. *The positive sign implies Pt-H.*

This calculation was only carried out at this bond distance. *All total energies are reported for \( R = 1.31 \) Å.

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Figure 5. Open-shell orbitals for the \(^1\)A\(_2\) state for linear Pt(PhH).

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Figure 6. GVB orbitals for diatomic PtH.

Experimental characterization of PtH includes the bond length and vibrational frequency but only an upper bound for the bond energy. This compares well with the experimental geometry (1.5% long) but is 15% low for the vibrational frequencies. The best theoretical bond energy of 60.6 kcal/mol was obtained from a dissociation-consistent configuration interaction (DC-Cl) calculation. This calculation involves all single and double excitations from the active space defined by the Pt-H bond pair from a GVB-PP(1/2) calculation times all single excitations from the semiautomatic space defined by the remaining platinum valence electrons. This calculation was carried out at only a single point (1.51 Å), so a vibrational frequency is not reported for this level of calculation. This calculated bond energy is 20 kcal/mol smaller than the experimental upper bound of 80 kcal/mol. The calculated Mulliken populations and dipole moments show that the PtH bond is essentially covalent. This is consistent with the small difference in Pauling electronegativities of Pt (2.2) and H (2.1). However, detailed comparison of the dipole moment and Mulliken populations appears to give conflicting results. The dipole moment indicates a transfer of 0.26 e\(^{-}\) to the hydrogen atom, while the Mulliken populations indicate a transfer of 0.10 e\(^{-}\) from the H. This apparent conflict is partly due to the Pt part of the bond orbital being a Pt \( \sigma \) hybrid with some Pt p character so that it is polarized toward the hydrogen. This polarization contributes to the dipole moment but not to the Mulliken charge transfer. To obtain a quantitative measure of the polarization taking place, we calculated the dipole moment of the platinum orbitals from a GVB(1/2) calculation on PtH. This calculation included the localized Pt-GVB orbital from the Pt-H GVB bond pair and the other five Pt-like nonbonding \( \sigma \) orbitals (four doubly occupied and the singly occupied \( d_{z^2} \) orbital), where in each case any hydrogen character was deleted (and the orbitals were renormalized). This calculation on the Pt atom yields a dipole moment of 1.08 D, over half the total dipole moment of Pt-H. Subtracting

---

(31) We have used C\(_2\) symmetry to classify the states in this discussion. At a P-Pt-P angle of 180° the Pt(PhH\(_2\)) complex would actually have D\(_\infty\) symmetry. The \(^1\)A\(_2\) state would be one component of the \(^1\)E state.

Oxidative Addition and Reductive Elimination

Table IV. Geometries along the Reaction Coordinate 1-13

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<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
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<th>10</th>
<th>11</th>
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<tbody>
<tr>
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<td>121.3</td>
<td>121.1</td>
<td>120.7</td>
<td>120.7</td>
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</table>

*All R is Å. *All θ in deg.

Figure 7. Plot of energy along the reaction coordinate for HF, GVB-Cl(2/6), and RC(4/8)+GVB-Cl(2/6) wavefunctions.

This dipole moment due to Pt atom polarization from the total dipole moment leads to a residual molecular moment of 0.81 D, corresponding to a transfer of only 0.11 e⁻ to the hydrogen atom. Therefore, a large fraction of the dipole moment is due to polarization of the Pt valence orbitals. The remaining discrepancy of Θ = 1.11 e⁻ from the dipole moment vs. Θ = 0.90 e⁻ from the Mulliken populations represents a deficiency in the Mulliken analysis, namely, the equal partitioning of overlap terms tends to underestimate the population on H. Summarizing, the charge transfer in the Pt-H bond is small so that the Pt-H bond should be described as covalent.

The Mulliken populations for the GVB orbitals (see Figure 6) of the Pt-H bond show that the GVB orbital localized on the Pt atom is about 60% Pt d character and 40% Pt p character. This hybridization of the Pt d₅ orbital makes the density along the z axis larger than it would be for either a pure Pt 6s orbital or a pure Pt d₅ orbital. This increases the overlap (and conformation) between the platinum orbital and the hydrogen orbital.

D. H₃Pt(PH₃). The changes in the electronic structure that occur during oxidative addition can most easily be elucidated by following a reaction path from reactants to products. We used the distinguished coordinate method to find a good approximation to the reaction coordinate at various levels of calculation. The distinguished coordinate method freezes one internal coordinate of the system to be studied while optimizing all the others for lowest energy. By repeating this procedure for a number of values for the frozen coordinate, one can generate a potential curve that is only a function of one variable and changes continuously from products to reactants. These optimizations were performed at the HF level with use of an analytic gradient technique. HF

Figure 8. Changes in the P-Pt-P bond angle and H-H distance along the reaction coordinate.

This provides accurate equilibrium geometries for various platinum complexes and leads to exothermicities and barrier heights similar to correlated wave functions.

The geometries resulting from the distinguished coordinate method are listed in Table IV. For more details on how these calculations were carried out, see section IV. The distinguished coordinate used in these calculations was the Pt-H₁ distance. The HF potential as a function of Pt-H₁ distance is shown in Figure 7.

As the Pt-H₁ distance was varied, only two other internal coordinates changed significantly. The P-Pt-P angle changed from 180° to 100° through the reaction path. The H-H distance increased a small amount as the hydrogen molecule approached the Pt(PH₃)₃ complex up to a Pt-H distance of 2.0 Å. For Pt-H₂
distances less than 2.0 Å, the H–H distance increased rapidly from 0.76 to 1.92 Å. These geometry changes as a function of Pt–H distance are shown in Figure 8.

E. Charge Populations. The Mulliken populations of the Pt d, Pt 5s and H1 orbitals are plotted as a function of Pt–H2 distance in Figure 9. This plot shows that the amount of Pt 6s character increases and the amount of Pt 5d character decreases as H2 approaches the Pt(PH3)3 complex. At the dissociated limit, the Pt population has 9.51 d electrons and 0.38 s electrons. At equilibrium, the population has 9.10 d electrons and 0.96 s electrons. Although Mulliken populations are not truly quantitative measures for the character and locations of the electrons, as shown above for Pt–H, they can be used to provide qualitative ideas of how charge is distributed. At equilibrium, the Mulliken populations show that the platinum atom is in a d5s state. At the dissociated limit and at the transition state, the platinum atom is in a state that is mainly d5 and singlet.

In Noel’s population analysis,28 charges are assigned to atoms by partitioning space. All charge within the covalent radius of the Pt atom was assigned to this center. The space outside this sphere was partitioned into cones with 45° angles of rotation about each ligand. The charge in a particular cone was assigned to the ligand that was contained in the cone. The remaining charge outside the covalent radius of the platinum atom was assigned to the platinum atom. This partitioning resulted in a positively charged platinum atom (1.22 e–), negatively charged hydrogen atoms (–0.29 e–), and negatively charged PH3 groups (–0.32 e–). Noel feels that this is a more reasonable assignment because it is closer to the formal oxidation states of the platinum and hydrogen atoms. One problem with Noel’s analysis is that a relatively large fraction of the platinum atom d basis (11%) and sp basis (37%) is outside the covalent radius of the platinum atom.

When the platinum atom is in a s4d state, this result would result in 1.36 e– being assigned to the ligands! Clearly this is not a fair division of density.

Comparing the Pauling electronegativities13 of platinum (2.2) and hydrogen (2.1), we see that the hydrogen atom should be slightly negatively charged. But such a small difference in the electronegativity should lead to a bond that is essentially covalent (less than 4% ionic by Pauling’s formula). The dipole moment of Pt–H indicates that the Pt–H bond is more polar than Pauling would predict, as discussed in section III. This is due largely to the polarization of the Pt valence electron rather than to charge transfer. Although the Mulliken population leads to the wrong polarity (Pt4H), it is particularly useful in determining the relative amounts of Pt 5p, d, and d character in a wave function. Qualitatively, the Mulliken populations indicate that there is not a large amount of charge transfer, and this is in agreement with the dipole moments.

F. Forms for the Wave Function. In analyzing the character of bond orbitals, it is important to use wave functions that change smoothly as one goes from one extreme with a doubly occupied Pt d orbital and H–H bond pair to the other extreme with Pt–H bonds. The simplest wave function providing a good description of the Pt–H bonds is the GVB wave function. This wave function contains one GVB pair for each Pt–H bond, as shown in Figure 10. These orbitals involve combinations of the platinum 5d α and 6s orbitals and of the two hydrogen atomic orbitals. The best GVB orbitals at the dissociated limit are shown in Figure 10. These orbitals involve combinations of a tight Pt d5 orbital, a diffuse d orbital, and two hydrogen atomic orbitals. Thus the GVB wave function is not consistent throughout the reaction path because different types of correlation are required to describe the electrons localized on the platinum atom at the different limits. At the dissociated limit, the pair of Pt electrons involved in the Pt–H bonds are both in d orbital and are correlated in-out. In other words, one electron is in close to the platinum atom while the other is further away. After the two Pt–H bonds are formed, the bonding Pt electrons are both in s hybrid orbitals.

A more consistent wave function for this reaction would be to allow the Pt pair of bonding electrons to use a tight d orbital, a

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Table V. Energies along the Reaction Path

<table>
<thead>
<tr>
<th>R [Å]</th>
<th>HF, kcal/mol</th>
<th>GVB-CI(2/6), kcal/mol</th>
<th>GVB-Cl(2/6)−*RCI(4/8), kcal/mol</th>
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<tr>
<td>1.166</td>
<td>16.21</td>
<td>23.79</td>
<td>−15.90</td>
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<td>1.417</td>
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<td>1.36</td>
<td>0.92</td>
<td>1.40</td>
</tr>
<tr>
<td>3.167</td>
<td>0.15</td>
<td>0.02</td>
<td>0.52</td>
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</table>

*The total energies at the dissociated limit (+) are −713.330 533 hartrees at the HF level, −713.363 061 hartrees at the GVB-CI(2/6) level, and −713.449 931 hartrees at the GVB-Cl(2/6)/RCI(4/8) level.

diffuse d orbital, and a Pt 5 orbital. This would allow this pair of electrons to have both in-out correlation and the optimum d5 mixture throughout the reaction. In order that the two GVB pairs involved in the bonding be treated equivalently, we have permitted each of them to have three natural orbitals (rather than two). At the dissociated limit, this corresponds to a Pt pair, as was described above, and to an H2 molecule described at the GVB(1/3) level (in-out plus left-right correlation).

In considering the effects of electron correlation on this reaction, we examined the HF, GVB-CI(2/6), and GVB-Cl(2/6)/RCI(4/8) wave functions. The GVB-CI(2/6) wave function includes electronic correlation terms differential in describing the Pt–H bonds. The GVB-CI(2/6)/RCI(4/8) wave function includes both the Pt–H bonding terms of the GVB-CI(2/6) level as well as the d–d correlations important in determining the d5s–d5s splitting on the platinum atom. For more calculation details, see section IV.
Oxidative Addition and Reductive Elimination

Table VI. Transition State as a Function of Electronic Correlation for Pt\((PH_3)_2\) + H_2 → H-Pt\((PH_3)_2\)

<table>
<thead>
<tr>
<th>level of electronic correlation</th>
<th>Pt-H distance, Å</th>
<th>activation energy, kcal/mol</th>
<th>exothermicity, kcal/mol</th>
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<tr>
<td>HF</td>
<td>2.199</td>
<td>4.04</td>
<td>-16.21</td>
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<tr>
<td>GVB-CI(2/6)</td>
<td>2.417</td>
<td>1.96</td>
<td>-23.79</td>
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<td>ROHCIP(2)/GVB</td>
<td>2.417</td>
<td>2.34</td>
<td>-15.90</td>
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</table>

Table VII. Comparison of the HF Activation Barrier for Pt\((PH_3)_2\) + H_2 → H-Pt\((PH_3)_2\) and Important Geometric Parameters at the Transition State Obtained in Various ab initio Studies

<table>
<thead>
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<th>Method</th>
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<th>(R_{H-P})</th>
<th>(\theta_{P-P-H})</th>
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<td>1.81</td>
<td>0.90</td>
<td>120</td>
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<td>Kitaura et al\textsuperscript{28}</td>
<td>5.2</td>
<td>2.066</td>
<td>0.766</td>
<td>147.7</td>
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<td>This work</td>
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<td>2.199</td>
<td>0.750</td>
<td>137.4</td>
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</table>

\textsuperscript{*}Reference 30. \textsuperscript{28}Reference 39.

The potential curves are shown in Figure 7, and the calculated energies are tabulated in Table V. The main effect of correlating the Pt-H bonds at the GVB-CI(2/6) level is to increase the exothermicity of the reaction and to move the transition state to longer distances. Correlating the nonbonding \(d\) electrons at the GVB-CI(2/6)'s RCI(4/8) level makes the exothermicity for the reaction smaller than for the GVB-CI(2/6) level wave function, but gets essentially the same transition-state geometry and barrier. Correlating the nonbonding \(d\) electrons does not affect the long-range behavior of the Pt-H bonds. The GVB-CI(2/6) wave function (in which the nonbonding \(d\) electrons are doubly occupied) does as well as the GVB-CI(2/6)'s RCI(4/8) wave function (which has the nonbonding \(d\) electrons correlated) near the transition state. This implies that this transition-state geometry is less sensitive to the \(s^d-d^2\) splitting than is the exothermicity.

Qualitatively, these potential curves all have similar shapes. The potential curves for the correlated wave functions can be divided into three regions similar to those for the HF surface. This implies that the HF level wave function could have been used to elucidate the electronic structure of the mechanism. Unfortunately HF yields orbitals that are delocalized and difficult to interpret, whereas the GVB types of wave functions lead to orbitals that are localized and easier to interpret. Also, the GVB wave function allows one to interpret the various types of correlation and to see how each one affects the wave function. The GVB-CI(2/6) wave function leads to an improved description of the long-range attractive terms in the wave function, leading to a lower activation energy, and a longer Pt-H bond distance at the transition state. At the GVB-CI(2/6)'s RCI(4/8) level, we also include interpair correlations of the nonbonding \(d\) electrons on the platinum atom. The calculations were not important at the transition state as the Pt atom still has a \(d^8\)-like configuration. On the other hand, these \(d\)-\(d\) correlations have a big effect on the \(s^d-d^2\) separation, and hence they have a big effect on the reaction exothermicity. These correlation effects stabilize \(d^2\) relative to \(s^d\) and have led to a smaller exothermicity. In Table VI we present a summary of the energetics for oxidative addition at the different levels of calculation.

Comparison with Previous Results. The previous two ab initio studies of this system gave different results for activation barriers and transition state. A comparison of the results presented in this paper with the results from Noell and Hay and from Kitaura et al.\textsuperscript{28} is shown in Table VII.

The transition-state geometry found in our studies and by Kitaura et al.\textsuperscript{28} is much closer to products than Noell and Hay's\textsuperscript{29} transition state. Also, our HF activation barrier (4.04 kcal/mol) for oxidative addition is close to the value (5.2 kcal/mol) found by Kitaura et al.\textsuperscript{28} Noell and Hay\textsuperscript{29} on the other hand, found a significantly larger activation barrier (17.4 kcal/mol). Since we have used the same effective potential as Noell and Hay\textsuperscript{29} and completely optimized the geometry for every fixed value of Pt-H bond length, Noell and Hay's\textsuperscript{29} high activation barrier must be due to their partial optimization, which apparently did not converge to the lowest energy point along the reaction coordinate.

The differences between our transition-state geometry and that of Kitaura et al.\textsuperscript{28} must be due to the different effective potentials and basis sets used. Our results should be more reliable for the following reasons. (1) We have used Noell and Hay's\textsuperscript{29} Pt potential, which includes the \(f\)-projected terms required when \(f\) electrons are included in the effective potential, whereas the Kitaura et al.\textsuperscript{28} calculations used an effective potential with only \(s\) and \(p\) projections. (2) We have used a larger hydrogen basis set than Kitaura et al.\textsuperscript{28} This larger basis set includes the more diffuse character needed to describe the long-range Pt-H interactions at the transition state.

The energies of reaction found from HF calculations in these three studies were also very different. Our \(\Delta E\) (-16.2 kcal/mol) is larger than that found by Noell and Hay\textsuperscript{29} (-6.7 kcal/mol), but smaller than the \(\Delta E\) (-36.9 kcal/mol) of Kitaura et al.\textsuperscript{28} We obtain a larger \(\Delta E\) than Noell and Hay for this reaction because we allowed the Pt-P bond lengths to change along the reaction path. Noell and Hay held this parameter fixed at a value closer to the optimum for Pt\((PH_3)_2\), which should favor the dissociated limit and give a smaller \(\Delta E\). The Pt potential used by Kitaura et al.\textsuperscript{28} is known to give Pt-H bonds that are 11.6 kcal/mol too strong.\textsuperscript{30} Applying this correction factor to Kitaura's 3P \(\Delta E\) leads to a corrected \(\Delta E\) of 13.7 kcal/mol, which is very close to our value.

Comparing geometries with the available X-ray structures, we see that our Pt-P bond distances are too long by 0.1 to 0.2 Å. For Pt\((PCy_3)_2\), the experimental distance was found to be 2.21 Å,\textsuperscript{31} while our calculated Pt-P bond distance for Pt\((PH_3)_2\) is 2.32 Å. Typical Pt-P bond distances for Pt(II) complexes are 2.25 Å for \(\eta^5\)-H,Pt\((PCy_3)_2\),\textsuperscript{32} 2.268 Å for \(\eta^5\)-H,Pt\((PCy_3)_2([Cy_4]H_2)\),\textsuperscript{33} and 2.248 Å for \(\eta^5\)-H,Pt\((PCy_3)_2(Cy_3)\).\textsuperscript{34} Our calculated Pt-P bond distance for \(\eta^5\)-H,Pt\((PH_3)_2\) is 2.45 Å, which is 0.2 Å too long. This elongation of the Pt-P bond length was also found by Noell and Hay\textsuperscript{35} when they optimized the geometry of Pt\((PH_3)_2\) and found a Pt-P distance of 2.36 Å (using a different effective potential and basis set on the phosphorus). This effect appears to be systematic for phosphorus Lewis acid/Lewis base bonds treated at the HF level with a valence double-\(f\) basis.

In BH\(_2\)PH\(_3\), where phosphorus is making a similar Lewis acid/Lewis base bond, we find a B-P bond length of 2.180 Å at the HF level using a double-\(f\) basis.\textsuperscript{36} When the geometry was optimized with polarization functions on both the phosphorus and boron,\textsuperscript{40} the B-P bond distance was found to be 2.055 Å. The experimental\textsuperscript{40} B-P distance in BH\(_2\)PH\(_3\) is 1.937 Å. Therefore, approximately 0.1 Å of the error observed in \(P\) Lewis acid/Lewis base bonds is due to the use of an unoptimized basis. Abridge and Koch\textsuperscript{41} have carried out calculations on BH\(_2\)PH\(_3\), using a smaller basis set with both HF and correlated wave functions (CEPA). The smaller basis set yields a shorter B-P bond distance of 1.99 Å at the HF level. For the correlated wave function, their B-P bond distance is 0.04 Å shorter than their HF results. This indicates a large part of the remaining discrepancy must be due to electronic correlation.

Kitaura et al.\textsuperscript{28} found Pt-P bonds that were short by 0.1 Å, but this is most likely due to the small basis set (STO-2G) used to calculate their geometries, which would underestimate bond distances for Lewis acid/Lewis base bonds.

Hoffmann and co-workers\textsuperscript{3} have performed an analysis of reductive elimination reactions using the extended Hückel method. Three major conclusions were presented in this work: (1) The better the $e$-donating capability of the leaving group, the more readily the elimination proceeds. (2) Stronger donor ligands trans to the leaving groups give a higher barrier for the elimination reaction. (3) A lower positioning of the MA$_2$B$_2$ orbital facilitiates the reductive elimination of R$_3$. A lower MA$_2$B$_2$ energy will be given by a lower metal d orbital energy.

Our studies concur with the third conclusion of Hoffmann et al. A more stable d orbital implies a more stable d$^5$ state of the metal relative to s$^6$ that will in turn increase the driving force for reductive elimination. This should also decrease the barrier for reductive elimination. Our results do not bear on the first two points since we have studied only the one system.

Balazs et al.\textsuperscript{48} have also studied (1) using the SCF-Xo-SW approach. However, they do not report calculated geometries or transition states nor do they report calculated bond energies or activation energies; thus there is little with which to compare our work. The electronic densities from Xo agree with our results, indicating neutral H atoms (charge of $-0.04$ e).

### IV. Calculational Details

#### A. Potentials and Basis Sets

On platinum we used the relativistic effective potential of Noël and Hay.\textsuperscript{49} For the hydrogen atoms bonded directly to the Pt atom we used a triple-$
\text{f}$ contraction of Huzinaga's six-Gaussian basis.\textsuperscript{44} For phosphorus we used the SHC effective potentials of Rappe et al.\textsuperscript{44} with a minimum basis set contraction based on the atomic orbitals. The hydrogen atoms bonded to P were described with a minimum basis set based on Huzinaga's four-Gaussian basis (unscaled). To determine whether the use of minimum basis phosphines affected the geometries or energetics for oxidative addition, we carried out geometry optimizations on H$_3$Pt(PH$_3$)$_2$ and Pt(PPH)$_3$ using full double-$
\text{f}$ basis sets on the phosphine ligands. The results are shown in Figures 11 and 12. The exothermicity calculated for this reaction with double-$
\text{f}$ phosphines is 13.84 kcal/mol, only 2.47 kcal/mol smaller than the result with minimum basis set phosphines. This represents only a 1.25 kcal/mol error per Pt-H bond.

B. GVB-PP (Generalized Valence Bond with Perfect Pairing Restrictions).\textsuperscript{44} In this wave function each correlated pair of electrons is described as a spin singlet state $\psi = \psi_+ + \psi_-$. This description can be transformed to a natural orbital description $c_1|\phi_1^+\rangle - c_2|\phi_2^+\rangle$

where

$$
\phi_1 = \frac{(\phi_+ + \phi_-)}{(2(1 + S))^{1/2}} \quad \phi_2 = \frac{(\phi_+ - \phi_-)}{(2(1 - S))^{1/2}}
$$

$c_1/c_2 = (1 - S)/(1 + S)$. $c_1^2 + c_2^2 = 1$, and $S = \langle \phi_+|\psi_\phi \rangle$. These natural orbitals are then used in higher level CI calculations.

C. GVB-RCI (Restricted Configuration Interaction). The GVB-RCI calculation includes the configurations $\phi_1^2$, $\phi_2^2$, and $\phi_1\phi_2$ for each GVB pair. When the configuration $\phi_1\phi_2$ is multiplied by similar configurations in the other GVB pairs, more general spin couplings are included that will optimize the total spin eigenfunction of the electronic wave function. This spin optimization can be important in describing the dissociation of multiple bonds and in describing the changes in the spin multiplicity in different atomic states. This wave function also includes interpair correlations important in the atomic d$^{50}$-s$^{50}$ splittings. This type of wave function is useful because it still maintains orthogonal GVB pairs of electrons, facilitating the interpretation of the wave function.

When comparing singlet and triplet states of the platinum atom and of Pt(PH$_3$)$_2$ we counted the two open-shells orbitals as a GVB pair in the RCI(1/10) nomenclature. This is consistent since the triplet wave function contains all the configurations that the singlet contains except for those that have two electrons in one of the open-shell orbitals.

D. GVB-Cl (Generalized Valence Bond Configuration Interaction). This type of CI is carried out by using all possible configurations that can be formed from the various occupations of the GVB orbitals from the GVB-PP calculation. This wave function includes all the terms of the RCI wave function plus terms that allow the GVB pairs to overlap and to change shape by allowing linear combinations between pairs. Such terms are particularly important near the region where the Pt-H bonds are just starting to form. Omission of such terms (as in a GVB-PP or RCI calculations) would lead to an artificial hump in the transition region.

Figure 13 demonstrates the importance of full correlation among the four electrons that are involved with the oxidation/reduction process. The GVB-PP wave function can describe the two Pt-H bonds at equilibrium or the doubly occupied d orbital and H-H bond at the dissociated limit. Near the region where both of the above VB descriptions are important, the energy of the GVB-PP wave function becomes artificially high. This gives a transition state near 1.55 Å for the GVB-PP wave function that disappears
for the GVB-CI wave function (which can describe both VB wave functions).

E. Geometry Optimizations. All of the geometry optimizations were obtained by using an analytic gradient procedure (GVBGRAD). This program was based on (a) the GVB program to evaluate density matrices for restricted HF and GVB-PP wave functions, (b) the HONDO program to calculate derivatives of the ab initio energy expressions, and (c) routines from the GAUSSIAN program and the Lee-Kong effective potential programs to calculate the effective potential terms of the derivative. For the optimization of the geometries we used a relatively simple Newton-Raphson technique in which the second derivative matrix is updated after every gradient calculation (except for the starting geometry). The end-on approach of $H_2$ to $Pt(PH_3)_2$ was not considered in this work since the side-on approach of $H_2$ to $Pt(PH_3)_2$ gave a lower barrier. The end-on approach should give a higher barrier because it would require breaking an H-H bond (104 kcal/mol) and promoting PtL to a triplet state (~50 kcal/mol) while only getting ~72 kcal/mol back in the Pt-H bond. [Kitaura et al., found that the C$_3$ transition state is a true saddle point (i.e., there is only one negative root in the curvature matrix).]

F. Hybrid Wave Functions. In examining the effect of electronic correlation along the reaction path, we calculated a GVB-CI(2/6)$^d$RCI(4/8) wave function where the orbitals were optimized for the full 1360 configuration (GVB spin eigenfunctions) wave function by using the GVB3 program. We used this wave function to examine the effects of correlating the nonbonding d electrons on the energetics along the reaction coordinate. The electrons in the Pt-H bonds were treated at the GVB-CI level for the reasons described above. The d nonbonding orbitals were treated at the RCI(4/8) level because this level was needed to get reasonable triplet–singlet splittings for the atom. The resulting wave function is therefore a product of the GVB(2/6) wave function for the Pt-H bonds and a RCI(4/8) for the nonbonding d electrons. This wave function was optimized self-consistently by using the GVB3 multiconfigurational self-consistent-field program because the nonbonding d natural orbitals did not change smoothly from equilibrium to the dissociated limit at the GVB-PP level unless they were optimized at the CI level. Often it is sufficient to use the orbitals from the GVB-PP wave function for RCI or GVB-CI wave functions. For example, orbitals obtained at the GVB-PP level were adequate for the GVB-CI(2/6) wave function. Optimizing the orbitals at the GVB-CI level lowered the energy of the GVB-CI wave function by less than 0.002 Hartree (1.255 kcal/mol) relative to the GVB-CI calculation by using orbitals obtained at the GVB-PP level. This energy lowering remained essentially constant along the reaction path. Thus, although the GVB-PP wave function yields an unreasonable potential curve in the transition region, it does provide orbitals yielding a proper description of Pt-H bonding formation. This occurs because the GVB-CI includes the recoupling of bonding electrons necessary in describing the reaction. However, for the GVB-CI(2/6)$^d$RCI(4/8) wave function it is essential to self-consistently reoptimize the orbitals for the full wave function, as illustrated in Figure 14. The upper potential curve was obtained from the fully self-consistent wave function, while the lower curve is for a wave function for which the orbitals were optimized at the GVB-PP level. Use of incompletely optimized orbitals (GVB-PP) is biased against the Pt d$^5$ state (the dissociated limit) and leads to an irregularly stepped potential curve. The reason for this behavior is that for Pt(PH$_3$)$_2$, the RCI wave function includes terms differential in the d$^5$-$d^6$ splitting. When the orbitals are optimized for a wave function including these terms, orbital shape changes occur that are differential for these state splittings. These differential terms affect the shape of the potential curve (and the transition state) because the platinum atom changes its electronic state during the reaction.

Acknowledgement. This work was supported in part by a grant from the National Science Foundation (No. CHE80-17774). One of the authors (J.J.L.) wishes to acknowledge financial support in the form of a fellowship from Exxon.

Registry No. Pt(H$_3$)(PH$_3$)$_2$, 76832-29-6; Pt(PH$_3$)$_3$, 76830-85-8; H$_2$, 1333-74-0.
CHAPTER 2

Theoretical Studies of Oxidative Addition and Reductive Elimination:

II. Reductive Coupling of H-H, H-C, and C-C Bonds
from Pd and Pt Complexes

The following chapter has been submitted for publication to Organometallics
I. Introduction

The concepts of oxidative addition

\[ M + \begin{array}{c} \text{A} \\ \text{B} \end{array} \rightarrow M \begin{array}{c} \text{A} \\ \text{B} \end{array} \]  \hspace{1cm} (1) \]

and reductive elimination

\[ \begin{array}{c} \text{A} \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\ \text{B} \end{array} \] \hspace{1cm} (2) \]

are prevalent in the literature on organometallic chemistry.\(^1\) Thus, catalytic hydrogenation of alkenes often requires oxidative addition of \( \text{H}_2 \) to form the activated complex \( \text{MH}_2 \),\(^2\) e.g.,

\[ \text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6 \hspace{1cm} \text{RhCl(PPh}_3\text{)}_3 \] \hspace{1cm} (3) \]

involves formation of \( \text{Rh(H)}_2\text{(Cl)(PPh}_3\text{)}_3 \). Similarly, an important step in the H-D exchange in alkanes\(^3\) is the oxidative addition of C-H bonds, e.g.,

\[ \text{CH}_4 + \text{D}_2\text{O} \rightarrow \text{CH}_3\text{D} + \text{HOD} \hspace{1cm} \text{K}_2\text{PtCl}_4 \] \hspace{1cm} (4) \]

may involve formation of \( \text{Pt(H)(CH}_3\text{)(Cl)}_4\). In addition, reductive coupling to form C-C bonds is an important step in the cross coupling reaction catalyzed by Ni(II) and Pd(II),\(^4\) e.g.,

\[ \text{Ar-Cl} + \text{RMgCl} \rightarrow \text{Ar-R} + \text{MgCl}_2 \hspace{1cm} \text{NiCl}_2\text{L}_2 \] \hspace{1cm} (5) \]

involves \( \text{Ni(Ar)(R)L}_2 \rightarrow \text{NiL}_2 + \text{Ar-R} \).

Because of the central role of oxidative addition/reductive elimination in organometallic chemistry, a number of recent experimental studies have been directed toward elucidating the details of such reactions.
However, a number of puzzles remain and there is yet no unified theoretical framework for understanding such processes for H-H, H-C, and C-C systems. The purpose of this paper is to add toward building this framework.

Current experimental evidence relating to these reactions is as follows.

A. *Experimental Evidence for Mechanism*

Mechanistic studies have been carried out on activation of H₂ by Ir(I) complexes,

\[
H_2 + \text{IrCl(CO)(PPh}_3)_2 \rightarrow \text{Ir(H)}_2\text{Cl(CO)(PPh}_3)_2
\]  \hspace{1cm} (6)

C-H activation by Ir(I)⁶ and Rh(I)⁷ complexes,

\[
\text{CH}_4 + \text{Ir(C}_5\text{Me}_5)(\text{PMe}_3) \rightarrow \text{IrH(CH}_3)(\text{C}_5\text{Me}_5)(\text{PMe}_3)
\]  \hspace{1cm} (7)

reductive coupling of C-H bonds from Pt(II)hydridomethyl complexes,⁸

\[
\text{PtH(CH}_3)(\text{PPh}_3)_2 \rightarrow \text{Pt(PPh}_3)_2 + \text{CH}_4
\]  \hspace{1cm} (8)

and reductive coupling of C-C bonds from Pd(II)⁹

\[
\text{Pd(CH}_3)_2(\text{PPh}_3)_2 \rightarrow \text{Pd(PPh}_3)_2 + \text{C}_2\text{H}_6
\]  \hspace{1cm} (9)

and Ni(II)¹⁰ complexes.

\[
\begin{array}{c}
\text{Me}_2 \begin{array}{c}
\text{P} \\
\text{Me}_2 \\
\text{Me}
\end{array} \\
\text{Ni} \\
\text{Ph} \\
\text{Me}_2 \\
\text{P}
\end{array} \quad \xrightarrow{2L} \quad \begin{array}{c}
\text{Me}_2 \begin{array}{c}
\text{P} \\
\text{Me}_2 \\
\text{L}
\end{array} \\
\text{Ni} \\
\text{L} \\
\text{Me}_2 \\
\text{P}
\end{array} + \text{MePh}
\]  \hspace{1cm} (10)

In all cases there is good evidence that these H-H, C-H, and C-C coupling or activation processes are concerted. Some of the evidence is as follows.

The activation of H₂ by Ir(I) complexes, (6), is believed to be concerted because (i) the oxidative addition of H₂ to Ir(I) complexes almost
always yields a cis-product,\textsuperscript{5,11} (ii) the kinetics of the addition reaction are first-order in both H\textsubscript{2} and the Ir(I) complex,\textsuperscript{5ab} and (iii) the entropy of activation $\Delta S^\ddagger \approx -23 \pm 3$ e.u. for oxidative addition of H\textsubscript{2} is very close to the entropy of reaction, $\Delta S \approx -28 \pm 3$ e.u. (which is dominated by the loss of the translational and rotational entropy of the H\textsubscript{2} molecule).\textsuperscript{5b}

Activation of C-H bonds by Ir(I) complexes, (7), has been observed by a number of different research groups.\textsuperscript{6} Janowics and Bergman\textsuperscript{6c} conducted crossover experiments and measured the relative rates of insertion in different types of C-H bonds. Their results appear to be most consistent with a concerted process.

The mechanism of reductive elimination from Pt(II) hydridoalkyls, (8), has been studied by two research groups.\textsuperscript{6} Abis, Sen, and Halpern\textsuperscript{6a} used isotope labeling experiments to follow the decomposition of various Pt(H)(Me)L\textsubscript{2} complexes and found that reductive elimination is intramolecular. Michelin et al.\textsuperscript{6b} studied the decomposition of cis-Pt(H)(CH\textsubscript{2}CF\textsubscript{3})(PPh\textsubscript{3})\textsubscript{2} [which decomposes at a slower rate than the hydridomethyl Pt(II) complexes] and found that (i) the rate of decomposition is first-order in the reaction, and (ii) the reaction has low values for the entropy of activation $\Delta S^\ddagger$ (2-8 e.u.). These results are consistent with a concerted unimolecular reductive elimination.

The mechanism of reductive elimination from Pd(II) dimethyl complexes, (9), has been studied by Stille et al.\textsuperscript{9a-c} and by Ozawa et al.\textsuperscript{9d} The lack of crossover products in the decomposition of Pd(CH\textsubscript{3})\textsubscript{2}L\textsubscript{2} and Pd(CD\textsubscript{3})\textsubscript{2}L\textsubscript{2} and the unimolecular kinetics observed in these experiments are consistent with a concerted process. Note, however, that the corresponding Pt complex will not reductively eliminate ethane;

$$L_2Pt(CH_\text{3})_2 \rightarrow L_2Pt + C_2H_6$$

(11)
it can, in fact, be sublimed before it will decompose.\textsuperscript{12}

\textbf{B. Theoretical Strategy}

Four issues we wish to address here are:

(i) Are the processes concerted?

(ii) What are the relative barriers for H-H, H-C, and C-C coupling (and activation)?

(iii) How does the nature of the metal affect the reaction? [Why is Pt(II) so different from Pd(II)?]

(iv) What relation should there be between the processes for metal complexes versus those for metal atoms?

For reasons to be discussed below, we wanted to consider two related classes of systems where one class has exothermic reductive coupling for all three cases of \( R_1, R_2 = H, CH_3 \), and where the other class has exothermic oxidative addition for all three cases. Consequently, we examined the following reactions:

\[
Pd(H)_2 \leftrightarrow Pd + H_2 \quad (12)
\]

\[
Pd(H)(CH_3) \leftrightarrow Pd + CH_4 \quad (13)
\]

\[
Pd(CH_3)_2 \leftrightarrow Pd + C_2H_6 \quad (14)
\]

\[
Pt(H)_2 \leftrightarrow Pt + H_2 \quad (15)
\]

\[
Pt(H)(CH_3) \leftrightarrow Pt + CH_4 \quad (16)
\]

\[
Pt(CH_3)_2 \leftrightarrow Pt + C_2H_6 \quad (17)
\]

where the first three are exothermic (to the right) while the last three are endothermic. The Pd-H, Pd-CH\(_3\), Pt-H, and Pt-CH\(_3\) bonds in these sys-
tems should typify the M-H and M-C bonds of other organometallic complexes involving metals of comparable electronegativity and oxidation state.

From various previous studies,\textsuperscript{13} we concluded that the reactions

\begin{equation}
\begin{array}{c}
L \quad M \quad R_1 \\
L \quad M \quad R_2
\end{array}
\leftrightarrow
\begin{array}{c}
L \\
M \\
L
\end{array}
+ \begin{array}{c}
R_1 \\
L \\
R_2
\end{array} \quad (18)
\end{equation}

[where \(R_1, R_2 = H, \text{CH}_3\) and \(M = \text{Pt}(0), \text{Pd}(0)\)] involve a change in the effective electronic configuration of \(M\) from an \(s^1d^9\) configuration for \(M(R_1)(R_2)L_2\) to a \(d^{10}\) configuration for \(ML_2\). Since the ground state of the Pd atom is \(d^{10}\) (with the lowest \(s^1d^9\) state lying 22 kcal/mol higher),\textsuperscript{14} the Pd atom should be a fair model for facile reductive elimination from various low valent Group VIII transition metal complexes (18). On the other hand, the ground state of the Pt atom is \(s^1d^9\) (with the \(d^{10}\) state lying 11 kcal/mol higher),\textsuperscript{14} favoring oxidative addition and making the Pt atom a good model for facile oxidative addition processes.

The theoretical results for reactions (12)-(17) are described in Section II, compared with experiment in Section III, and compared with other theoretical work in Section IV and Appendix A. Calculational details are described in Section V.
II. Summary of Results

A. Electronic Promotion Versus Charge Transfer

A major conclusion from these studies is that oxidative addition requires promotion of the metal from the d^{10} atomic configuration to the s^1d^9 configuration. We find for R = H, CH₃, that the M-R bonds are covalent for both M = Pd and Pt, with each bond involving one electron in an orbital on R and one electron in an sd hybrid orbital on the metal. The d^{10} configuration cannot make covalent bonds since all five d orbitals are doubly-occupied; however, the s^1d^9 configuration with two singly-occupied orbitals can mix these two orbitals to form two sd hybrids capable of forming covalent bonds to the two ligands. Thus the metal atom is not oxidized during the oxidative addition of H₂, CH₄, and C₂H₆ to Pd and Pt. Rather, the metal is promoted from the d^{10} state incapable of forming covalent bonds to the s^1d^9 state capable of forming two covalent bonds.

Generalized valence bond (GVB) orbitals for the complexes studied in this work are shown in Figures 1, 2, and 3, with the hybridization of each orbital indicated just above the lower boundary of each orbital plot (these populations of GVB orbitals are summarized in Table I). In each case the ligand GVB orbital has 0.80±0.03 electrons on the ligand with 0.17±0.02 electrons on the Pt atom. For the Pt complexes, the metal GVB orbital has 0.08±0.01 electrons on the ligand, 0.62±0.02 electrons in a Pt d orbital, and 0.30±0.02 electrons in Pt 6s and 6p orbitals (94% s and 5% p). Thus the metal orbitals are sd^2 hybrids. In the Pd complexes there is more variety in the character of the GVB orbital describing the metal part of the metal-carbon bond pair, with 0.24 electrons on the CH₃ for Pd(CH₃)₂, but 0.12 for Pd(H)(CH₃). In addition, the sd hybrid character varies [from s^1d^{1.7} for PdH₂ to s^1d^{1.3} for the Pd-H bond of Pd(H)(CH₃) and
from $s^1d^{3.8}$ for the Pd-C bond of PdH(CH$_3$) to $s^1d^{2.9}$ for Pd(CH$_3$)$_2$. We do not believe that these variations are as significant as the general result that the GVB orbitals for both Pt and Pd use sd hybrid orbitals to form bonds to H and CH$_3$ groups. These sd hybrids are similar in all cases, with somewhat more d than s character. The carbon atoms in methyl groups bonded to the metal are tetrahedral (within 1°) and sp$^3$ hybridized (see Appendix B). From total Mulliken populations (see Table II), the Pt complexes on the average have 9.03 d electrons and 1.06 s electrons, while Pd complexes have 9.23 d electrons and 0.69 s electrons (a difference expected from the preference of Pd for d electrons).

The fact that Pd-H, Pd-C, Pt-H, and Pt-C bonds are covalent is consistent with the Pauling electronegativities: Pd(2.2) and Pt(2.2) versus H(2.1) and C(2.5).$^{15}$ Crabtree et al.$^{5f,i}$ have also suggested that the addition of H$_2$ to Ir(I) complexes is not oxidative based on observations that the oxidative addition of H$_2$ to cationic Ir(I) cyclooctadiene complexes is promoted by electron-withdrawing ligands and inhibited by electron donors.$^{5f}$ and that an upfield shift of the vinyl carbon resonance occurs in the $^{13}$C NMR of Ir(COD)$_2$ (COD = 1,5-cyclooctadiene) on addition of H$_2$.$^{5g}$

Summarizing, the oxidative addition of H$_2$, CH$_4$, and C$_2$H$_6$ to d$^{10}$ metal centers should be thought of in terms of promoting an electron from a doubly-occupied d orbital to an unoccupied s orbital in order to accommodate the formation of two covalent bonds rather than the transfer of one electron to each ligand. For Pd and Pt this promotion corresponds to the electronic transition from d$^{10}$ to s$^1$d$^9$ instead of ionizing two electrons from d$^{10}$ M(0) to form a d$^8$ M(II).
B. Reaction Energetics and Bond Energies

1. Reaction Energetics

Before discussing the details of the reactions, we will examine the overall energetics (see Figures 4 and 5). For Pd, H-H, H-C, and C-C coupling is exothermic (with \( \Delta H_{298}^{16} \) of \(-4.0\), \(-17.2\), and \(-19.0\) kcal/mol resulting from \( \Delta E \)'s of \(-3.6\), \(-20.1\), and \(-16.0\) kcal/mol, respectively), while for Pt these processes are endothermic (with \( \Delta H_{298}^{16} \) of \(33.2\), \(19.0\), \(15.5\) kcal/mol resulting from \( \Delta E \)'s of \(33.6\), \(16.1\), and \(18.3\) kcal/mol \( \Delta E \), respectively; see Table III). (For Pt these energies are for the lowest spin-allowed process, leading to \(d^{10}\) Pt atom.) These differences between Pd and Pt are easily understood on the basis of relative atomic excitation energies. Reductive coupling changes the metal from \(s^1d^9\) to \(d^{10}\), but for Pd the \(s^1d^9\) state is 22 kcal/mol higher than \(d^{10}\), while for Pt the \(s^1d^9\) state is 11 kcal/mol below \(d^{10}\). Thus, reductive coupling from Pd should be favored by 33 kcal/mol (theoretical value 32 kcal/mol) over comparable reductive coupling from Pt. Indeed, we find the differences \([\Delta H_{298} \text{ for } (2)]\) to be 37.2 kcal/mol for the dihydrides, 36.2 kcal/mol for hydridomethyl complexes, and 34.3 kcal/mol for the dimethyl complexes. Thus the GVB model of bonding allows one to use atomic excitation energies and the relative energetics of reductive coupling for one metal complex to estimate the energetics for other metals.

2. Average Bond Energies

For semi-quantitative comparisons of various systems, it is often useful to have an idea of average bond energies for various types of bonds. There are two simple ways of doing this:
Method 1: Adiabatic Bond Energies

The adiabatic bond energy is defined as

$$D_A(M-R) = \frac{1}{2}[\Delta H_{298}(MR_2 \rightarrow M + R_2) + \Delta H_{298}(R_2 \rightarrow 2R)]$$

The calculated reaction enthalpy for the reductive coupling is added to the $R_2$ bond energy\textsuperscript{17} for a free $R_2$, and then the total is divided in half to give the adiabatic bond energy. This leads to $D_A(Pt-H) = 69$ kcal/mol, $D_A(Pt-C) = 53$ kcal/mol, $D_A(Pd-H) = 50$ kcal/mol, and $D_A(Pd-C) = 36$ kcal/mol. As a check on the consistency of average bond energies, we can use the bond energies calculated from the $\Delta H_{298}$ of reactions (12), (14), (15), and (17) to predict $\Delta H_{298}$ for reactions (13) and (16). This yields predicted values of $\Delta H_{298}$ of -19 kcal/mol for reaction (13) and 17 kcal/mol for reaction (16), which are both 2 kcal/mol lower than the calculated values of -17.2 and 19.0 kcal/mol. Overall, the Pd-$R$ bonds are 19 and 17 kcal/mol weaker than the corresponding Pt-$R$ bonds, which just represents the preference of Pd for d\textsuperscript{10} over s\textsuperscript{1}d\textsuperscript{9}.

Method 2: Intrinsic Bond Energies

In order to eliminate the effect of s\textsuperscript{1}d\textsuperscript{9}–d\textsuperscript{10} state splittings on the average bond energies, we define an intrinsic bond energy as

$$D_I(M-R) = \frac{1}{2}[\Delta H_{298}(MR_2 \rightarrow M + R_2) + \Delta H_{298}(R_2 \rightarrow 2R) + \Delta E(d^{10} \rightarrow s^{1}d^{9})]$$

where the final state of the metal atom is taken as the s\textsuperscript{1}d\textsuperscript{9} state. This is the intrinsic bond strength where the electronic state of the atom is not allowed to relax to a d\textsuperscript{10} state. In this case, we obtain very similar bond energies for Pd and Pt, with $D_I(Pd-H) = 60$ kcal/mol and $D_I(Pt-H) = 62$ kcal/mol, while $D_I(Pd-CH_3) = 45$ kcal/mol, and $D_I(Pt-CH_3) = 47$ kcal/mol (see Table IV). Thus, these intrinsic energies plus atomic excitation energies should be most useful in using results for one metal to predict
results for another.

3. **Energetics on Metal Surfaces**

For metal surfaces, one might expect that metal-metal bonding would tend to keep the surface atoms for the Ni triad in s\(^1\)d\(^9\) states. If so then the \(D_7\) should provide a reasonable estimate for the bond energy at metal surfaces.\(^{18}\) (Band calculations for Pd and Pt have been interpreted in terms of an average s\(^{0.4}\)d\(^{0.6}\) configuration,\(^{19}\) somewhat more d occupation than in our complexes.) The predicted results for

\[
\begin{array}{c}
\text{R}_1 - \text{R}_2 \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\end{array}
\begin{array}{c}
\text{R}_1, \text{R}_2 \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\hline \\
\end{array}
\]

are

\[\Delta H_{298} = -15 \text{ kcal/mol (Pd) and } -20 \text{ kcal/mol (Pt) for H}_2\]
\[\Delta H_{298} = -4 \text{ kcal/mol (Pd) and } -8 \text{ kcal/mol (Pt) for H-CH}_3\]
\[\Delta H_{298} = -10 \text{ kcal/mol (Pd) and } -14 \text{ kcal/mol (Pt) for H-C}_2\text{H}_5\]

and

\[\Delta H_{298} = 0 \text{ kcal/mol (Pd) and } -5 \text{ kcal/mol (Pt) for CH}_3-\text{CH}_3.\]

The experimental heats of adsorption for H\(_2\) on Pt and Pd surfaces are 20.8 kcal/mol,\(^{20}\) on Pd(111), 24.4 kcal/mol, on Pd(110),\(^{20}\) 9.5 kcal/mol, on Pt(111),\(^{21}\) and 12 kcal/mol on Pt[9(111) \times (111)].\(^{21}\) Thus our one-center Pd numbers predict surface Pd-H bonds about 3 kcal/mol weaker than experiment, whereas our numbers for Pt indicate surface Pt-H bonds about 5 kcal/mol stronger than observed.

Using the experimental results on H\(_2\) to calibrate the predictions for the other reactions leads to
\[ \Delta H = -10 \text{ kcal/mol (Pd)} \text{ and } +1 \text{ kcal/mol (Pt) for H-CH}_3 \]
\[ \Delta H = -16 \text{ kcal/mol (Pd)} \text{ and } -6 \text{ kcal/mol (Pt) for H-C}_2\text{H}_5 \]
\[ \Delta H = -6 \text{ kcal/mol (Pd)} \text{ and } +4 \text{ kcal/mol (Pt) for CH}_3\text{-CH}_3 \]

As experimental data become available for such surface reactions, it will be interesting to see how energetics can be extrapolated between homogeneous and heterogeneous systems.

4. Barriers for Reductive Coupling

For the Pd(R\textsubscript{1})(R\textsubscript{2}) complexes, it is exothermic to reductively couple H-H, H-C, or C-C bonds; however, the barriers for these processes depend dramatically upon the nature of the ligands (see Figure 6):

\[ \Delta E^\ddagger_{\text{H-H}} = 1.6 \text{ kcal/mol, } \Delta H^\ddagger_{298 \text{ H-H}} = 0.4 \text{ kcal/mol} \]
\[ \Delta E^\ddagger_{\text{H-C}} = 10.4 \text{ kcal/mol, } \Delta H^\ddagger_{298 \text{ H-C}} = 9.5 \text{ kcal/mol} \]
\[ \Delta E^\ddagger_{\text{C-C}} = 22.6 \text{ kcal/mol, } \Delta H^\ddagger_{298 \text{ C-C}} = 23.6 \text{ kcal/mol.} \]

Similarly, for the corresponding Pt complexes (see Figure 7), the barriers for H-C and C-C coupling are far larger than the endothermicity

\[ E^\ddagger_{\text{H-C}} = 29.0 \text{ kcal/mol, } H^\ddagger_{298 \text{ H-C}} = 28.1 \text{ kcal/mol} \]
\[ E^\ddagger_{\text{C-C}} = 53.5 \text{ kcal/mol, } H^\ddagger_{298 \text{ C-C}} = 54.5 \text{ kcal/mol.} \]

Such dramatically different barriers would explain why Pt(H)(CH\textsubscript{3})(PH\textsubscript{3})\textsubscript{2} will reductively couple H-C bonds, whereas Pt(CH\textsubscript{3})\textsubscript{2}(PH\textsubscript{3})\textsubscript{2} will not reductively couple C-C bonds. However, the question now is why the dramatic differences in barriers?

As discussed in more detail in Section II.6, the reductive coupling process starts with a configuration having two covalent bonds involving sd hybrids on the metal,
and converts this to a wavefunction with one covalent bond between the ligands and a doubly-occupied d orbital on the metal,

\[ (19) \]

\[ \text{d}^{10} \text{ Resonance Configuration} \]

At the transition state geometry, both configurations must come into the wavefunction, wherein lies the difficulty. A hydrogen s orbital at the transition state is equally suited for either bonding configuration (19) or (20); however, for methyl the bonding orbital is an sp\(^3\) hybrid that can be directed \textit{either} for making an M-C bond,

\[ (21) \]
or for making a C-C bond

![molecular structure](image)

but not both. This is illustrated in Figures 8 and 9, which show the various orbitals for (12), (13), and (14) at a geometry near the saddle point. The CH₃ radical orients itself to a position intermediate between the geometries appropriate for (21) and for (22), leading to too weak a bond for either. The consequence of these effects is that each methyl group leads to a doubling of the barrier.

Clearly this methyl orientation effect can account for the observed differences in the efficacy of H-C versus C-C coupling in Pt phosphine complexes. These results are consistent with the facile H-C coupling on Pt and C-C coupling on Pd, with the apparent lack of stability of the cis-Pd(H)(CH₃)(PH₃)₂ complex, and with the difficulty of C-C coupling from Pt dimethyl complexes.

5. Geometries

The bond distances for Pd-CH₃ and Pt-CH₃ bonds are nearly identical [1.96 ± 0.01 Å] for all complexes. For M-H bonds there is more variation with Pd-H = 1.51 ± 0.01 Å and Pt-H = 1.48 ± 0.01 Å. On the other hand, the bond angles for the various M(H)₂, M(H)(CH₃), and M(CH₃)₂ complexes vary considerably, being 73°, 80°, and 92° for Pd and 82°, 89°, and 96° for Pt.
The ideal bond angle between two bonds formed with symmetric linear combinations of a Pt s and a Pt d orbital is 90°. Thus, if the repulsive steric interactions were solely responsible for the trend of bond angle with methyl substitution, one would expect to find R-M-R angles greater than 90°, but most of the equilibrium geometries have R-M-R angles less than 90°. Of course the actual hybridization is not exactly sd, and the calculated angles between the lobes of the metal-like GVB orbitals vary between 86° and 100° [86° for PtH₂, 91° for Pt(H)(CH₃), and 100° for Pt(CH₃)₂, leading to the an average of 92°] for Pt complexes and the average for Pd complexes is 88°±1°. The observed angles between the metal-like GVB orbitals for Pt track closely with the actual bond angle (80, 91, and 100 versus 82, 89, and 98, respectively); however, this does not constitute an explanation since we have not provided an a priori criterion for predicting the hybridization leading to these angles (other than being s¹0d¹⁰ to correspond to the s¹d⁹ state). Thus, compared with the 90° expected from the s¹d⁹ configuration, there must be attractive interactions between the ligands bound to the metal atom. This attractive interaction can be explained by noting that the d¹₀ resonance structure has an R-R bonding interaction. The more important the d¹₀ resonance structure, the more attractive the interaction between ligands and the smaller the R-M-R angle. Since the d¹₀ resonance structure is more important in PdR₂ than in PtR₂, there will be greater bonding character between the R groups in PdR₂, providing a rationalization for the R-Pd-R bond angles being 10° smaller than the corresponding bond angles in the PtR₂ complexes (see Figures 4 and 5).
6. Changes Along Reaction Path

As discussed above, there are two important resonance structures in the M(R₁)(R₂) complexes responsible for determining the relative amounts of s and d character. The dominant resonance structure for PdR₂ and PtR₂ has the metal atom in an s¹d⁹ configuration, shown schematically in (19) and denoted as the s¹d⁹ resonance structure. Here the singly-occupied s and d orbitals rehybridize to form sd hybrid orbitals that spin-pair (or form bonds) to the singly-occupied orbitals of the R group. The second resonance structure, which dominates the wavefunction at the dissociated limit, has the metal atom in a d¹⁰ configuration and an R-R bond, as shown schematically in (20). This is referred to as the d¹⁰ resonance structure. As oxidative addition proceeds, the dominant resonance structure changes from the d¹⁰ structure to the s¹d⁹ structure. Since Pd prefers d¹⁰ while Pt prefers s¹d⁹, PdR₂ should have more of the d¹⁰ resonance structure than PtR₂. This is consistent with the observation that PdR₂ complexes have larger d populations than PtR₂ complexes.

The Mulliken populations as a function of reaction coordinate for reaction (12) (see Table V) show that at the dissociated limit the Pd atom is in a d¹⁰ state, and as the hydrogen molecule approaches, the Pd atom mixes in s¹d⁹ character. Finally, when two Pd-H bonds have formed, the Pd atom has 75% s¹d⁹ character (defined by the occupation of the Pd s orbital).

The spherically symmetric H₁₈ orbital allows it to form bonds in more than one direction at a time. This multi-centered bonding increases the H-H bonding character of the d¹⁰ resonance structure, causes the H atoms to have an attractive interaction in the dihydrides, and leads to
smaller H-M-H bond angles.

The sp³ hybrid orbital of the CH₃ group is more directional than the H₁s orbital. The shape of this orbital makes it difficult for this orbital to bond in more than one direction at a time. Consequently, there will be less bonding character in the d¹⁰ resonance structure of the hydridomethyl complexes than in the dihydrides. This will cause the hydridomethyl complexes to have larger bond angles than the dihydrides.

Since the sp³ orbitals of the methyl groups are directed at the metal, they have trouble forming the C-C bond in the d¹⁰ structure. Consequently, the dimethyl complexes have the least amount of bonding character in the d¹⁰ resonance structure. Therefore, the dimethyl complexes should have the largest bond angles.

The increased ligand-ligand bonding in the d¹⁰ resonance structure should stabilize it relative to the s¹d⁹ resonance structure. This will cause metal d populations to be larger for dihydride complexes and smaller for the dimethyl complexes, which is consistent with the Mulliken populations in Table II.

The potential curves along the reaction paths are shown in Figures 6 and 7. In each of the potential curves the R₁-M-R₂ bond angle (θᵣ₁ᵣ₂) was fixed, and all other geometric parameters were fully optimized (see Section V). In this manner, we were able to obtain the energy as a function of θᵣ₁ᵣ₂ from the MR₂ complex to the dissociated limit (θᵣ₁ᵣ₂ = 0°).

The potential curves for reactions (12)-(14), (16), and (17) can be partitioned into three regions:

1. The MR₂ complex region, where the metal atom has s¹d⁹ character and each R group forms a covalent bond to the metal.
2. The transition state region, where the M-R bonds are breaking and the R-R bond is forming (or vice versa), with a strong mixture of both the $d^{10}$ and $s^1d^9$ resonance structures.

3. The dissociated limit, where the R-R bond is fully formed and the metal is in the $d^{10}$ state.

In region 1 the M-R bond lengths change by less than 0.02 Å as the $\theta_{R_1R_2}$ is varied, indicating that the M-R bond is still intact. As the complex enters region 2, the M-R bonds begin to stretch and the methyl groups in the hydridomethyl and dimethyl complexes rotate so that their $sp^3$ orbitals are directed more toward the other R group.

At the transition state, the ligand-ligand bond distances are generally closer to the bound complex geometry than to the dissociated limit. Pd complexes have smaller distortions (they are more reactant-like) than the corresponding Pt complexes (see Figures 4 and 5) at the transition state, as would be expected from the Hammond Postulate. The dimethyl complexes have the largest distortions. Pt + $H_2 \rightarrow $ PtH$_2$ differs from the other reactions studied here in that there is no barrier to oxidative addition (it is quite exothermic, 33.6 kcal/mol).

Past the transition state there exists a second minimum for the Pd + $H_2$, Pd + CH$_4$, and Pt + CH$_4$ cases. In this bound complex, the H-H or C-H bonds are intact and behave as Lewis bases, while the $d^{10}$ configuration of the transition metal serves as a Lewis acid (empty valence s orbital). The geometries for the Lewis acid/Lewis base complex are shown in Figure 10. These geometries were not separately optimized but were interpolated from the calculations along the reaction path. [Notice the lack of symmetry in the $M(CH_4)$ complexes.] As a result, the geometry obtained for each complex is not particularly accurate [the internal coordinates of $H_2$
and CH$_4$ in these complexes should be accurate, while the error in metal-ligand distance ($\pm 0.2$ Å) and in orientation ($\pm 10^\circ$) will be larger. However, Lewis acid/Lewis base complexes in these systems are clearly stable with respect to the dissociated limit. There seems to be a small increase in the H-H bond length (0.07 Å) and very little distortion in the C-H bond lengths of methane (two CH bonds of methane interact with the metal atom in this region). Our reaction path restricted the orientation of the methyl group in such a way that at most two C-H bonds could complex to the metal atom. Therefore, the Lewis acid/Lewis base complexes, with three C-H bonds complexed to the metal atom (probably the most stable), were not examined.

Previous calculations found a similar bound complex for PdH$_2$\textsuperscript{22} and described it as a van der Waals complex. Since our wavefunction does not include the electronic configurations involved in the dynamic polarizations responsible for van der Waals forces (nor the f functions needed on the Pt for a proper description of such effects), our results cannot be explained in terms of a van der Waals complex.\textsuperscript{23} Rather, they should be thought of as weak Lewis acid/Lewis base complexes. Similar $\eta^2$ bonding of H$_2$ to a transition metal has been observed experimentally in M(CO)$_3$(PR$_3$)$_2$H$_2$ (M = Mo,W; R = Cy,i-Pr) complexes studied by Kubas \textit{et al.}\textsuperscript{24a} and theoretically by Hay.\textsuperscript{24b}

The interactions responsible for these Lewis base/Lewis acid complexes of CH$_4$ to metal atoms are probably identical to those involved in "agostic" \textsuperscript{25a} interactions of C-H bonds and transition metals observed experimentally\textsuperscript{25a} and theoretically\textsuperscript{25b} in several complexes. This type of interaction has thus far only been observed for C-H bonds of ligands that are also covalently bound to the complex. The very small binding ener-
gies found in our calculations [5 kcal/mol for Pd(H₂), 2 kcal/mol for Pd(CH₄), and 4 kcal/mol for Pt(CH₄)] are insufficient to balance the entropic contribution to the free energy of binding at room temperature (~10 kcal/mol), indicating that such bonds to alkyl groups that are not already part of the complex will in gas phase only be observed at low temperatures.
III. Comparison With Experiment

The results presented in the previous section explain many of the experimentally observed trends. Halpern et al.\textsuperscript{8a} and Michelin et al.\textsuperscript{8b} observed intramolecular reductive coupling from various hydridoalkyl-bisphosphine Pt(II) complexes. However, reductive coupling from Pt(II) dialkyls to form C-C bonds has never been reported, even though this reaction is thought to be thermodynamically favored.\textsuperscript{26} Rather, the Pt(II) dialkyls prefer β-hydride elimination,\textsuperscript{27}

\[
\begin{align*}
&\text{(PR\textsubscript{3})\textsubscript{2}Pt} + \text{H}_2\text{C=CH}_2 \rightarrow \text{(PR\textsubscript{3})} + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 \quad (23) \\
&\text{(PR\textsubscript{3})\textsubscript{2}Pt} + \text{CH}_3\text{CH} = \text{CH}_3 \rightarrow \text{(PR\textsubscript{3})} + \text{CH}_3\text{CH} = \text{CH}_3 \\
&\text{(PR\textsubscript{3})\textsubscript{2}Pt} + \text{CH}_2\text{CH} = \text{CH}_2 \rightarrow \text{(PR\textsubscript{3})} + \text{CH}_3\text{CH} = \text{CH}_3
\end{align*}
\]

despite the fact that (24) is favored thermodynamically (by \(\Delta H\textsubscript{300} = -22.5\) kcal/mol and \(\Delta G\textsubscript{300} = -11.0\) kcal/mol).\textsuperscript{28} These observations are consistent with our findings that C-H reductive coupling leads to a barrier half that for CC reductive coupling. This trend should be applicable to concerted addition/elimination reactions for other Group VIII metals because it depends primarily on the relative shapes of H 1s and CH\textsubscript{3} sp\textsuperscript{3} orbitals.

Unlike their Pt analogs, Pd(II) dimethyl complexes do reductively eliminate ethane, a result we attribute to the strong preference (by 34 kcal/mol relative to Pt) of Pd for the d\textsuperscript{10} configuration, which leads to a greatly reduced barrier [we estimate 10 kcal/mol for Pd(CH\textsubscript{3})\textsubscript{2}(PH\textsubscript{3})\textsubscript{2} compared with 40 kcal/mol for Pt(CH\textsubscript{3})\textsubscript{2}(PH\textsubscript{3})\textsubscript{2}].\textsuperscript{29} This is in agreement with observed reductive elimination of ethane from Pd(CH\textsubscript{3})\textsubscript{2}L\textsubscript{2} complexes\textsuperscript{9a,d} (where L = PPh\textsubscript{3}, PPh\textsubscript{2}CH\textsubscript{3}, L\textsubscript{2} = PPh\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}) and the
fact that hydrogen will not oxidatively add to a Pd bispiphosphate complex but does add to the corresponding Pt complex.\textsuperscript{30}

Oxidative addition of H\textsubscript{2} to square planar Ir(I) complexes is the most thoroughly studied system experimentally, and it is believed to involve a concerted mechanism.\textsuperscript{5} In contrast to the results presented here for the addition of H\textsubscript{2} to Pt and Pd and earlier work for H\textsubscript{2} addition to Pt(PH\textsubscript{3})\textsubscript{2}, the Ir(I) complexes have a relatively high barrier to oxidative addition (10-12 kcal/mol for Vaska's complex\textsuperscript{5a,b,d}) and reductive elimination (25 kcal/mol). This difference probably arises from the difference in electronic configurations, with Pt and Pd having a spherically symmetric d\textsuperscript{10} shell of electrons on the metal atom, while Ir(I) leads to square planar four-coordinate complexes. Thus Pt(PH\textsubscript{3})\textsubscript{2},\textsuperscript{13} has a P-Pt-P angle of 180°, being determined by steric interactions between phosphines. Promoting the Pt(PH\textsubscript{3})\textsubscript{2} complex to a triplet state leads to a P-Pt-P bond angle of 100°, where the phosphine lone pairs maximize their overlap with the singly-occupied d\textsubscript{yz} orbital of the triplet state.\textsuperscript{13} On the other hand, Ir(I) has a strong preference for square planar geometries. Addition of H\textsubscript{2} to such complexes should lead to a distortion of ligands toward the six-coordinate Ir(III) product.\textsuperscript{5b} Here a significant distortion away from square planar is required at the transition state in order to allow the d\textsuperscript{2} \rightarrow s\textsuperscript{1}d\textsuperscript{1} excitation required for formation of the new Ir-ligand covalent bonds. Thus the higher barrier in Ir(I) is attributed to the lack of a symmetric d\textsuperscript{10} shell and the concomitant strong preference for square planar geometries. Indeed, Vaska and Werneke\textsuperscript{5b} proposed a similar effect, the "reorganization or rehybridization energy," whose magnitude was deduced from the trends observed in ΔH\textsuperscript{‡} and ΔH for oxidative addition of H\textsubscript{2} to Ir(I) complexes. They equated this reorganization energy to the ΔH\textsuperscript{‡}
for reductive elimination of H₂. We find low barriers for concerted reactions of H₂ with Pd, Pt(¹S), and Pt(PH₃)$_2$; therefore, the reorganization energy must be very small (~2 kcal/mol) for these d$^{10}$ systems.

It has generally been believed that oxidative addition (being oxidative) should be promoted by electron-rich metals. However, C-H activation of C-H bonds has been observed to occur for both electron-rich and electrophilic Ir systems. Since the electronegativity$^{14}$ of Ir(2.2) is the same as for Pt(2.2) and Pd(2.2), we expect it to form covalent bonds to H and CH₃ so that the electron density on the metal should have little effect on the energetics for oxidative addition (as observed).

In every case where stable hydridoalkyl complexes have been formed by oxidative addition of M to sp$^3$ C-H bonds, a photochemically generated Cp*ML (L = CO or PMe$_3$) (M =Ir$^{6a-d}$ or Rh$^7$) (Cp* =cC$_5$Me$_5$) complex has been involved. The Cp* ligand can easily occupy three coordination sites of the octahedral complex for Ir(III) or Rh(III). However, Cp* cannot occupy three coordination sites of a square planar complex. Thus, the Cp*ML complexes are distorted significantly away from the square planar preferred by Ir(I) and Rh(I), and hence have smaller reorganization energy for oxidative addition than does Vaska's complex [they are much closer to the octahedral geometry favored by Ir(III) and Rh(III) complexes].$^{31-33}$ Therefore, these complexes will have lower activation barriers and greater driving forces favorable for oxidative addition. Constraining the geometry of the ligands appears to be a more important effect than the electron richness of the metal center. Similar analyses have also been given by Saillard and Hoffmann,$^{31}$ Sevin,$^{32}$ and Dedieu and Strich.$^{33}$

We find that oxidative addition of H₂, CH₄, and C₂H₆ to the Pd atom is
uphill energetically. These results suggest that the Pd atom is unreactive with respect to H₂, CH₄, and C₂H₆. This is consistent with the results of Klabunde and Tanaka³⁴c who found no reaction of Pd codeposited with CH₄ at 10⁵K. This lack of reactivity of Pd at low temperatures is due to the unreactive nature of the d¹⁰ state of Pd and the large excitation energy (21.9 kcal/mol) needed to promote the Pd atom to the s¹d⁹ configuration that can make two covalent bonds.

In fact, no transition metal in its ground state has been found to be reactive with CH₄ at low temperatures.³⁴ This can be easily explained despite the diverse nature of transition metal atoms. Every transition metal except Pd has either a singly- or doubly-occupied valence s orbital in its ground state. In reactions (12), (13), and (16), the empty s orbital gave rise to attractive Lewis acid/Lewis base interactions at long M-R distances, resulting in an decreased barrier for oxidative addition. For a metal where the s orbital is occupied, this orbital must become orthogonal to the incoming R-R bond, leading to a repulsive interaction at long M-R₂ distances. Thus, one would expect every transition metal in its ground state to have an activation barrier to oxidative addition.

For excited states of transition metal atoms, one can have states in which the s orbital is unoccupied and for which oxidative addition is exothermic. For example, we find that Pt(¹S) + H₂ → PtH₂(¹A₁) leads to no barrier. These predictions are consistent with experiments³⁴ that find photoexcited metal atoms reactive with methane at low temperatures. [Extended Hückel calculations of Sevin and Chaquin³⁵ lead to similar results.]
IV. Comparison With Other Theoretical Work

Several previous theoretical studies\textsuperscript{22b,23,36,37} have addressed various issues relevant to the oxidative addition/reductive elimination of H\textsubscript{2}, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6} to transition metal complexes, although most have not examined the full reaction surfaces. Using fixed bond distances, Tatsumi \textit{et al.}\textsuperscript{36a} calculated activation energies at the extended Hückel level for reductive elimination of C\textsubscript{2}H\textsubscript{6} from Pd(CH\textsubscript{3})\textsubscript{2}(PH\textsubscript{3})\textsubscript{2} and H\textsubscript{2} from (PdH\textsubscript{4})\textsuperscript{−4} models. They found higher barriers for reductive couplings for C-C bonds (39.1 kcal/mol) than for H-H bonds (4.6 kcal/mol) because of the "weakening necessitated by the rocking motion"\textsuperscript{36a} of the methyl group.

Balacz \textit{et al.}\textsuperscript{36b} carried out muffin-tin Xα calculations at assumed geometries for various complexes and suggested, on the basis of the shapes of the molecular orbitals, that three-center bonding might be more important in the reductive elimination of H\textsubscript{2} from H\textsubscript{2}PtL\textsubscript{2} than for CH\textsubscript{4} from H(CH\textsubscript{3})PtL\textsubscript{2} or for C\textsubscript{2}H\textsubscript{6} from (CH\textsubscript{3})\textsubscript{2}PtL\textsubscript{2}. (They did not calculate barriers or geometries.)

Previous theoretical studies\textsuperscript{22,23} of Pd(H)\textsubscript{2} did not find the local minimum corresponding to the Pd-H bonded complex. However, these calculations did \textit{not} include relativistic effects and consequently the s\textsuperscript{1}d\textsuperscript{9} (3\textit{D}) state [important in the Pd(H)\textsubscript{2} complex] is 15 kcal/mol too high\textsuperscript{38} relative to the d\textsuperscript{10} state. Since our calculated barrier for reductive coupling is only 1.5 kcal/mol, it is not surprising that nonrelativistic calculations of this minimum do not find a Pd-H bonded complex.

Obara \textit{et al.}\textsuperscript{16a} have recently reported \textit{ab initio} calculations on oxidative addition of H\textsubscript{2} and CH\textsubscript{4} to Pt(PH\textsubscript{3})\textsubscript{2}. Their transition state geometry for H\textsubscript{2} addition is in reasonable agreement with our previously published results on the same system.\textsuperscript{13} The transition state geometry for CH\textsubscript{4}
addition calculated by Obara et al.\textsuperscript{16a} (C-Pt-H angle = 36°, Pt-CH\textsubscript{3} distance = 2.27 Å, and Pt-H distance = 1.59 Å) is remarkably close to ours (C-Pt-H angle = 42°, Pt-CH\textsubscript{3} distance = 2.12 Å, and Pt-H distance = 1.57 Å), considering the lack of phosphines in our model. Their energetics, however, are difficult to compare with ours since the Pt effective core potential used by Obara et al.\textsuperscript{39} is known to give stronger Pt-H bonds that are far too strong.\textsuperscript{40} [We used the Hay\textsuperscript{41} effective core potential which gives excellent bond energies and excitation energies.] The similarity of the transition states indicates that the PH\textsubscript{3} ligands do not significantly affect the reaction path for reductive coupling of C-H bonds. We would expect PH\textsubscript{3} ligands to lower the barrier for reductive elimination, since phosphines stabilize the d\textsuperscript{10} configuration relative to s\textsuperscript{1}d\textsuperscript{9} and increase the driving force for reductive elimination from Pt(H)\textsubscript{2}(PH\textsubscript{3})\textsubscript{2}.\textsuperscript{13} Pt(H)(CH\textsubscript{3})(PH\textsubscript{3})\textsubscript{2},\textsuperscript{29} Pt(CH\textsubscript{3})\textsubscript{2}(PH\textsubscript{3})\textsubscript{2},\textsuperscript{29} and Pd(CH\textsubscript{3})\textsubscript{2}(PH\textsubscript{3})\textsubscript{2}.\textsuperscript{29}

No other \textit{ab initio} theoretical studies on oxidative addition/reductive elimination to Pd and Pt atoms have been reported; however, similar studies have been reported for oxidative addition of H\textsubscript{2}, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6} to the lowest singlet state of the Ni atom.\textsuperscript{22b,37a,b} These results on Ni differ considerably from ours on Pd and Pt. For example, Siegbahn et al.\textsuperscript{22b,37a,b} find oxidative addition barriers of 4.2 kcal/mol for H\textsubscript{2}, 54.1 kcal/mol for CH\textsubscript{4}, and 42.3 kcal/mol for addition to the CC bond of C\textsubscript{2}H\textsubscript{6}. In addition, they report an unusually small equilibrium bond angle of 57° for NiH\textsubscript{2}. There are significant differences in the properties of Ni versus Pd and Pt, even though they are in the same column. For example, Ni is much more electropositive than Pd or Pt (Pauling electronegativities\textsuperscript{15} of 1.8 versus 2.2 and 2.2). In addition, the ground state of Ni has nearly degenerate s\textsuperscript{2}d\textsuperscript{8} (\textsuperscript{3}F) and s\textsuperscript{1}d\textsuperscript{9} (\textsuperscript{3}D) triplet states, with the d\textsuperscript{10} (\textsuperscript{1}S) state 40 kcal/mol
higher.\textsuperscript{14} For Ni the lowest singlet state is s\textsuperscript{1}d\textsuperscript{9} (1D) at 7.7 kcal/mol.\textsuperscript{14} On the other hand, Pd has a d\textsuperscript{10} (1S) ground state with the s\textsuperscript{1}d\textsuperscript{9} (3D) triplet at 22 kcal/mol, while the lowest singlet for Pt is also d\textsuperscript{10} (1S) with s\textsuperscript{1}d\textsuperscript{9} (3D) 11 kcal/mol lower.\textsuperscript{14} Consequently, we include in Appendix A some calculations performed on the Ni + H\textsubscript{2} system for comparison purposes.

Siegblahn and co-workers\textsuperscript{22b,37b} calculated potential surfaces at the contracted CI level for the reactions

\begin{equation}
\text{Ni} + \text{CH}_4 \rightarrow \text{NiH(CH}_3) \quad (26)
\end{equation}

\begin{equation}
\text{Ni} + \text{C}_2\text{H}_6 \rightarrow \text{Ni(CH}_3)_2 \quad (27)
\end{equation}

They find, in contrast to our results, higher barriers for C-H activation than for C-C activation. Since this trend parallels the trend in C-H versus C-C bond energies, it is possible that Siegbahn's calculations are modelling nonconcerted additions of Ni to CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}\textsuperscript{37b} To estimate the \(\Delta E\)'s for the formation of the radical intermediates (\(\Delta E_{\text{rad}}\)), we used Siegbahn's \(\Delta E\) for Ni + H\textsubscript{2} \rightarrow NiH\textsubscript{2}\textsuperscript{37a} (-9.6 kcal/mol) and Ni + C\textsubscript{2}H\textsubscript{6} \rightarrow Ni(CH\textsubscript{3})\textsubscript{2}\textsuperscript{37b} (5.3 kcal/mol) to estimate average Ni-H (\(D_1 = 56\) kcal/mol) and Ni-CH\textsubscript{3} bond energies (\(D_1 = 45\) kcal/mol).\textsuperscript{42}

\begin{equation}
\text{Ni}(1D) + \text{CH}_4 \rightarrow \cdot \text{Ni-H} + \cdot \text{CH}_3 \quad \Delta E_{\text{rad}} = 50 \text{ kcal/mol} \quad (28)
\end{equation}

\begin{equation}
\text{Ni}(1D) + \text{C}_2\text{H}_6 \rightarrow \cdot \text{Ni-CH}_3 + \cdot \text{CH}_3 \quad \Delta E_{\text{rad}} = 43 \text{ kcal/mol} \quad (29)
\end{equation}

These \(\Delta E_{\text{rad}}\)'s are very close to the \(\Delta E^+\)'s for C-H activation (54 kcal/mol) and C-C activation (42 kcal/mol), as calculated by Siegbahn et al.,\textsuperscript{37b} suggesting that their calculations are not modelling the concerted processes. On the other hand, for our studies on Pd and Pt, a similar analysis leads to energies of formation for radical intermediates far higher than our calculated barriers for the concerted processes. The sole
exception is for C-C activation of Pt where the $\Delta H_{\text{red}}$ is 43 kcal/mol, which is close to the $\Delta H^\ddagger$ for oxidative addition of 39 kcal/mol. This suggests that radical processes are competitive with concerted processes for reactions (17), (26), and (27).

For the organometallic systems being modeled in this paper, the metal atoms will generally have other ligands (e.g., phosphines) on them. We have shown\textsuperscript{13} that the effect of phosphines is to stabilize the $d^{10}$ versus $s^1d^9$ states in Pt(PH$_3$)$_2$ and expect the same effect for Pd(PH$_3$)$_2$ and Ni(PH$_3$)$_2$. The lowest singlet states of Pd and Pt are $d^{10}$, like the M(PR$_3$)$_2$ complexes that we are modelling, whereas the lowest singlet state of Ni is $s^1d^9$. Thus, the calculations for oxidative coupling of Pd and Pt atoms are more relevant for organometallic chemistry than similar calculations\textsuperscript{37a,b} on Ni. Since the lowest singlet state of Ni differs so much from the lowest singlet state of Pd, Pt, and M(PR$_3$)$_2$ (M = Ni, Pd, Pt), it is not surprising that Siegbahn's results are different from ours and run counter to the observed experimental trends.
V. Calculational Details

A. Potentials and Basis Sets

We used \textit{ab initio} effective core potentials (ECP) to represent the core electrons of Ni, Pd, and Pt. For Ni we used the ECP of Melius \textit{et al.}\(^{43}\) with the five-gaussian d basis of Rappé \textit{et al.}\(^{44}\) and the sp basis associated with the SHC potential of Rappé.\(^{45}\) The relativistic effective core potentials (RECP) and basis of Hay\(^{41}\) were used on Pd and Pt with a valence double zeta basis. The Dunning\(^{46}\) double zeta contraction of the Huzinaga (9s5p) gaussian basis was used on carbon. The active hydrogens bound directly to metal atoms were described by a triple zeta contraction of the Huzinaga six-gaussian basis.\(^{47}\) The nonactive methyl hydrogen atoms were described by a double zeta contraction of the Huzinaga four-gaussian hydrogen basis scaled by a factor of 1.2.\(^{46,47}\) For highly accurate bond energies and geometries, f functions should be included on the metal center, d functions on the C atoms, and p functions on the H atoms. However, the present basis is expected to be adequate for extracting the important issues about these various reactions.

B. Configuration Interaction Calculations

For PdH\(_2\) and PtH\(_2\) there are 12 valence electrons with four electrons involved in M-H bonds and eight involved in four pairs of metal d orbitals. As the H\(_2\) molecule is eliminated, the four bonding electrons change dramatically, leading to two electrons describing H-H bonding and two describing a doubly-occupied d orbital on the metal, while the other eight electrons change little. \[\text{Note that the spin-allowed product } \text{M(H)}_2 \rightarrow \text{M} + \text{H}_2 \text{ involves a } \text{d}^{10} \text{ singlet state for both Pd and Pt.}\] Thus, to provide a balanced description of this system, we described each of the four fairly constant pairs of electrons in terms of a standard (one orbital
per electron) GVB description. This is denoted as GVB(1/2) for each pair and GVB-PP(4/8) to indicate four pairs of electrons, each with two GVB orbitals for a total of eight. The PP (for perfect-pairing) indicates that the spin coupling is that of a simple valence bond wavefunction with each of these four pairs singlet-spin paired. Expanded as a configuration interaction (CI) wavefunction in terms of natural orbitals, the GVB-PP(4/8) wavefunction leads to $2^4 = 16$ configurations. Instead, we allowed the two electrons of each pair to recouple in all three possible ways using two orbitals, leading to a total of $3^4 = 81$ configurations, a calculation referred to as GVB-RCI(4/8). This GVB-RCI level of wavefunction allows the spin-coupling terms often important in transition metal systems and allows the interpair correlation so important for doubly-occupied d orbitals.

The other four electrons have very different requirements for Pd(H$_2$) versus Pd + H$_2$. Thus, for Pd(H)$_2$, a standard GVB wavefunction leads to two localized orbitals for describing each Pd-H bond pair (as shown in Figure 1). In terms of symmetry orbitals, this would lead to two $a_1$ and two $b_2$ orbitals. On the other hand, for separated H$_2$ and Pd, the standard GVB(2/4) description has two localized orbitals on the H$_2$ (leading to one $a_1$ and one $b_2$) and a correlated $d_{yz}$ orbital (leading to two $b_2$ orbitals). In order to provide an unbiased description of these reactions all along the reaction path, we used a wavefunction with three $a_1$ and three $b_2$ orbitals for the four bonding electrons. Allowing all possible occupations of the four electrons among these six orbitals leads to a wavefunction with 48 configurations and is referred to as GVB-CI(2/6). For all points along the reaction path we combined the GVB-RCI(4/8) and GVB-CI(2/6) wavefunctions to obtain a composite containing 8568 configurations and denoted
as GVB-RCI(4/6)×GVB-CI(2/6). The orbitals for this wavefunction were
optimized for this 8568 configuration wavefunction using the GVB3 pro-
gram.49

For calculations involving methyl groups, the inactive C-H bonds were
uncorrelated [as in Hartree-Fock (HF)], and the M-C, active C-H and C-C
bonds were included in the GVB-CI space. All the other metal electrons
were described in the same manner as MH₂.

A special virtue of this GVB approach to wavefunctions is that since
the orbitals are divided into active (GVB-CI), semi-active (GVB-RCI), and
inactive (HF) orbitals, the number of configurations does not increase
when ligands are added, so large systems [e.g., Pt(CH₃)₂(PH₂)₂]²⁹ can be
treated nearly as easily as small ones.

Often it has been convenient to calculate the GVB-RCI wavefunction
using orbitals from corresponding GVB-PP calculations. This saves con-
siderable time because the GVB-PP calculation does not require transfor-
mation of electron repulsion integrals to the molecular orbital basis.
Indeed, such GVB-RCI calculations, using orbitals from GVB wavefunc-
tions, yield atomic state splittings that are in good agreement with state
splittings calculated self-consistently at the GVB-RCI level (see Table VI).
However, it is necessary to optimize orbitals at the full GVB-
RCI(4/8)×GVB-CI(2/6) level of wavefunction in order to self-consistently
include the resonance between the d¹⁰ and s¹d⁹ configurations near the
transition states for reactions (12)-(17).

To indicate how well this type of wavefunction does for atomic state
splittings, we show in Table VII comparisons with experiment for HF and
GVB-RCI(5/10)¹³,⁵⁰ state splittings. Here the GVB-RCI involves a total of
ten optimized GVB orbitals for each state (d¹⁰, s¹d⁹, or s²d⁸), and we see
that GVB-RCI does quite well, with errors of 1 to 3 kcal/mol in the $^1S(d^{10})$ to $^3D(s^1d^9)$ excitation, and 0 to 6 kcal/mol in the energy of $^1D(s^1d^9)$ relative to $^4D(s^1d^9)$. These three states describe the dominant character of the wavefunction for the reactions studied in this paper. [Larger errors occur for the $s^2d^8$ state because angular correlation of the s pair of electrons, which is important for this state, was not included in this wavefunction. However, the $s^2d^8$ state is destabilized by addition of phosphine ligands, and it will not play a significant role in the chemistry of such complexes.] In contrast, HF wavefunctions lead to errors of 20 to 60 kcal/mol in the $^1S(d^{10})$ to $^3D(s^1d^9)$ excitation and 2 to 11 kcal/mol in the position of $^1D(s^1d^9)$ relative to $^3D(s^1d^9)$.

Configurations with more than six singly-occupied orbitals in the GVB-RCI wavefunction lead to numerous spin eigenfunctions (SEF) (e.g., a triplet with ten open shells has 90 SEF's). In order to save computer time, it is convenient to restrict the wavefunction so that there is a maximum of six open shells in any configuration. Thus the GVB-RCI for the $^1S$ state of Pt restricted to six open shells contains 72 configurations and 328 SEF's, whereas the full GVB-RCI contains 81 configurations with 642 SEF's. Table VI shows the differences in state splittings of Pt atom for calculations in which the number of open shells was restricted to a minimum of six compared with the case where no restrictions were made (up to ten open shells. The restriction of a maximum of six open shells leads to errors of only $\sim 0.2$ kcal/mol in the atomic state splitting relevant for this work, an error quite tolerable for our studies. We should emphasize that inclusion of at least six open shells is required in order to describe inter-pair correlations (a single excitation within one GVB pair times a single excitation within another GVB pair) for both the triplet and open-shell
singlet states of the atom. In conclusion, the use of the six-open-shell restriction is justified for these studies, and all wavefunctions reported here are restricted to a maximum of six open shells unless otherwise noted.

C. Geometry Optimization

We used a distinguished coordinate method\textsuperscript{51} to follow the potential curve from reactants to products. Each geometry was calculated by holding the R-M-R angle fixed and optimizing all other geometric parameters for the HF wavefunction. Using this sequence of geometries, we then carried out the self-consistent GVB-RCI(4/8)×GVB-Cl(2/6) calculations. This allowed us to follow a continuous path from reactant to products for each system studied and to extract the concepts permitting us to explain the various features and to interpret the experiments. To obtain various critical points (minima and saddle points), we fitted the variations in energy and all other geometric parameters along the reaction path to cubic splines and interpolated the geometric parameters for the optimum energy. Thus, the geometries are not as accurate as they would be if separate energy optimizations had been carried out.

To determine the effect of electronic correlation on geometry, we calculated (see Table VIII) the equilibrium bond angles for PdH\textsubscript{2}, PtH\textsubscript{2}, PdH(CH\textsubscript{3}), and NiH\textsubscript{2} at the HF, GVB-Cl(2/6) and GVB-RCI(4/8)×GVB-Cl(2/6) levels. For Pd and Pt complexes, the bond angle determined at the HF level is within 5° of the GVB-RCI(4/8)×GVB-Cl(2/6) level. On the other hand, the equilibrium geometry of NiH\textsubscript{2} is strongly affected by electronic correlation, as discussed in Appendix A.

In order to test the effects of correlation on the transition state geometries, we reoptimized the geometry of PdH\textsubscript{2} at the GVB-RCI(4/8)×GVB-Cl(2/6) level. This optimized transition state has a Pd-H
distance of 1.595 Å and an H-Pd-H bond angle of 50.6°, with an activation energy of 0.74 kcal/mol (versus 1.547 Å, 50.8°, and 1.551 kcal/mol for interpolated value based on the HF distinguished coordinate studies followed by GVB-RCI). These changes of 0.048 Å in Pd-H distance, 0.2° in bond angle, and 0.81 kcal/mol in activation barrier indicate that use of the GVB calculations along the HF reaction path provides a reasonable description for these reactions.

Our calculations for reductive elimination of dimethyl and dihydride complexes assume a transition state with $C_{2v}$ symmetry. It is possible that the transition state for these reactions has lower symmetry. However, it has been shown that the $C_{2v}$ transition state is a true saddle point in recent ab initio calculations on a similar system, oxidative addition of H$_2$ to Pt(PH$_3$)$_2$. Therefore it is plausible that the $C_{2v}$ transition state for H-H coupling from PdH$_2$ and C-C coupling from Pd(CH$_3$)$_2$ is also a true saddlepoint; however, we did not demonstrate this (by solving for the eigenvectors of the Hessian and showing there to be one negative eigenvalue).

Acknowledgments: This work was supported by a grant from the National Science Foundation (No. CHE83-18041). One of the authors (J. J. L.) was an Exxon Education Foundation Fellow (1983) and then an Atlantic Richfield Foundation Summer Fellow (1984) during part of the time the project was in process.
Appendix A.

Although not strictly required for the studies of this paper, we carried out some limited calculations on NiH₂ in order to compare with a series of studies carried out by Siegbahn and co-workers^{22b,37a,b} on Ni(R₁)(R₂) → Ni + R₁−R₂ processes.

The calculations by Siegbahn and co-workers^{37a} on NiH₂ started with a CASSCF in which three pairs of electrons are correlated. Thus, of the 12 valence electrons, six are in doubly-occupied orbitals, while the other six are described by a full CI in which six electrons are distributed among five orbitals. All orbitals are solved for self-consistently in this wavefunction [denoted as CASSCF (3/5)], which corresponds closely to our GVB-Cl(2/6) wavefunction, except that we have four doubly-occupied orbitals (rather than three) and four electrons distributed among six orbitals (rather than six electrons distributed among four orbitals), all of which are optimized self-consistently [thus our wavefunction could be denoted CASSCF(2/6)]. In addition, we also calculated the wavefunction in which all four doubly-occupied orbitals were correlated simultaneously at the GVB-RCI(4/8) level. This calculation is denoted GVB-RCI(4/8)×GVB-Cl(2/6) (see Section V), where all orbitals are solved for self-consistently for the full wavefunction. We find that the GVB-RCI wavefunction gives a balanced description of the s²d⁸, s¹d⁹, and d¹⁰ atomic states (see Section V), and this is the level used in the various calculations on Pd and Pt systems.

However, Siegbahn and co-workers^{37} considered an alternative wavefunction in which several dominant configurations from the CASSCF were selected (all configurations with coefficients larger than 0.05),^{37a} and all single and double excitations from the dominant configurations to
all virtuals were allowed. Siegbahn's contracted CI method\textsuperscript{55} was used to solve for this CI wavefunction. On top of this, the multi-reference analog of Davidson's correction\textsuperscript{56} was used to estimate the effect of quadruple excitations.

To mimic Siegbahn's CI calculation, we carried out a CI calculation (denoted CISD) that involved all single and double excitations from the three dominant spatial configurations of the CASSCF wavefunction, accounting for about 99.0±0.1\% of the CASSCF wavefunction for the geometries considered. This size-consistent CI involved 6324 spatial configurations and 19,740 spin eigenfunctions.\textsuperscript{57} We also added the multi-reference analog of Davidson's correction\textsuperscript{56} for quadruple excitations (denoted CISD+Q). We also carried out HF, GVB-CI(2/6), GVB-RCI(4/8)×GVB-CI(2/6), and CASSCF calculations (without p functions on the hydrogens to be consistent with how PdH\textsubscript{2} and PtH\textsubscript{2} were calculated). CASSCF, CISD, and CISD+Q levels were also calculated with polarization functions on each hydrogen to be consistent with the basis set used by Blomberg and Siegbahn.\textsuperscript{37a} The effect of hydrogen p functions is to make the H-Ni-H angle larger by 2° at the CASSCF level. (All calculations with p functions of hydrogens will henceforth have an apostrophe after their names, e.g., CASSCF'.) These results are presented in Figure 11, where we see that the equilibrium H-Ni-H bond angle decreases as the level of correlation increases. Since the H-Ni-H angle is the same at the CISD' and CISD+Q' levels, this angle has probably converged to 69° with respect to electronic correlation. This bond angle is significantly different from the 57° bond angle found by Blomberg and Siegbahn\textsuperscript{37a} and is closer to the GVB-RCI(4/8)×GVB-CI(2/6) result of 76°.

We believe that the smaller bond angle found by Blomberg and
Siegahn\textsuperscript{37a} is due to the fact that their CI calculation was not a "fully variational CI calculation".\textsuperscript{37c} Siegbahn's contracted CI method has been shown to give errors of 2\% of the total correlation energy in simple systems such as CH\textsubscript{2}, CH\textsubscript{3}, and CH\textsubscript{6}.\textsuperscript{55} In NiH\textsubscript{2}, the total correlation energy is on the order of 0.30 hartrees (HF energy minus CISD+Q energy). Thus, 2\% errors in the contracted CI would lead to changes of about 6 millihartrees = 3.8 kcal/mol. Since the difference in energy between the 57\textdegree{} geometry and the 69\textdegree{} geometry (from CISD+Q) is only 0.5 millihartrees, we conclude that the contracted CI should not be reliable for such geometric quantities.

It is appropriate to examine why electron correlation has such a large effect on the bond angle in NiH\textsubscript{2} (99\textdegree{} at HF, 76\textdegree{} at GVB-RCI, and 69\textdegree{} at the best CI; see Table A-1). For all three systems, NiH\textsubscript{2}, PdH\textsubscript{2}, and PtH\textsubscript{2}, the dominant resonance structure is the same, s\textsuperscript{1}d\textsuperscript{9}. However, the second resonance structure for NiH\textsubscript{2} is different from PdH\textsubscript{2} and PtH\textsubscript{2} [see (19) and (20)], as should be expected since the lowest singlet state for Pd and Pt is d\textsuperscript{10}, whereas it is s\textsuperscript{1}d\textsuperscript{9} (\textsuperscript{1}D) for Ni. Thus, while the second resonance structure of PdH\textsubscript{2} and PtH\textsubscript{2} is d\textsuperscript{10}, it is expected to be s\textsuperscript{1}d\textsuperscript{9} for the Ni atom. But the s\textsuperscript{1}d\textsuperscript{9} open-shell singlet cannot be described by the closed-shell HF wavefunction. This bias against the s\textsuperscript{1}d\textsuperscript{9} singlet state of the Ni atom leads to repulsive interactions between hydrogen atoms and a large H-Ni-H bond angle at the HF level. The CI wavefunction includes a good description of s\textsuperscript{1}d\textsuperscript{9} singlet and hence leads to significantly smaller bond angles. Therefore, HF bond angles should be accurate for the Pd and Pt complexes but not for NiH\textsubscript{2}.
Appendix B.

We report here (in Tables B.1-VI) the optimized geometries along the reaction path for the various reactions studied in this paper. All of the geometries were optimized at the HF level (described in Section V). We also report energies for HF, GVB-CI(2/6), and GVB-RCI(4/8)×GVB-CI(2/6) wavefunctions, all of which were found\textsuperscript{13} to be consistent levels of calculation for the reaction $H_2 + Pt(PH_3)_2 \rightarrow H_2Pt(PH_3)_2$.

The following trends can be observed from these results. In going from HF to GVB-CI(2/6), oxidative addition always becomes more favorable (or reductive elimination is made less favorable). This occurs because the GVB-CI(2/6) wavefunction includes terms that provide a better description of the two M-R bonds, which have larger correlation errors than the corresponding pairs for the dissociated limit (involving a metal d pair and an H-H bond pair). In going from the GVB-CI(2/6) level to the GVB-RCI(4/8)×GVB-CI(2/6) level, we have added terms to describe the correlation effects between d electrons. These terms are needed to get accurate $d^{10}-s^1d^9$ splittings. These correlation terms always stabilize the $d^{10}$ (1S) state relative to the $s^1d^9$ (3D) state and make oxidative addition less favorable (and reductive elimination more favorable). Thus there is some degree of cancellation in the correlation errors for HF.

Table B.VII shows the effect of electron correlation on $\Delta E^\dagger$, R-M-R angle at the transition state, and $\Delta E$. The trends in $\Delta E^\dagger$ follow the same general trend as the $\Delta E$ for these reactions except with smaller magnitudes.
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(11) Harrod *et al.* have observed a trans product from H₂ addition to Ir(I).⁵⁵ however, this is believed not to be an initial product of the oxidative addition but rather the result of a rearrangement of one of the initial cis-products.⁵¹


(14) Moore, C. E. "Atomic Energy Levels," NBS: Washington, D.C., 1971; Vol. III. (These state splittings were averaged over j states to cancel out spin-orbit coupling.)


(16) The vibrational frequencies used to estimate the zero point energies were taken from those calculated for Pt(H₂)₂(PH₃)₂ and PtH(CH₃)(PH₃)₂.¹⁶a
(b) The C-Pt-C bend was calculated using the angle bending force
constant derived from the potential of reaction (14). This gave a frequency for the \( \text{H}_3\text{C} - \text{Pt} - \text{CH}_3 \) bend of 190 cm\(^{-1}\).

(17) The \( D_{298} \) used in these calculations are \( D_{298}(\text{H-H}) = 104.2 \text{ kcal/mol} \), \( D_{298}(\text{H-CH}_3) = 105.1 \text{ kcal/mol} \) and \( D_{298}(\text{H}_3\text{C-CH}_3) = 90.4 \text{ kcal/mol} \). These bond energies were derived from spectroscopic measurements of \( \text{H}_2 \)^{17a} and the reported \( D_{298} \)^{17b} for \( \text{H}_3\text{C-CH}_3 \) and \( \text{H-CH}_3 \).


(18) The vibrational frequencies (550, 1230, and 1230 cm\(^{-1}\)) used to calculate the zero point energy correction of chemisorbed H are those from the EELS spectra of H on Pt(111).\(^{18a}\) The zero point energy correction for chemisorbed \( \text{CH}_3 \) is that calculated and estimated for \( \text{CH}_3 \) chemisorbed on Ni(001).\(^{18b}\)


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(28) Pt(II)2(PPh3)2 is known to decompose via β-hydride elimination to yield ethylene ($\Delta H_{300}^0 = 12.5$ kcal/mol, $S_{300} = 52.4$ e.u.) and ethane ($\Delta H_{300}^0 = -20.2$ kcal/mol, $S_{300} = 54.9$ e.u.) rather than by reductive elimination to give n-butane ($\Delta H_{300}^0 = -30.2$ kcal/mol, $S_{300} = 74.1$ e.u.) even though n-propane is the thermodynamically favored product ($\Delta H_{300} = -22.5$ kcal/mol, $\Delta S_{300} = -34.2$ e.u., $\Delta G_{300} = -11.0$ kcal/mol for $C_2H_4 + C_2H_6 \rightarrow n-C_4H_{10}$). The $\Delta H_{300}^0$ and $S_{300}^0$ were taken from Benson, S. W. "Thermochemical Kinetics," 2nd ed.; J. Wiley and Sons: New York, 1976.


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(42) It is important to point out here that the multi-reference singles and doubles CI method is not size-consistent at every section of the potential surface. The number of configurations reported in ref. 37a "varied between 30,000 and 130,000 for Ni(CH₃)₂ depending on the part of the potential surface." Small inconsistencies at different geometries can generate large errors in the optimum geometries if the potential surface has small curvatures. It appears that the energetics derived from these calculations are reasonable and useful in discussing the properties of Ni atom vs Pd and Pt. We have used the following Dₑ and state splitting to calculate average bond energies and energetics; Dₑ(H-H) = 109.6, Dₑ(H₂C-H) = 112.6, Dₑ(H₂C-CH₃) = 95.0, and ³D-¹D splitting of 7.1 kcal/mol.¹²a


(45) Rappé, A. K., unpublished results.

We have tested the SHC basis sp basis by reoptimizing the H-Ni-H angle with the 5p basis associated with the one-electron MEP of Upton and Goddard [Upton, T. H.; Goddard III, W. A. "Chemistry and Physics of Solid Surfaces," Vanselow, R; England, W.; Eds.; CRC Press: Boca Raton, 1982; Vol. 3, pp 127-162]. The MEP basis yielded an H-Ni-H angle of 83.2° at the GVB-Cl(2/6) level, while the SHC gave 81.0° at the same level of calculation.


(48) This Cl level was restricted to allow only six open shells. This was found to be an adequate level for the state splittings of Ni, Pd, and Pt atoms.


(50) This level is very close to atomic wavefunctions at the dissociated limit of reactions (1)-(6).

(b) Williams, I. H.; Maggiora, G. M. J. Mol. Structure, THEOCHEM, 1982, 89, 365-376. Williams and Maggiora have shown that the distinguished coordinate method can yield a discontinuous reaction path if multiple local minima exist for the same value of distinguished coordinate. Since the M-H and M-CH₃ equilibrium bond
lengths are much longer than the corresponding R-H and R-CH₃ bond lengths, it is not likely that more than one local minimum can exist for any value of R₁-M-R₂ bond angle in the bound complex to transition state region. The M-R bond lengths in this region are close to those of the bound complex. If another minimum existed, it would have an R₁-R₂ distance closer to those of the products, which would force unphysically short M-R bond lengths. The typical symptom of a discontinuous reaction path would be a discontinuous change in geometric parameters, which is not evident in our results (see Appendix B).

52. A similar energy lowering would be expected for the PdH₂ complex if the geometry was reoptimized at the RCI(4/8)×GVB-CI(2/6) level.

(b) Stanton, R. E.; McIver, J. W. *J. Am. Chem. Soc.* 1975, 97, 3632-3646;  
(c) Pechukas, P. *J. Chem. Phys.* 1976, 64, 1516-1521.


57. Unfortunately no total energies or number of configurations were reported for Siegbahn’s calculations on NiH₂, so a comparison of how closely our calculations mimic his results is not possible.
Table I. Mulliken Populations for the GVB Bond Pairs of M(R₁)(R₂). For each bond there are two listings, the top one is the metal-like GVB orbital and the bottom one is the ligand-like orbital.

<table>
<thead>
<tr>
<th>System</th>
<th>Populations of GVB Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M - H</td>
</tr>
<tr>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II. Mulliken Total Populations for $M(R_1)(R_2)$.

<table>
<thead>
<tr>
<th>System</th>
<th>Metal Total Population</th>
<th>Total Population</th>
<th>Overlap of GVB Bond Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{sp}$</td>
<td>$M_d$</td>
<td>$H$</td>
</tr>
<tr>
<td>M</td>
<td>0.76</td>
<td>9.36</td>
<td>0.94</td>
</tr>
<tr>
<td>Pd</td>
<td>0.71</td>
<td>9.19</td>
<td>1.05</td>
</tr>
<tr>
<td>Pd</td>
<td>0.60</td>
<td>9.15</td>
<td>9.13</td>
</tr>
<tr>
<td>Pt</td>
<td>1.16</td>
<td>9.15</td>
<td>0.85</td>
</tr>
<tr>
<td>Pt</td>
<td>1.05</td>
<td>9.03</td>
<td>0.89</td>
</tr>
<tr>
<td>Pt</td>
<td>0.97</td>
<td>8.91</td>
<td>9.06</td>
</tr>
</tbody>
</table>
Table III. Summary of Energetics. Double dagger indicates transition state for the reaction.

The separate atomic state for Pt is the spin-allowed singlet (d^{10}).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE</th>
<th>ΔE‡</th>
<th>Zero Point Energy</th>
<th>ΔH_{298}^0</th>
<th>ΔH_{298}‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(H)₂ → Pd + H₂</td>
<td>-3.6</td>
<td>1.6</td>
<td>7.9 (MR₂)</td>
<td>1.2 (MR₂‡)</td>
<td>-4.0</td>
</tr>
<tr>
<td>Pd(H)(CH₃) → Pd + CH₄</td>
<td>-20.1</td>
<td>10.4</td>
<td>28.4 (MR₂)</td>
<td>1.2 (MR₂‡)</td>
<td>-17.2</td>
</tr>
<tr>
<td>Pd(CH₃)₂ → Pd + C₂H₆</td>
<td>-16.0</td>
<td>22.6</td>
<td>47.6 (MR₂)</td>
<td>0.9 (MR₂‡)</td>
<td>-18.8</td>
</tr>
<tr>
<td>Pt(H)₂ → Pt + H₂</td>
<td>33.6</td>
<td>--</td>
<td>7.9 (MR₂)</td>
<td>1.2 (MR₂‡)</td>
<td>33.2</td>
</tr>
<tr>
<td>Pt(H)(CH₃) → Pt + CH₄</td>
<td>16.1</td>
<td>29.0</td>
<td>28.4 (MR₂)</td>
<td>1.2 (MR₂‡)</td>
<td>19.0</td>
</tr>
<tr>
<td>Pt(CH₃)₂ → Pt + C₂H₆</td>
<td>18.3</td>
<td>53.5</td>
<td>47.6 (MR₂)</td>
<td>0.9 (MR₂‡)</td>
<td>15.5</td>
</tr>
</tbody>
</table>

H₂ → Pt

H₂ → Pt

ΔH_{298}^0 = -2.1, ΔH_{298}‡ = -15.2

CH₄ → Pt

CH₄ → Pt

ΔH_{298}^0 = -2.1, ΔH_{298}‡ = -8.3

C₂H₆ → Pt

C₂H₆ → Pt

ΔH_{298}^0 = -1.8, ΔH_{298}‡ = -5.3

a) We have assumed that methyl groups bonded to the metal atom have free rotation about the M-C bond.
Table IV. Average M-R Bond Energies.

<table>
<thead>
<tr>
<th></th>
<th>Adiabatic Bond Energy</th>
<th>Intrinsic Bond Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>R</td>
<td>$D_A$ (kcal/mol)</td>
</tr>
<tr>
<td>Pd</td>
<td>H</td>
<td>50</td>
</tr>
<tr>
<td>Pt</td>
<td>H</td>
<td>69</td>
</tr>
<tr>
<td>Pd</td>
<td>CH₃</td>
<td>38</td>
</tr>
<tr>
<td>Pt</td>
<td>CH₃</td>
<td>53</td>
</tr>
</tbody>
</table>

a) State splittings are those determined at the GVB-RCI level (see Section V).
Table V. Mulliken Populations and Geometries Along Reaction Path for Pd + H₂ → PdH₂. The transition state is at a H-Pd-H angle of 51°.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.80</td>
<td>9.28</td>
<td>0.958</td>
<td>1.51</td>
<td>2.14</td>
</tr>
<tr>
<td>80</td>
<td>0.79</td>
<td>9.31</td>
<td>0.949</td>
<td>1.51</td>
<td>1.94</td>
</tr>
<tr>
<td>70</td>
<td>0.76</td>
<td>9.36</td>
<td>0.940</td>
<td>1.51</td>
<td>1.73</td>
</tr>
<tr>
<td>60</td>
<td>0.71</td>
<td>9.41</td>
<td>0.939</td>
<td>1.52</td>
<td>1.52</td>
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<tr>
<td>50</td>
<td>0.62</td>
<td>9.49</td>
<td>0.948</td>
<td>1.55</td>
<td>1.31</td>
</tr>
<tr>
<td>40</td>
<td>0.50</td>
<td>9.59</td>
<td>0.957</td>
<td>1.60</td>
<td>1.10</td>
</tr>
<tr>
<td>30</td>
<td>0.36</td>
<td>9.71</td>
<td>0.963</td>
<td>1.71</td>
<td>0.89</td>
</tr>
<tr>
<td>20</td>
<td>0.14</td>
<td>9.88</td>
<td>0.989</td>
<td>2.12</td>
<td>0.74</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>10.0</td>
<td>1.00</td>
<td>∞</td>
<td>0.73</td>
</tr>
<tr>
<td>Config.</td>
<td>Term</td>
<td>Exp&lt;sup&gt;a&lt;/sup&gt;</td>
<td>GVB-RCI&lt;sup&gt;b&lt;/sup&gt;</td>
<td>HF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Exp&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>--------</td>
<td>-----------------</td>
</tr>
<tr>
<td>s&lt;sup&gt;1&lt;/sup&gt;d&lt;sup&gt;8&lt;/sup&gt;</td>
<td>3D</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>d&lt;sup&gt;10&lt;/sup&gt;</td>
<td>1S</td>
<td>40.0</td>
<td>40.6</td>
<td>99.5</td>
<td>-21.9</td>
</tr>
<tr>
<td>s&lt;sup&gt;1&lt;/sup&gt;d&lt;sup&gt;8&lt;/sup&gt;</td>
<td>1D</td>
<td>7.7</td>
<td>7.9</td>
<td>18.4</td>
<td>11.4</td>
</tr>
<tr>
<td>s&lt;sup&gt;2&lt;/sup&gt;d&lt;sup&gt;8&lt;/sup&gt;</td>
<td>3F</td>
<td>0.7</td>
<td>21.3</td>
<td>-15.3</td>
<td>56.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reference 14.

<sup>b</sup> GVB-RCI(5/10) total energies in hartrees for the 3D states of Ni, Pd, and Pt, are -39.238987, -29.150011, -27.551978, respectively.

<sup>c</sup> Total energies in hartrees for the 3D states of Ni, Pd, and Pt are -39.152853, -29.111329, -27.506192, respectively, at the HF level.
Table VII. The Effect of Maximum Number of Open Shells and Level of Optimization on GVB-RCI(5/10) State Splittings in Pt Atom.

<table>
<thead>
<tr>
<th>State</th>
<th>State Splittings (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GVB-PP</td>
</tr>
<tr>
<td></td>
<td>Orbitals</td>
</tr>
<tr>
<td>$^3\text{D}(d^8s^1)$</td>
<td>0$^a$)</td>
</tr>
<tr>
<td>$^1\text{S}(d^{10})$</td>
<td>12.3</td>
</tr>
<tr>
<td>$^1\text{D}(d^9s^1)$</td>
<td>26.1</td>
</tr>
<tr>
<td>$^3\text{F}(d^8s^2)$</td>
<td>18.5</td>
</tr>
</tbody>
</table>

$^a$) Total energy in hartrees for the $^3\text{D}$ state of Pt is -27.551297 for GVB-RCI(5/10) with GVB-PP orbitals and restricted to six open shells.

$^b$) Total energy in hartrees for the $^3\text{D}$ state of Pt is -27.551978 for GVB-RCI(5/10) with optimized orbitals and restricted to six open shells.

$^c$) Total energy in hartrees for the $^3\text{D}$ state of Pt is -27.552461 for GVB-RCI(5/10) with optimized orbitals.
Table VIII. The Effect of Electron Correlation on $R_1$-$M$-$R_2$ Equilibrium Bond Angles.

<table>
<thead>
<tr>
<th>System</th>
<th>Bond Angle (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
</tr>
<tr>
<td>M</td>
<td>R$_1$</td>
</tr>
<tr>
<td>Pd</td>
<td>H</td>
</tr>
<tr>
<td>Pt</td>
<td>H</td>
</tr>
<tr>
<td>Pd</td>
<td>H</td>
</tr>
<tr>
<td>Ni</td>
<td>H</td>
</tr>
</tbody>
</table>

$^a$ Bond length frozen at geometry of Blomberg and Siegbahn.$^{37a}$
Table A-I. Results for NiH₂.

<table>
<thead>
<tr>
<th>Wavefunction a)</th>
<th>Total Energy at minimum (hartrees)</th>
<th>Optimum Angle (degrees)</th>
<th>Number of Configs.</th>
<th>Number of SEF's</th>
<th>Number of Nonzero CI Matrix Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-40.075637</td>
<td>99.4</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>GVB-Cl(2/6)</td>
<td>-40.152318</td>
<td>81.0</td>
<td>48</td>
<td>57</td>
<td>1,018</td>
</tr>
<tr>
<td>CASSCF(3/5)</td>
<td>-40.158219</td>
<td>82.3</td>
<td>25</td>
<td>28</td>
<td>287</td>
</tr>
<tr>
<td>CASSCF(3/5) b)</td>
<td>-40.161980</td>
<td>84.5</td>
<td>25</td>
<td>28</td>
<td>287</td>
</tr>
<tr>
<td>RCI(4/8)×GVB-Cl(2/6)</td>
<td>-40.317295</td>
<td>76.3</td>
<td>3,360</td>
<td>8,568</td>
<td>403,712</td>
</tr>
<tr>
<td>CISD b)</td>
<td>-40.333400</td>
<td>69.0</td>
<td>6,324</td>
<td>19,740</td>
<td>8,560,651</td>
</tr>
<tr>
<td>CISD+Q b)</td>
<td>-40.350557</td>
<td>69.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

a) All of these wavefunctions used orbitals belonging to irreducible representations of C₂v.

b) These wavefunctions included p's on the H atom.
Table B-1. Geometries and Energies Along Reaction Path for Pd + H₂ → PdH₂.

<table>
<thead>
<tr>
<th>Geometric Parameters&lt;sup&gt;a&lt;/sup&gt;)</th>
<th>Energy&lt;sup&gt;b&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
</tr>
<tr>
<td></td>
<td>(kcal/mol)</td>
</tr>
<tr>
<td>PdH₂ angle, Pd-H, H-H</td>
<td></td>
</tr>
<tr>
<td>(deg.)</td>
<td>Å</td>
</tr>
<tr>
<td>90</td>
<td>1.510</td>
</tr>
<tr>
<td>70</td>
<td>1.512</td>
</tr>
<tr>
<td>60</td>
<td>1.524</td>
</tr>
<tr>
<td>50</td>
<td>1.550</td>
</tr>
<tr>
<td>40</td>
<td>1.601</td>
</tr>
<tr>
<td>30</td>
<td>1.714</td>
</tr>
<tr>
<td>20</td>
<td>2.124</td>
</tr>
<tr>
<td>0</td>
<td>∞</td>
</tr>
</tbody>
</table>

<sup>a</sup>) Each geometry optimized at the HF level with H-Pd-H angle held fixed.

<sup>b</sup>) Total energies (in hartrees) at the dissociated limit are -30.237961 at the HF level, -30.265687 at the GVB-CI(2/6) level, and -30.336364 at the GVB-RCI(4/8)xGVBCI(2/6) level.
Table B-2. Geometries and Energies Along Reaction Path for Pd + CH₃ → Pd(H)(CH₃). All angles in degrees; all distances in angstroms; all energies in kcal/mol.

<table>
<thead>
<tr>
<th>Geometric Parameters</th>
<th>Energy ( ^{a}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Pd-C</td>
<td>Pd-H₢</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>86</td>
<td>1.51</td>
</tr>
<tr>
<td>80</td>
<td>1.53</td>
</tr>
<tr>
<td>70</td>
<td>1.52</td>
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<tr>
<td>60</td>
<td>1.55</td>
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<td>1.55</td>
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<td>30</td>
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<td>20</td>
<td>2.64</td>
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<tr>
<td>0</td>
<td>∞</td>
</tr>
</tbody>
</table>

\( ^{a}) \) Each geometry optimized at the HF level with the H-Pd-C-CH₃ held fixed.

\( ^{b}) \) Total energies in hartrees at the dissociated limit are -69. 327703 for HF, -69. 317023 for GVBCH(3/6), and -69. 307700 for RC\((4/8)^*\)GVBCH(3/6).

\( ^{c}) \) \( \theta_{\text{Me}} \) is defined to be the center of mass of the methyl protons.
<table>
<thead>
<tr>
<th>C-Pd</th>
<th>Pd-C distance</th>
<th>C-C distance</th>
<th>C-H_p distance</th>
<th>C-H_0 distance</th>
<th>H^Me-C-Pd angle</th>
<th>H^Me-C angle</th>
<th>H^Me-C-H_p angle</th>
<th>H^Me-C-H_0 angle</th>
<th>H^Me-C-H_p angle</th>
<th>H^Me-C-H_0 angle</th>
<th>H^Me-C-H_p angle</th>
<th>H^Me-C-H_0 angle</th>
<th>Energy</th>
<th>Energy</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>91.9</td>
<td>1.96</td>
<td>2.82</td>
<td>1.09</td>
<td>1.06</td>
<td>176</td>
<td>140</td>
<td>106</td>
<td>112</td>
<td>87</td>
<td>150</td>
<td>106</td>
<td>112</td>
<td>87</td>
<td>150</td>
<td>106</td>
</tr>
<tr>
<td>80</td>
<td>2.01</td>
<td>2.50</td>
<td>1.09</td>
<td>1.06</td>
<td>175</td>
<td>135</td>
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<td>155</td>
<td>105</td>
<td>112</td>
<td>84</td>
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<td>105</td>
</tr>
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<td>70</td>
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<td>2.34</td>
<td>1.09</td>
<td>1.06</td>
<td>169</td>
<td>136</td>
<td>112</td>
<td>103</td>
<td>94</td>
<td>157</td>
<td>103</td>
<td>112</td>
<td>90</td>
<td>157</td>
<td>103</td>
</tr>
<tr>
<td>60</td>
<td>2.20</td>
<td>2.20</td>
<td>1.09</td>
<td>1.06</td>
<td>148</td>
<td>131</td>
<td>122</td>
<td>100</td>
<td>83</td>
<td>143</td>
<td>100</td>
<td>83</td>
<td>98</td>
<td>143</td>
<td>100</td>
</tr>
<tr>
<td>50</td>
<td>2.33</td>
<td>1.97</td>
<td>1.06</td>
<td>1.06</td>
<td>133</td>
<td>133</td>
<td>113</td>
<td>93</td>
<td>83</td>
<td>143</td>
<td>102</td>
<td>83</td>
<td>85</td>
<td>143</td>
<td>102</td>
</tr>
<tr>
<td>40</td>
<td>2.70</td>
<td>1.85</td>
<td>1.08</td>
<td>1.08</td>
<td>119</td>
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<td>118</td>
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<td>70</td>
<td>118</td>
<td>118</td>
<td>110</td>
<td>118</td>
</tr>
<tr>
<td>30</td>
<td>4.43</td>
<td>1.54</td>
<td>1.08</td>
<td>1.08</td>
<td>100</td>
<td>180</td>
<td>121</td>
<td>132</td>
<td>113</td>
<td>112</td>
<td>107</td>
<td>112</td>
<td>107</td>
<td>112</td>
<td>107</td>
</tr>
<tr>
<td>0</td>
<td>∞</td>
<td>1.54</td>
<td>1.09</td>
<td>1.09</td>
<td>90</td>
<td>180</td>
<td>--</td>
<td>111.1</td>
<td>111</td>
<td>106</td>
<td>106</td>
<td>111.1</td>
<td>111</td>
<td>111</td>
<td>106</td>
</tr>
</tbody>
</table>

a) Geometry optimized at the HF level with the C-Pd-C angle held fixed except for the 91.9° angle, which was fully optimized.
b) Total energies in hartrees at the dissociated limit (C-Pd-C angle = 0°) are -108.315072 for HF, -108.34428 for GVB(2/8) and -108.405523 for RCI(4/8)*GVB(2/8).
c) H^Me is defined to be the center of mass of the methyl protons. Key:
Table B-IV. Geometries and Energetics Along Reaction Path for Pt + H₂ → PtH₂.

<table>
<thead>
<tr>
<th>Geometric Parameters a)</th>
<th>Energies b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtH₂</td>
<td>Pt-H</td>
</tr>
<tr>
<td>angle (deg.)</td>
<td>distance Å</td>
</tr>
<tr>
<td>90</td>
<td>1.47</td>
</tr>
<tr>
<td>82.5</td>
<td>1.46</td>
</tr>
<tr>
<td>70</td>
<td>1.47</td>
</tr>
<tr>
<td>60</td>
<td>1.48</td>
</tr>
<tr>
<td>50</td>
<td>1.50</td>
</tr>
<tr>
<td>40</td>
<td>1.55</td>
</tr>
<tr>
<td>20</td>
<td>2.12</td>
</tr>
<tr>
<td>0</td>
<td>∞</td>
</tr>
</tbody>
</table>

a) Geometry optimized at the HF level with the H-Pt-H angle held fixed except for the 82.5° H-Pt-H angle that was the result of a full geometry optimization.

b) Total energies (in hartrees) at the dissociated limit are -27.584343 for HF, -27.619193 for GVB-Cl(2/6), and -27.693296 for GVB-RCI(4/8)×GVB-Cl(2/6).
Table B-V. Geometries and Energetics Along Reaction Path for Pt + CH₃ → Pt(CH₃). All angles in degrees; all distances in angstroms; all energies in kcal/mol.

<table>
<thead>
<tr>
<th>H-Pt-CH₃ angle</th>
<th>Pt-C distance</th>
<th>Pt-H distance</th>
<th>C-H distance</th>
<th>H₂Me-C-Pt angle</th>
<th>H₂Me-C-H₂ distance</th>
<th>H₂Me-H distance</th>
<th>H₂-C-Pt distance</th>
<th>H₂-C-H₂ distance</th>
<th>H₂-C-H₂ angle</th>
<th>H₂-C-H₂ angle</th>
<th>H₂-C-H₂ angle</th>
<th>Energy a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.3</td>
<td>1.96</td>
<td>1.48</td>
<td>2.44</td>
<td>180</td>
<td>182</td>
<td>1.09</td>
<td>1.06</td>
<td>100</td>
<td>109</td>
<td>114</td>
<td>110</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>1.97</td>
<td>1.47</td>
<td>2.34</td>
<td>179</td>
<td>181</td>
<td>1.09</td>
<td>1.08</td>
<td>100</td>
<td>109</td>
<td>113</td>
<td>110</td>
<td>-1.7</td>
</tr>
<tr>
<td>70</td>
<td>1.98</td>
<td>1.45</td>
<td>2.32</td>
<td>178</td>
<td>180</td>
<td>1.08</td>
<td>1.09</td>
<td>107</td>
<td>110</td>
<td>150</td>
<td>87</td>
<td>110</td>
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<td>60</td>
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<td>1.08</td>
<td>105</td>
<td>111</td>
<td>149</td>
<td>87</td>
<td>110</td>
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<tr>
<td>50</td>
<td>2.04</td>
<td>1.48</td>
<td>1.57</td>
<td>164</td>
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<td>1.08</td>
<td>95</td>
<td>115</td>
<td>141</td>
<td>91</td>
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</tr>
<tr>
<td>40</td>
<td>2.15</td>
<td>1.59</td>
<td>1.39</td>
<td>152</td>
<td>160</td>
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<td>1.08</td>
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<td>1.09</td>
<td>1.08</td>
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<td>104</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>3.06</td>
<td>2.94</td>
<td>1.09</td>
<td>123</td>
<td>180</td>
<td>1.08</td>
<td>1.08</td>
<td>54</td>
<td>125</td>
<td>110</td>
<td>109</td>
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<td>1.08</td>
<td>--</td>
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<td>109</td>
<td>109</td>
<td>109</td>
<td>0</td>
</tr>
</tbody>
</table>

---

a) Geometry optimized at the HF level with the H-Pt-C angle held fixed except for the 89.3° H-Pt-C bond angle, which was the result of a full geometry optimization.

b) Total energies in the dissociated limit are -67.641853 for HF, -67.670529 for GVBCH(2/6), and -67.744632 for RC(4/6)*GVBCH(2/6).

c) H₂Me is defined to be the center of mass for the three methyl protons. Key:

\[
\begin{align*}
\text{H}_2\text{Me} & \quad \text{Pt} \\
& \quad \text{H}_2
\end{align*}
\]
<table>
<thead>
<tr>
<th>Geometric Parameters&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Energies&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;-Pt-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>HF</td>
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<tr>
<td>C-Pt distance</td>
<td>C-C distance</td>
</tr>
<tr>
<td>90</td>
<td>1.97</td>
</tr>
<tr>
<td>90</td>
<td>1.97</td>
</tr>
<tr>
<td>60</td>
<td>2.00</td>
</tr>
<tr>
<td>70</td>
<td>2.03</td>
</tr>
<tr>
<td>60</td>
<td>2.14</td>
</tr>
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<tr>
<td>40</td>
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</tr>
<tr>
<td>30</td>
<td>3.00</td>
</tr>
<tr>
<td>20</td>
<td>4.44</td>
</tr>
<tr>
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<td>∞</td>
</tr>
</tbody>
</table>

<sup>a</sup> Each geometry optimized at the HF level with the C-Pt-C bond angle held fixed except for the 90° bond angle for which a full geometry optimization was done.
<sup>b</sup> Total energies in hartrees at the dissociated limit are -106.652122 for HF, -106.697232 for GVBCH(3/8), and -106.783035 for RCI(4/8)*GVB-CCH(3/8).
<sup>c</sup> H<sub>Me</sub> is defined to be the center of mass of the methyl protons.
Table B-VII. Effect of Correlation on Reaction Energetics and on Transition State Geometry. a)

All angles in degrees; all energies in kcal/mol.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Hartree-Fock</th>
<th>GVB-CI(2/6)</th>
<th>RCI(4/8)×GVB-CI(2/6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE ( \dagger )</td>
<td>R-M-R ( \dagger ) angle</td>
<td>ΔE</td>
</tr>
<tr>
<td>Pd(H)(_2) → Pd + H(_2)</td>
<td>0.3</td>
<td>55.8</td>
<td>-17.6</td>
</tr>
<tr>
<td>Pd(H)(CH(_3)) → Pd + CH(_4)</td>
<td>7.2</td>
<td>53.3</td>
<td>-36.5</td>
</tr>
<tr>
<td>Pd(CH(_3))(_2) → Pd + C(_2)H(_6)</td>
<td>27.5</td>
<td>59.0</td>
<td>-33.0</td>
</tr>
<tr>
<td>Pt(H)(_2) → Pt + H(_2)</td>
<td>--</td>
<td>--</td>
<td>26.2</td>
</tr>
<tr>
<td>Pt(H)(CH(_3)) → Pt + CH(_4)</td>
<td>26.1</td>
<td>44.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Pt(CH(_3))(_2) → Pt + C(_2)H(_6)</td>
<td>42.8</td>
<td>52.0</td>
<td>5.1</td>
</tr>
</tbody>
</table>

a) \( \text{R-M-R} \dagger \) denotes angle at transition state.
Figure 1. The GVB orbitals for PdH₂ and PtH₂ [from GVB(2/4)-PP calculations]. Nuclei in the plane are indicated by asterisks. Positive contours are solid, negative contours are dotted, and nodal lines are long dashes. The spacing between contours is 0.05. Each GVB orbital is analyzed in terms of a Mulliken population.
Figure 2. The GVB orbitals for PdH(CH₃) and PdH(CH₃) based on GVB(2/4) calculations.
Figure 3. The GVB orbitals for Pd(CH$_3$)$_2$ and Pt(CH$_3$)$_2$ based on GVB(2,4) calculations.
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Transition State</th>
<th>( \Delta E^* ) (kcal/mol)</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 kcal/mol</td>
<td>0 kcal/mol</td>
<td>( \Delta E^* = 1.55 \text{kcal/mol} )</td>
<td>1.55Å Pd-H, 1.73Å H</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta E^* = 10.4 \text{kcal/mol} )</td>
<td>1.55Å Pd-H, 1.73Å H</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta E^* = 22.6 \text{kcal/mol} )</td>
<td>2.25Å Pd-H, 1.97Å CH₃, 2.11Å CH₃, methyl lifl = 25°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta E^* = -3.55 \text{kcal/mol} )</td>
<td>1.95Å CH₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta E^* = -20.1 \text{kcal/mol} )</td>
<td>1.95Å CH₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta E^* = -15.95 \text{kcal/mol} )</td>
<td>1.95Å CH₃</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.** Summary of geometries and energetics for Pd + H₂ + PdH₂, Pd + CH₄ + PdH₂CH₃, and Pd + C₆H₆ + Pd(CH₂)₂ based on CVB-RCI(4/8)×CVB(2/6) calculations.
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Transition State</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.46 Å H</td>
<td>0 kcal/mol</td>
<td>ΔE_r = 33.6 kcal/mol</td>
</tr>
<tr>
<td>Pt 82.5°; 1.93 Å H</td>
<td>Pt + 0.734 Å H</td>
<td></td>
</tr>
<tr>
<td>1.48 Å H</td>
<td>0 kcal/mol</td>
<td>ΔE_r = 16.1 kcal/mol</td>
</tr>
<tr>
<td>Pt 89.3°; 2.44 Å</td>
<td>Pt + 1.08 Å CH₃</td>
<td></td>
</tr>
<tr>
<td>1.96 Å CH₃ methyl tilt = 0°</td>
<td>1.57 Å H Pt 42°; 1.42 Å CH₃ methyl tilt = 25°</td>
<td></td>
</tr>
<tr>
<td>1.97 Å CH₃ methyl tilt = 2°</td>
<td>2.34 Å CH₃ Pt 50°; 2.14 Å CH₃ methyl tilt = 51°</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5.** Summary of geometries and energetics for Pt + H₂ → PtH₂.

Pt + CH₄ → PtH(CH₃), and Pt + C₂H₆ → Pt(CH₃)₂ based on GVB-RCI(4/8)×GVBCI(2/6) calculations.
Figure 6. Potential curves for Pd + H₂ → PdH₂, Pd + CH₄ → PdH(CH₃), and Pd + CH₂ → Pd(CH₂) based on CVP-RCH(4/8) × GVB(2/6) calculations.
Figure 7. Potential curves for $\text{Pt} + \text{H}_2 \rightarrow \text{PtH}_2$, $\text{Pt} + \text{CH}_4 \rightarrow \text{PtH(CH}_3)$, and $\text{Pt} + \text{C}_2\text{H}_6 \rightarrow \text{Pt}(.\text{CH}_3)_2$ based on GVB-RCI(4/6)$\times$GVBCl(2/6) GVB-RCI calculations.
Figure 8. The GVB orbitals for PdH₂ and Pd(CH₃)₂ near the transition state for reductive elimination based on GVB(2/4)-PP calculations.
Figure 9. GVB orbitals for PdH(CH₃) near the transition state for reductive elimination based on GVB(2/4)-PP calculations.
Figure 10. Geometries of Lewis acid/Lewis base complexes of Pd + H₂, Pd + CH₄, and Pt + CH₄. The bond energy with respect to dissociation is 5, 2, and 4 kcal/mol, respectively.
Figure 11. Total energy versus H-Ni-H angle for the lowest singlet state \(^{1}A_1\) of NiH\(_2\). The asterisks mark the minimum of each curve. The HF minimum is at 99° (off the scale plotted here).
CHAPTER 3

Theoretical Studies of Oxidative Addition and Reductive Elimination:

III. C-H and C-C Reductive Coupling from Pd and Pt Bisphosphine Complexes

The following chapter has been submitted for publication to the Journal of the American Chemical Society.
1. Introduction

In spite of the importance of oxidative addition and reductive elimination in organometallic chemistry,¹ a fundamental understanding of the electronic structure of these reactions is only just emerging.²⁻⁵ Focusing only on Pd and Pt complexes, some of the experimental observations are:

(i) C-C coupling from Pd dialkylbisphosphines⁶

\[
Pd(CH_3)_2(PR_3)_2 \rightarrow Pd(PR_3)_2 + CH_3-CH_3
\]  

and from dimethyl, trimethyl and tetramethyl Pt(IV)⁷ complexes, e.g.,

\[
Pt(CH_3)_2(Cl)_2(PR_3)_2 \rightarrow Pt(Cl)_2(PR_3)_2 + CH_3-CH_3
\]  

is intramolecular and consistent with a concerted process. Conversely,

(ii) Pt dialkyls tend to decompose through β-hydride elimination⁸ if this pathway is available, even though direct C-C reductive coupling is thermodynamically favored (by 11 kcal/mol).⁹

\[
\begin{align*}
&\text{H} \quad \text{H}_4C=CH_2 \\
&\text{H}_4C=CH_2 \\
&\text{H}_4C=CH_2 \\
&\text{H}_4C=CH_2
\end{align*}
\]

(iii) Pt(CH₃)₂(PR₃)₂ complexes are thus very stable and have never been observed to undergo reductive elimination,¹⁰ while
(iv) Pt(II) biphenyls, on the other hand, reductively couple to form C-C bonds.\textsuperscript{11}

(v) In contrast, reductive H-C coupling occurs readily from Pt(II) complexes,\textsuperscript{12,13}

\[ \text{Pt(H)(CH}_3\text{)(PR}_3\text{)}_2 \rightarrow \text{Pt(PR}_3\text{)}_2 + \text{CH}_4 \] (4)

and presumably would also occur from analogous Pd(II) and Pt(IV) complexes should they be formed.

(vi) On the other hand, the reverse (oxidative addition) reaction to (1), (2), and (4) has not been observed and oxidative addition has been observed\textsuperscript{14} only for

\[ \text{Pt(PR}_3\text{)}_2 + \text{H}_2 \rightarrow \text{Pt(H)}_2\text{(PR}_3\text{)}_2 \] (5)

[and not for the analogous Pd(II) species].

In order to elucidate the general trends about reductive elimination/oxidative addition, we have carried out ab initio calculations for the species

\[
\begin{array}{ccc}
\text{Pt(CH}_3\text{)}_2\text{(PH}_3\text{)}_2 & \text{Pd(CH}_3\text{)}_2\text{(PH}_3\text{)}_2 & \text{Pt(Cl)}_2\text{(CH}_3\text{)}_2\text{(PH}_3\text{)}_2 \\
\text{1} & \text{2} & \text{3} \\
\text{Pt(Cl)}_2\text{(PH}_3\text{)}_2 & \text{Pt(H)(CH}_3\text{)(PH}_3\text{)}_2 & \text{Pt(H)}_2\text{(PH}_3\text{)}_2 \\
\text{4} & \text{5} & \text{6}
\end{array}
\]

and for the reductive coupling products

\[
\begin{array}{ccc}
\text{Pt(PH}_3\text{)}_2 & \text{Pd(PH}_3\text{)}_2 \\
\text{7} & \text{8}
\end{array}
\]

These data plus the results from previous studies\textsuperscript{2} on the transition states and barriers for reductive coupling from Mt(H)\textsubscript{2}, Mt(H)(CH\textsubscript{3}), and Mt(CH\textsubscript{3})\textsubscript{2} complexes (where Mt = Pd, Pt) are used to estimate the energet-
ics and barriers for various reductive coupling processes in Pd and Pt bisphosphine complexes.
II. Summary of Results

A. Nature of the Chemical Bonds

As a basis for understanding the differences in energetics for C-C, C-H, and H-H reductive coupling from Pt(II), Pd(II), and Pt(IV) complexes, we first develop a qualitative picture for the bonding in these systems.

1. Mt(II) Systems

The Mt–CH₃ bond orbitals (from GVB calculations) of 1, 2, 3, and 5 are shown in Figures 1-4, the Pt-Cl orbitals of 3 and 4 are shown in Figures 5 and 6, and the Pt-H orbital of 5 is shown in figure 4. The GVB orbitals are analyzed in terms of Mulliken populations in Table I and in Figures 1-6; total populations are given in Table II. The overall qualitative description is as follows:

(1) The Mt–CH₃ bonds are covalent, with one electron in an sp³ hybrid orbital on the CH₃ and one electron in an spd hybrid orbital (60% to 75% d) mainly on the metal,

(2) The Mt-H bonds are covalent, with one electron in an H 1s orbital and one electron in an spd hybrid orbital on the metal,

(3) The Mt-Cl bonds are partially ionic, with one electron in a Cl pz orbital and the other electron in an orbital that is partly on the Cl and partly on the metal (spd hybrid with 30% to 50% d character),

(4) There are generally about ten electrons on the metal with character corresponding to either

(i) the atomic d¹⁰ configuration for 7 and 8 [generally denoted as Mt(0)].
(ii) the atomic s¹d⁹ configuration for 1, 2, 4, 5, and 6 [generally denoted as Mt(II)], or

(iii) the atomic s²d⁸ configuration for 3 [generally denoted as Mt(IV)].

This focus on the ten-electron atomic configuration on the metal arises naturally from the generalized valence bond description, and we find that it provides a means for quantitative comparison of the various reaction energetics.

A more quantitative analysis of the character in the GVB orbitals is as follows (see Tables I and II). For the Pt-CH₃ bond of 1, the metal orbital is 82% on the Pt and 17% on the C. The metal part of this orbital is 60% d, 28% s and 12% p character, very similar to other Mt-C and Mt-H bonds.¹⁵

The methyl orbital of the Pt-CH₃ bond pair is 89% on the C atom (16% s and 71% p or s¹p⁴). The HCH bond angles (108°, 108° and 110°) are very close to the tetrahedral bond angles expected for sp³ carbon. These orbitals are similar to the bond orbitals of Pt(CH₃)₂, where the metal orbital has 90% Pt character (69% d, 30% s and 1% p). The carbon in the methyl group in this complex is also sp³-like (18% s and 71% p or s¹p⁴), with H-C-H bond angles of 109°, 109° and 110°.² The preference for ~60% d character in covalent metal-carbon and metal-hydrogen bonds was also observed in Ti(H)₂(Cl)₂ [74%] and Zr(H)₂(Cl)₂ [58%] and has been rationalized in terms of maximal lowering of kinetic energy.¹⁵

The major effect of the phosphines here is to decrease the Pt d character (69% to 60%) and Pt s character (30% to 28%), to increase the Pt p character (1% to 12%), and to increase the charge transfer to the methyl (0.06 e⁻ to 0.13 e⁻). These changes arise because each phosphine lone pair forms a Lewis base/Lewis acid bond to the Pt by overlapping the
empty valence s and p space of the metal atom. Thus the Mt(PH₃)₂ complex favors the d¹⁰ configuration. However, with five doubly-occupied d orbitals, the d¹⁰ configuration cannot form covalent bonds to CH₃ or H⁻ ligands. Thus, in order to add to H-H, H-C, or C-C bonds, the metal must be promoted from d¹⁰ to s¹d⁹. With two singly-occupied orbitals (one s and one d that may be hybridized to form two sd hybrids pointing at 90° to each other), the s¹d⁹ state can form the requisite pair of covalent bonds. The singly-occupied sd bonding orbitals must become orthogonal to phosphine lone pairs [not required for Mt(CH₃)₂], which they do by mixing in p character. This destabilization by the phosphines of the metal bonding orbitals makes them easier to ionize and thereby increases the ionic character of the M-C bonds.

Although Mulliken populations are always somewhat ambiguous in identifying the absolute location of charges [e.g., the dipole moment for PtH indicates that Pt is positively charged (Pt⁺H⁻) by an amount corresponding to a transfer of 0.26 e⁻ to H, whereas the Mulliken population indicates a positive charge on H of 0.1 e⁻], we find these populations useful for comparisons with related systems. From Table II the total populations indicate that each phosphine in 1 is essentially neutral (-0.06 e⁻ total charge). The total populations on the Pt for 1 lead to (sp)⁰.⁷₅(d)⁰.₃⁰, reasonably consistent with the characterization as s¹d⁹. The description of the two M-C bonds as covalent is in reasonable agreement with the Pauling electronegativities (2.2 for Pt and 2.5 for carbon).

Changing the metal atom from Pt in 1 to Pd in 2 leads to a small increase in charge transfer to CH₃ (0.13 e⁻ versus 0.20 e⁻) and to PH₃ (0.06 e⁻ versus 0.10 e⁻), to decreased sp population (0.73 e⁻ versus 0.33
e\textsuperscript{-}), and to a slight increase in d population (8.89 e\textsuperscript{-} versus 9.09 e\textsuperscript{-}). These differences indicate that Pd has essentially the same electronegativity as Pt (the Pauling scale assigns both as 2.2) and that Pd is biased toward d\textsuperscript{10} relative to s\textsuperscript{1}d\textsuperscript{9}. (This is expected since the ground state of Pd atom is d\textsuperscript{10}, while that of Pt is s\textsuperscript{1}d\textsuperscript{9}.) The character of the GVB orbitals reflects these differences. Thus, comparing 1 (Pt) and 2 (Pd), the metal part of the Mt-CH\textsubscript{3} bond orbital has 0.17 e\textsuperscript{-} versus 0.24 e\textsuperscript{-} on the C, while the M sp character decreases by 0.09 e\textsuperscript{-} and the percentage d character on the metal part of the orbital increases from 60\% to 67\%.

Comparison of 1 and 4 allows us to analyse the differences between Pt-CH\textsubscript{3} and Pt-Cl bonds. The net effect of replacing both CH\textsubscript{3} by Cl is to decrease the charge on each PH\textsubscript{3} by 0.14 e\textsuperscript{-} and to decrease the charge on Pt by 0.07 e\textsuperscript{-}. Comparing the GVB orbitals, we see that the metal orbital is 27\% on the Cl (versus 17\% on the CH\textsubscript{3}) and that the percent d character of the metal part decreases from 60\% to 51\%. As would be expected, the Cl-like GVB orbital is nearly pure p character (95\%) with very little metal character (3\%).

Summarizing, all complexes that would be described as Mt(II) in the normal oxidation state formalism are unoxidized and have s\textsuperscript{1}d\textsuperscript{8} character on the metal. Thus oxidative addition of these metals to H-H, H-C, and C-C bonds is not oxidative! In the GVB description, we think of the two singly-occupied orbitals (s and d) as combined into sd hybrids (pointing at 90\textdegree\ from each other) and covalently paired with the singly-occupied ligand orbital (H, CH\textsubscript{3}, or Cl) to form a covalent bond pair. The presence of phosphines leads to destabilization of the M s orbital, with a concomitant increase in p character and increased charge transfer to the ligand.
Thus we use the notation Mt(II) to indicate the configuration (s\textsuperscript{1}d\textsuperscript{9}) capa-
ble of forming two covalent bonds.

2. Mt(IV) Systems

Before considering the Pt(IV) complex 3, it is appropriate to examine the GVB description of the s^2d^8 state of Pt (and Ni and Pd). In the d^{10} state of Pt, the Hartree-Fock (HF) description has five doubly-occupied valence orbitals, while the GVB description leads to five pairs of orbitals, each of which involves two overlapping orbitals of the same character (e.g., d_{yz}) orthogonal to the other four pairs. In each pair, one of these orbitals is more compact and the other is more diffuse (reflecting the tendency of the electrons to correlate their motions so as to reduce electron-electron interaction while keeping the electrons close to the nucleus). Thus GVB describes d^{10} in terms of ten orbitals for the ten electrons, while HF uses five orbitals. However, since the GVB orbitals within each pair have a high overlap (S = 0.91) and similar shape, the GVB description leads to the same qualitative description as HF, and we discuss the d^{10} state as if there were five doubly-occupied orbitals.

For the s^1d^9 configuration, the ground state is 3D, which in HF is described with four doubly-occupied d orbitals, a singly-occupied d orbital, and a singly-occupied s orbital (a total of six). In the GVB description, each of the four doubly-occupied HF orbitals leads to a pair of highly overlapping GVB orbitals so that GVB again has ten orbitals for the ten electrons. Although the shapes of the singly-occupied orbitals change slightly between HF and GVB, there is again no qualitative difference in the description of the s^1d^9 state.

However, for s^2d^8, there is a qualitative difference between HF and GVB. Here the ground state is 3F, leading in HF theory to three doubly-occupied d orbitals, a doubly-occupied s orbital, and two singly-occupied
d orbitals, for a total of six. In the GVB description there are once again ten orbitals with three pairs of highly overlapping d orbitals (corresponding to the HF pairs), two singly-occupied d orbitals, and a pair of orbitals corresponding to the HF s pair. However, this last pair of GVB orbitals differs remarkably from HF, leading to sp hybrids as shown in Figure 7. The overlap for this pair is 0.75, but most significantly these sp hybrids point to opposite sides of the atom so that they can each participate in separate covalent bonds. This is quite analogous to the situation in Zn, Cd, and Hg, where the valence s pair can make two covalent bonds (say to CH₃'s), leading to a 180° bond angle. Indeed, the triplet state of PtH₂, Pt(CH₃)₂, and PtCl₂ should be linear, being formed by bonding to these sp hybrids, leaving a d⁸ configuration (probably ²Δ). [For Ni there should also be similar strongly bound triplet states; however, for Pd the very high energy of the s²d⁸ state may lead to unstable triplet states.] Of course the two singly-occupied d orbitals can also be used for bonding, leading to a total of four possible covalent bonds for Pt s²d⁸. Electronegative ligands favor bonding to the sp hybrid orbital¹⁷ since the ionization potential of the s orbital is 2.79 eV lower (leading to Pt⁺ s¹d⁸) than the d orbital (leading to Pt⁺ s²d⁷). Thus in 3 we expect the Pt-Cl bonding to favor Pt sp, while Pt-CH₃ should favor Pt d. In addition, bonding both Cl to sp orbitals should favor trans Cl ligands.

Indeed, the geometry of 3 is essentially octahedral (vide infra). (We have assumed the Cl as trans and the CH₃ groups as cis.) Comparing the Mt-Cl bonds in 4 and 3 we see an increase in ionic character for 3 (for the metal-like orbital the number of electrons on the Cl increases from 0.27 e⁻ to 0.37 e⁻). Concomitantly, the d character on the metal part of the metal orbital decreases from 52% to 32%, while the ratio of p to s
increases from 2/3 to 4/3. Comparing the Mulliken populations in 1 and 3, we see a slight change in polarity from Pt\(^{+}\)C\(^{-}\) to Pt\(^{-}\)C\(^{+}\), while remaining essentially covalent (the Pt component of the metal orbital increases from 0.82 to 0.93 e\(^{-}\), while the component of C character of the methyl orbital decreases from 0.89 to 0.78 e\(^{-}\)). Simultaneously, the d character in the metal part of the bond pair increases dramatically (60% to 74%), as expected.

To simplify the description we will refer to the Pt-C bond in 3 as a covalent bond to a Pt 5d orbital and the Pt-Cl bond as a partially ionic bond to a Pt 6sp hybrid orbital. In this simplified picture we visually represent the Pt(IV) complexes as having the Pt atom promoted to the \(s^2d^8\) configuration, having two sp hybrid pairs as in Mg, Al, and Si,

\[\text{\(6\)}\]

This state is the only one that can allow Pt atom to form four covalent bonds, two bonds to singly-occupied d orbitals and two bonds to the pair of sp lobe orbitals.\(^{18}\)

The Mulliken populations for 3 are ambiguous in assigning the electronic configuration of Pt atom. Significant amounts of charge transfer from the Pt sp orbitals to the chlorines (0.56 e\(^{-}\)) and from the methyl groups to the Pt d orbitals (0.29 e\(^{-}\)) make Pt atom appear intermediate between \(s^2d^8\) and \(s^1d^9\) (8.33 e\(^{-}\) in d orbitals and 1.12 e\(^{-}\) in s and p orbitals). Adjusting the Mulliken populations by assigning the excess charge on the chlorines as Pt sp and replacing the charge deficiency on the methyl groups with charge from the Pt d\(\pi\) orbitals, we obtain a charge of 1.68 for sp and 8.05 for d, reasonably close to \(s^2d^8\).
The bonding in this Pt(IV) complex is essentially covalent, which should not be too surprising since the Pauling electronegativity \(^1\) for Pt is 2.2 versus 3.0 for Cl and 2.5 for carbon.

3. \(\text{Mt}(0)\) Systems

The ground state of Pd(0) is \(d^{10}\), with the (triplet) \(s^1d^9\) configuration 21.9 kcal/mol higher \(^2\) (calculated value 19.6 kcal/mol). The ground state of Pt is \(s^1d^9\) with the \(d^{10}\) state 11.0 kcal/mol higher \(^3\) (calculated value 12.3 kcal/mol). For both Pd and Pt, reductive coupling involves \(s^1d^9\) for the reactant and \(d^{10}\) for the product, and hence reductive coupling should be more exothermic for Pd than for Pt by 19.6 + 12.3 = 31.9 kcal/mol (experimental value 32.9 kcal).

The lowest \textit{singlet} state of Pt(0) is \(d^{10}\) so that the spin-allowed product of

\[
\text{Mt}(R_1)(R_2) \rightarrow \text{Mt} + R_1 - R_2
\]  

is \(d^{10}\) in both cases. Adding two phosphines stabilizes \(d^{10}\) with respect to \(s^1d^9\) so that the ground state of \(\text{Mt}(\text{PH}_3)_2\) is the linear \(d^{10}\) singlet for both \(\text{Mt} = \text{Pd}\) and Pt. This stabilization of \(d^{10}\) arises from overlap between the phosphine lone pair and the metal valence s orbital. If the Mt s orbital is empty (\(d^{10}\)), the phosphine lone pair can donate into this orbital (Lewis base-Lewis acid interaction), leading to extra bonding. If the metal s orbital is occupied, it must be orthogonalized to the phosphine lone pair, increasing the energy. The result is that reductive coupling from \(\text{Mt}(\text{PH}_3)_2\) is about 20-25 kcal/mol more exothermic for both \(\text{Mt} = \text{Pd}\) and Pt.

4. Summary

Our conclusion is that the oxidation state formalism for Pt and Pd
complexes should be interpreted in terms of maximum covalency rather than degree of oxidation. Thus, Pt(II) and Pd(II) should be considered as neutral atoms with a s^1d^9 configuration forming two covalent bonds, while Pt(IV) should be described as a neutral platinum atom in an s^2d^8 configuration forming four covalent bonds. We will find this view to be quite useful in rationalizing the relative reaction energetics of Pt(II) versus Pd(II) and of Pt(II) versus Pt(IV) (Section II.C), where appropriate atomic excitation energies provide excellent predictions.

B. Energetics

The energetics for various reactions were obtained by calculating GVB correlated wavefunctions (which give accurate s^1d^9–d^10 state splittings) at geometries optimized for HF wavefunctions (see Section IV for calculational details). The results are summarized in Table III.

1. Calculated Energetics for C-C Reductive Coupling

Considering C-C coupling processes, we find

\[
\text{Pt(CH}_3)_2(\text{PH}_3)_2 \rightarrow \text{Pt(PH}_3)_2 + \text{C}_2\text{H}_6
\]

with \( \Delta H_8 = -11.3 \text{ kcal/mol} \) \hspace{1cm} (8)

which can be compared to

\[
\text{Pt(CH}_3)_2 \rightarrow \text{Pt} + \text{C}_2\text{H}_6
\]

with \( \Delta H_9 = 15.5 \text{ kcal/mol} \). \hspace{1cm} (9)

Thus, the presence of two phosphines favors reductive coupling by an extra 26.8 kcal/mol. The reason for this is that the Pt has a s^1d^9 configuration for the reactant side of (8) and (9) but a d^10 configuration for the product side. As discussed in Section II.A.3, phosphines stabilize d^10 relative to s^1d^9, leading to a more exothermic reaction.

Consider next the analogous reactions with Pd,
\[ \text{Pd(CH}_3\text{)}_2(\text{PH}_3)_2 \rightarrow \text{Pd(HP}_3\text{)}_2 + \text{C}_2\text{H}_6 \]  
with \( \Delta H_{10} = -45.6 \text{ kcal/mol} \),

which can be compared to

\[ \text{Pd(HP}_3\text{)}_2 \rightarrow \text{Pd} + \text{C}_2\text{H}_6 \]  
with \( \Delta H_{22} = -18.8 \text{ kcal/mol} \).

The reaction enthalpies differ dramatically from those of Pt; however, these differences are easily explained. All four reactions involve converting the metal from \( s^1d^9 \) to \( d^{10} \), but using \( d^{10} \) as the reference Pt favors \( s^1d^9 \) by 12.3 kcal/mol, whereas Pd disfavors \( s^1d^9 \) by 19.6 kcal/mol. Thus, relative to Pt, Pd has a bias against \( s^1d^9 \) of 31.9 kcal/mol. Consequently, the driving force for Pd reductive coupling should be exothermic by 31.9 kcal/mol more than for Pt. Indeed, we calculate a difference of 34.5 kcal/mol for the bisphosphine and 34.3 kcal/mol for the unsubstituted metal.

These results for Mt(II) can be compared to the Mt(IV) reaction,

\[ \text{Pt(HP}_3\text{)}_2(\text{Cl}_2\text{)}_2(\text{PH}_3)_2 \rightarrow \text{Pt(HP}_3\text{)}_2(\text{PH}_3)_2 + \text{C}_2\text{H}_6 \]  
with \( \Delta H_{12} = -27.0 \text{ kcal/mol} \).

Here the metal changes from \( s^2d^8 \) to \( s^1d^9 \), which for the free atom is exothermic by 17.2 kcal/mol. Comparing to reaction (8) involving \( s^1d^9 \) to \( d^{10} \), which is endothermic in the atom by 12.3 kcal/mol, we would expect from atomic considerations that (12) should be 29.5 kcal/mol more exothermic than (8). Of course the four-coordinate Pt(II) and six-coordinate Pt(IV) also differ in other respects; however, we find that (12) is 16 kcal/mol more exothermic than (8), so that the atomic change of configuration effects dominate.

Based on differential atomic excitation energies, the Pd analog of (12) should be exothermic by an extra 45 kcal/mol, leading to a total
exothermicity (ΔE) of about 70 kcal/mol. We estimate that there is no barrier for this decomposition and hence that this species is unstable.

Summarizing, we find that reductive CC coupling is exothermic by 45.8 kcal/mol for Pd(II), by 27.0 kcal/mol for Pt(IV), and by 11.3 kcal/mol for Pt(II), differences that can be understood in terms of the relative atomic energies of $s^1d^9$, $d^{10}$, and $s^2d^8$ configurations.

2. Calculated Energetics for C-H Reductive Coupling

We calculate that

$$\text{Pt(H)(CH}_3\text{(PH}_3\text{)}_2 \rightarrow \text{Pt(PH}_3\text{)}_2 + \text{CH}_4$$

with $\Delta H_{13} = -5.8$ kcal/mol,

whereas

$$\text{Pt(H)(CH}_3\text{)} \rightarrow \text{Pt + CH}_4$$

with $\Delta H_{14} = 19.0$ kcal/mol.

Thus two phosphines promote H-C reductive coupling by 24.8 kcal/mol, which can be compared with a promotion of 26.8 kcal/mol for C-C reductive coupling on Pt and 27.0 for C-C reductive coupling on Pd. For Pd we studied reductive coupling for the free atoms, finding

$$\text{Pd(H)(CH}_3\text{)} \rightarrow \text{Pd + CH}_4$$

with $\Delta H_{15} = -17.2$ kcal/mol

but did not calculate the H-C coupling from the bisphosphine. However, the above results suggest that for Pd the bisphosphine would promote H-C reductive coupling by $\sim 25.0$ kcal/mol, leading to

$$\text{Pd(H)(CH}_3\text{(PH}_3\text{)}_2 \rightarrow \text{Pd(PH}_3\text{)}_2 + \text{CH}_4$$

with $\Delta H_{16} \approx -42.2$ kcal/mol.

We did not calculate the energetics for H-C coupling from Pt(IV) or Pd(IV) complexes; however, comparisons with the C-C coupling cases sug-
gest that
\[ \text{Pt(H)(CH}_3\text{)(Cl)}_2(\text{PH}_3)\text{)}_2 \rightarrow \text{Pt(Cl)}_2(\text{PH}_3)\text{)}_2 + \text{CH}_4 \]
(17)
with \( \Delta H_{17} \approx -19.5 \text{ kcal/mol} \),

while the analogous Pd complex would not be stable.

3. **Calculated Energetics for H-H Reductive Coupling**

We calculate that
\[ \text{Pt(H)}_2(\text{PH}_3)\text{)}_2 \rightarrow \text{Pt(PH}_3\text{)}_2 + \text{H}_2 \]
(18)
with \( \Delta H_{18} = 12.3 \text{ kcal/mol} \),

whereas
\[ \text{Pt(H)}_2 \rightarrow \text{Pt} + \text{H}_2 \]
(19)
with \( \Delta H_{19} = 33.2 \text{ kcal/mol} \).

Thus the phosphines promote H-H reductive coupling by 20.9 kcal/mol, which can be compared with 24.8 kcal/mol for H-C and 26.8 kcal/mol for C-C. For Pd we studied reductive coupling from the free atom, finding
\[ \text{Pd(H)}_2 \rightarrow \text{Pd} + \text{H}_2 \]
(20)
with \( \Delta H_{20} = -4.0 \text{ kcal/mol} \)

but did not calculate the reductive H-H coupling from the bisphosphine. However, the above results suggest that the phosphines would promote H-H coupling on Pd by about 21.1 kcal/mol, leading to
\[ \text{Pd(H)}_2(\text{PH}_3)\text{)}_2 \rightarrow \text{Pd(PH}_3\text{)}_2 + \text{H}_2 \]
(21)
with \( \Delta H_{21} \approx -25 \text{ kcal/mol} \).

We did not calculate the energetics of H-H coupling from Pt(IV) or Pd(IV) complexes; however, we estimate that
\[ \text{Pt(H)}_2(\text{Cl)}_2(\text{PH}_3)\text{)}_2 \rightarrow \text{Pt(Cl)}_2(\text{PH}_3)\text{)}_2 + \text{H}_2 \]
(22)
with \( \Delta H_{22} \approx 2.5 \text{ kcal/mol} \)

and that the analogous Pd complex is unstable.
4. Adiabatic Bond Energies

Since the C-C bond energy in ethane is 90.4 kcal/mol, the exothermicity of 11.3 kcal/mol for (8) leads to an average Pt-C bond energy of

\[ \tilde{D}_{298}[(\text{PH}_3)_2\text{Pt}-\text{CH}_3] = 38.6 \text{ kcal/mol.} \] (23)

Similarly, since the H-H bond energy is 104.2 kcal/mol, the energetics in (18) correspond to an average Pt-H bond energy of

\[ \tilde{D}_{298}[(\text{PH}_3)_2\text{Pt}-\text{H}] = 58.3 \text{ kcal/mol.} \] (24)

As a check upon the utility of such average bond energies, we can use (23) and (24) plus the C-H bond energy in CH₄ (105.1 kcal/mol) to predict

\[ \Delta H_{13} = 39.6 + 58.3 - 105.1 = -7.2 \text{ kcal/mol,} \]

in reasonable agreement with the calculated value of -5.8 kcal/mol.

The average bond energies for the bare metal are obtained from (9) and (19) as

\[ \tilde{D}_{298}(\text{Pt}-\text{CH}_3) = 53.0 \text{ kcal/mol} \] (25)

\[ \tilde{D}_{298}(\text{Pt}-\text{H}) = 68.7 \text{ kcal/mol,} \] (26)

which leads to a prediction of

\[ \Delta H_{14} = 53.0 + 68.9 - 105.2 = +16.5 \text{ kcal/mol,} \]

in reasonable agreement with the calculated value of \( \Delta H_{14} = 19.0 \) kcal/mol.

The average bond energies for Pd complexes are calculated to be about 18 kcal/mol lower (see Table IV) because of the propensity for Pd to form d^{10} configurations.
Averaging the results for Pd and Pt, we find that M-H bonds are 18 kcal/mol stronger than M-CH₃ bonds for the bisphosphine and 15 kcal/mol stronger for the bare metal. Thus, the phosphines lead to a relative weakening of M-CH₃ versus M-H bonds. This could be simply a steric effect. If so, the bulky phosphines endemic to experiments might have even a greater bias against M-CH₃ bonds.

The Pt(IV) system leads to weaker Pt-CH₃ bonds,

\[ \overline{D}_{298}[(\text{Cl})_2(\text{PH}_3)_2\text{Pt-CH}_3] = 31.7 \text{ kcal/mol}. \]  (27)

As discussed above, this 8 kcal/mol decrease from the value for Pt(II) is dominated by the preference of Pt to convert from \(s^2d^6\) to \(d^9s^1\).

5. Intrinsic Bond Energies

It is often useful to define an intrinsic bond strength as the energy to break a bond A-B without allowing the fragments to relax. This intrinsic bond strength is then reduced by various relaxation effects that occur in the fragments A and B after the bond is broken. These relaxation effects can involve geometric relaxation and electronic relaxation. The final bond energy including all these effects is the adiabatic bond energy \(\overline{D}_{298}\). Thus, for example, the C-H bond energy of cyclopropane is 11 kcal/mol stronger²⁰ than for H-CH(CH₃)₂ partly because geometric constraints prevent most of the geometry relaxation in cyclopropane.

A good example for the role of electronic relaxation upon bond energy is in the difference in carbon-carbon double bond strengths in C₂H₄ and C₂F₄.²¹ The double bond requires a singly-occupied \(\sigma\) and \(\pi\) orbital on each carbon corresponding to the \(^3\text{B}_1\) state of free CH₂ or CF₂. For CH₂, the triplet state is the ground state and hence the observed (adiabatic) bond energy of 172.2 kcal/mol²² is electronically diabatic (it
involves a small amount of geometric relaxation). However, for \( \text{CF}_2 \), the \( ^3\text{B}_1 \) state is 56.6 kcal/mol\(^{23}\) above the ground state \( ^1\text{A}_1 \). Thus, if the diabatic C-C double bond energy is assumed unchanged (172.2 kcal/mol), we would expect the adiabatic bond energy in \( \text{C}_2\text{F}_4 \) to be 172.2 - 2(56.6) = 59.0 kcal/mol. This is in good agreement with the observed bond energy of 69.0 ± 2.7 kcal/mol,\(^{22}\) demonstrating the power in using the concept of electronic relaxation in estimating bond energies.

The adiabatic bond energies calculated in the previous section included both geometrical and electronic relaxation effects. In order to correct the average bond energies for these relaxation effects, we must add the atomic excitation energy \( \text{d}^{10} \rightarrow \text{d}^9 \text{s}^1 \) or \( \text{s}^1 \text{d}^9 \rightarrow \text{s}^2 \text{d}^8 \) in the complex to the driving force for reductive elimination. We calculate the energy of the triplet at the geometry of the \( \text{Mt} \text{(PH}_3)_2 \) [or \( \text{MtCl}_2 \text{(PH}_3)_2 \)] fragment in the \( \text{MtR}_2 \text{(PH}_3)_2 \) [or \( \text{MtR}_2 \text{Cl}_2 \text{(PH}_3)_2 \)] complex. Of course the energy of the \( \text{Mt} \text{(PH}_3)_2 \) [or \( \text{MtCl}_2 \text{(PH}_3)_2 \)] singlet was calculated at the equilibrium geometry. The singlet-triplet splittings calculated with these reference states include all differential relaxation effects which occur during reductive elimination from these complexes. Thus the intrinsic bond energy is defined as

\[
D_t = \frac{1}{2} \Delta H (\text{MR}_2 \rightarrow \text{M} + \text{R}_2) + \delta E (\text{M} \rightarrow \text{M}) + D_{298} (R-R),
\]

(28)

where \( \delta E (\text{M} \rightarrow \text{M}) \) is the singlet-triplet excitation energy described above, \( \text{M} \) is the singlet metal complex product in its ground state geometry, and \( \text{M} \) is the triplet state of the same complex frozen at the geometry it had in the reactant complex.

Average bond energies and the relevant state splittings are presented in Table IV. The corrected bond energies show that the intrinsic strengths of Pt-C and Pd-C bonds are very similar and that the
relative stability toward reductive coupling is dominated by the relative
energies of the s^1d^9 and d^{10} states and of bent versus linear phosphines.
Comparing the intrinsic Mt-R bond strengths of bisphosphine complexes
[e.g., 56 kcal/mol for Pt(CH_3)_2(PH_3)_2] and the corresponding MtR_2
complexes^{2c} (e.g., 47 kcal/mol for PtMe_2), indicates that the presence of
phosphines strengthens the intrinsic Mt-R bonds by 6-12 kcal/mol. This
is because the metal spd hybrid orbitals used to form the M-R bonds
must be orthogonalized to the phosphines, leading to an increase in the p
character of the metal hybrid. This in turn increases the overlap of the
M-R bond,^{15} increasing the intrinsic bond strength. On the other hand,
the phosphines lead to a decrease in the adiabatic bond energies [from 53
kcal/mol for Pt(CH_3)_2 to 40 kcal/mol for Pt(CH_3)_2(PH_3)_2]. This is prob-
ably because the phosphines greatly favor the d^{10} form of the product.

The intrinsic Pt(IV)-C bond is 5 kcal/mol weaker than the Pt(II)-C
bond in bisphosphine complexes. This is probably because the Pt 6s char-
acter of the Pt(IV)-C bonds is used up in the Pt-Cl bonds. Consequently,
the methyl group in Pt(IV) is forced to bond to metal orbitals that have
mainly d character rather than the optimal hybridization^{15} (~60% d and
40 % sp) that is available in the Pt(II) bisphosphine complex.

Few bond strengths are known experimentally for Pt-C or Pd-C.
From studies of the decomposition of PtMe_3Cp,^{24} an experimental Pt-CH_3
bond energy of 39±5 kcal/mol has been determined. This is an adiabatic
bond energy,

$$\text{PtMe}_3\text{Cp} \rightarrow \cdot\text{Me} + \cdot\text{PtMe}_2\text{Cp},$$

but the Pt atom no doubt retains s^2d^8-character. Thus the exothermicity
of (29) should be less than the intrinsic bond energy (51 kcal/mol) but
probably larger than our estimated adiabatic bond strength of 32
kcal/mol, which involves relaxation to $s^1d^9$. Thus the theory and experiment are in reasonably agreement.

C. Barriers and Rates

In previous studies of

$$\begin{align*}
\text{Mt} & \xrightarrow{R_1} \text{Mt} + \frac{R_1}{R_2} \\
\text{Mt} & \xrightarrow{R_2} \text{Mt} + \frac{R_1}{R_2}
\end{align*}$$

(30)

where Mt = Pd,Pt and $R_1,R_2 = H$ and CH$_3$, we showed that the intrinsic barrier (i.e., the barrier exceeding the endothermicity) is

(i) large for CC coupling (e.g., 23 kcal/mol for Pd, 54 kcal/mol for Pt),

(ii) intermediate for CH coupling (e.g., 10 kcal/mol for Pd, 29 kcal/mol for Pt), and

(iii) small for HH coupling (e.g., 2 kcal/mol for Pd).

The origin for such dramatic differences for H-H, H-C, and C-C coupling is found in the shapes of the H 1s and C sp$^3$ orbitals. At the transition state, the wavefunction involves a mixture of the $s^1d^9$ resonance structure (31) for the reactant

$$\begin{align*}
\text{s}^1\text{d}^9 \text{ Resonance Configuration}
\end{align*}$$

(31)

and the d$^{10}$ resonance structure (32) of the product
d^{10} Resonance Configuration

Since the H 1s orbital is spherical, it can simultaneously overlap either the Mt sd hybrid orbital in (31) or the valence orbital of the other R group in (32). The result is that these two resonance structures have a high overlap for R_1 = R_2 = H, leading to a large resonance stabilization and a low barrier. If R_1 = H and R_2 = CH_3, then the directed form of the valence orbital for CH_3 is such that one CH_3 orientation favors (31)

while a different CH_3 orientation favors (32)

Consequently, at the transition state the CH_3 group has an intermediate
orientation which is less favorable for both (31) and (32), leading to a
significant barrier. If \( R_1 = R_2 = \text{CH}_3 \), then there is a similar problem for
both ligands, leading to a barrier that is roughly twice as large.

Adding two phosphines to the metal stabilizes the \( d^{10} \) state over \( s^1d^9 \),
making reductive coupling about 23 kcal/mol more exothermic (27
kcal/mol for H-H, 23 kcal/mol for H-C, and 21 kcal/mol for C-C) and
should similarly decrease the activation barrier. Assuming that the transition state involves about equal parts of the \( d^{10} \) and \( s^1d^9 \) configurations,
it is plausible that the barrier will be decreased by about half as much as is
the reactive enthalpy. This leads to the estimated activation energies
in Table III and Figure 8.

Particularly clean experiments have been carried out for H-C coupling from Pt(II),\(^{12,13}\) (13), for which we estimate

\[
\Delta H_f = 15.7 \text{ kcal/mol.}
\]

This can be compared to

\[
cis-\text{Pt(H)(CH}_2\text{CF}_3)(\text{PPPh}_3)_2 \to \text{Pt(PPPh}_3)_2 + \text{CH}_3\text{CF}_3,
\]  

where in benzene solvents \( \Delta H^\dagger = 24.6 \pm 0.6 \) and \( \Delta S^\dagger = 4.9 \pm 2 \), and to

\[
cis-\text{Pt(H)(CH}_3)(\text{PPPh}_3)_2 \to \text{Pt(PPPh}_3)_2 + \text{CH}_4,
\]  

where (in toluene at -25°C) \( \Delta G^\dagger = 18.2 \).\(^{12}\) Assuming \( \Delta S^\dagger \approx 5 \), this latter value leads to \( \Delta H^\dagger = 17.0 \text{ kcal/mol, in good agreement with our predictions.} \)

Other relevant activation energies have been measured by Moravskiy
and Stille\(^6^c\) for reductive elimination of ethane from cis-
\text{Pd(CH}_3)_2(\text{PPPh}_2(CH}_3)_2. They find activation energies (\( E_a \)) of 6-11 kcal/mol
in polar-coordinating solvents (Me_2SO-d_6, Me_2CO-d_6, and CD_3CN) and 25-
28 kcal/mol in aromatic solvents (C₆D₅CD₃ and C₆D₆). It is uncertain how
to compare these numbers with our calculations since it is likely that
reductive elimination does not proceed directly from the bisphosphine
complex (see Section III.A). However, we estimate

$$
\Delta H^{\ddagger}_{f0} = 10.4 \text{ kcal/mol}
$$

(at 300°K), and hence the estimated barrier (at 300°K) is $E_a = \Delta H^{\ddagger} + RT =
10.7 \text{ kcal/mol}$, surprisingly close to the $E_a$ measured in coordinating sol-
vent.

On the other hand, our estimates lead to

$$
\Delta H^\ddagger = 41 \text{ kcal/mol}
$$

for C-C coupling on Pt(II), certainly consistent with the lack of observa-
tion of this reaction.

The calculated endothermicity ($\Delta H_{18} = 12.3 \text{ kcal/mol}$) and barrier
($\Delta H^\ddagger_{f0} = 14.0 \text{ kcal/mol}$) for H-H coupling from Pt(II) are consistent with
the equilibrium observed in such systems by Trogler.¹⁴ On the other
hand, our calculations suggest that cis-Pd(H)₂(PH₃)₂ and cis-
Pd(H)(CH₃)(PH₃)₂ would have no barrier for decomposition and hence
should not be stable.

The estimated barriers for Mt(IV) complexes are much more uncer-
tain since barriers were not calculated even for complexes without phos-
phines. In this case we have assumed that half of the addition exothermi-
city relative to Mt(II) goes into the transition state.

Brown et al.⁷b have measured $E_a$ for reductive elimination of ethane
from various Pt(IV) trimethyl complexes. They find $E_a = 27.7 \pm 1.2$ for
reductive elimination from PtCl(CH₃)₃(PMe₂Ph)₂ at 353°K. Our estimate is
$E_a = 34.9 \text{ kcal/mol}$ ($\Delta H^\ddagger_{f2} = 34.2 \text{ kcal/mol}$) for elimination from
PtCl₂(CH₃)₂(PH₃)₂. The good agreement between experiment and theory may be fortuitous since it appears experimentally that the reductive elimination takes place from a five-coordinate intermediate formed by loss of phosphine. Similar estimates for H-H and H-C coupling from Pt(IV) lead to ΔH° = 9 kcal/mol for both reactions, indicating rather unstable species. The analogous Pd(IV) complexes are predicted to be unstable.

Experimentally it is known that Pt(II) dimethyl complexes are much more stable than Pd(II) dimethyl complexes, with C-C coupling facile for Pd(II)⁶ and unobserved for Pt(II).¹⁰ In addition, it is known that Pt(IV) dimethyl, trimethyl, and tetramethyl complexes will reductively eliminate ethane,⁷ while Pt(II) dimethyl complexes do not.¹⁰ Our results are consistent with these experimental observations.

As indicated, the theoretical results are consistent with current experimental knowledge concerning reductive coupling and oxidative addition of Pt(II), Pd(II), and Pt(IV) complexes. These experiments can be understood on the basis of the changes in the electronic configuration of the metal plus simple ideas on the relative barriers for C-C versus C-H versus H-H coupling. Given results for one metal, these ideas may be used to predict the results on other metals using only atomic data.

D. Geometries

The geometries for all molecules studied in this work have been optimized for the HF wavefunctions using analytic gradient techniques. The fully optimized HF geometries of 1 Pt(Me)₂(PH₃)₂, 2 Pd(Me)₂(PH₃)₂, and 3 Pt(Me)₂(Cl)₂(PH₃)₂ are shown in Figures 9 and 10, and the calculational details are described in Section IV. The internal coordinates around the metal atom for the complexes studied in this work are presented in Table V. Cartesian coordinates for each molecule are given
in the Appendix. We find very good agreement between our calculated geometries and x-ray structures on related molecules, as described below.

The calculated Pt-C bond distance (2.06 Å) in 1 is very close to the sum of covalent radii\(^{16}\) (Pt-Csp\(^3\)) 2.09 Å and is in the range observed in x-ray structures of Pt(II) dialkyl complexes:\(^{25}\) [an average of 2.05 Å in Pt\(_2\)Me\(_4\) (μ-\(\mu\)-dppm)\(^2\)]\(^{25c}\) [dppm = Ph\(_2\)PCH\(_2\)PPh\(_2\)]; 2.18 Å and 2.15 Å in PtMe\(_2\) (tripod) [tripod = 1,1,1-tris(diphenylphosphinomethyl)ethane];\(^{25a}\) and 2.05 Å and 2.12 Å in Pt(C\(_4\)H\(_8\))(PPh\(_3\))\(^2\).\(^{25b}\)

The calculated C-Pt-C bond angle in 1 of 89° is \(~10°\) larger than the C-Pt-C angles observed in the x-ray structure of Pt\(_2\)Me\(_4\) (μ-\(\mu\)-dppm) (81.6°) and Pt(C\(_4\)H\(_8\))(PPh\(_3\))\(^2\) (80.9°).\(^{25}\) This difference is most likely due to the PH\(_3\) ligands having less steric bulk than substituted phosphines.

The calculated Pt-Cl bond distance in 4 of 2.35 Å and the Cl-Pt-Cl bond angle of 91° match very well with the observed Pt-Cl distances (2.368 Å and 2.377 Å) observed in the x-ray structure of cis-Pt(PMe\(_3\))\(_2\)Cl\(_2\).\(^{26}\)

The calculated Pt-P bond distances are 0.1-0.2 Å longer than experiment [Pt-P = 2.23 and 2.24 Å in PtCl\(_2\)(PMe\(_3\))\(^2\)]\(^{26}\) versus 2.44 Å calculated for (4); 2.279 and 2.285 Å in Pt(C\(_4\)H\(_8\))(PPh\(_3\))\(^2\)\(^{25b}\) versus 2.46 Å calculated in (1)]. This is systematic for Pt-P bonds at this level of calculation\(^{26a}\) and may be partially due to the effect of substituted phosphines versus PH\(_3\).

The P-Pt-P bond angle is apparently less sensitive, and good matches to the experimentally observed P-Pt-P angles are found [101° in (1) versus 98.9° in Pt(C\(_4\)H\(_8\))(PPh\(_3\))\(^2\) and 102° in (6) versus 96.2° in PtCl\(_2\)(PMe\(_3\))\(^2\)].\(^{26}\)

Noell and Hay\(^{4b}\) were the first to show that HF wavefunctions yield geometries of Pt and Pd complexes which compare well with x-ray
structures, indicating that HF is a reasonable level of wavefunction with which to optimize geometries.
III. Discussion

A. The Effect of Added Phosphine on the Rate of Reductive Elimination

One of the unresolved questions in the experimental literature is the effect of added phosphines on the rate of C-C coupling. There are three classes of systems:

(A) For PdMe₂L₂⁶ and AuMe₃L³b,⁷ experiment shows that reductive elimination of ethane is retarded by added phosphine. This led Hoffman et al.³a,b to propose a mechanism by which reductive elimination proceeds through a three-coordinate intermediate, an interpretation supported by Extended Hückel (EH) calculations.

(B) Contrasted with these results are

\[ \text{Pd(CH₃)(CH=CHPh)(PPh₃)₂} \rightarrow \text{CH₃CH=CHPh + Pd(PPh₃)₂} \quad (37) \]

\[ \text{Ni(CH₃)₂(DIPHOS) \rightarrow Ni(DIPHOS) + C₂H₆} \quad (38) \]

[DIPHOS = Ph₂P(CH₂)₂PPh₂] where the addition of phosphine has no affect on the rate of C-C coupling.²⁸,²⁹ These systems apparently can reductively eliminate directly from the original four-coordinate complex.

(C) There are also Ni(II) and Pt(II) complexes such as

\[ \text{cis-NiPh(CH₃)(DPE)} \quad (39) \]

and

\[ \text{cis-Pt(C₆H₄Me-4)₂(PPh₃)₂,} \quad (40) \]

where reductive coupling of C-C bonds is promoted by the addition of phosphines.¹¹,²⁸ This led Braterman and Cross³⁰ to propose a mechanism by which reductive elimination proceeds through a
five-coordinate intermediate, a mechanism that was also supported by EH calculations of Tatsumi et al.\textsuperscript{3d}

Our calculations on reductive elimination of ethane from PdR\textsubscript{2} and PtR\textsubscript{2} show that reductive elimination is favored energetically from PdR\textsubscript{2} because Pd prefers the d\textsuperscript{10} configuration.\textsuperscript{2c} It is interesting to note that the difference in ΔH\textsuperscript{θ} for elimination of C\textsubscript{2}H\textsubscript{6} from Pd(CH\textsubscript{3})\textsubscript{2} and Pt(CH\textsubscript{3})\textsubscript{2} (30.9 kcal/mol) is very close to the difference in the driving force for each reaction (34.3 kcal/mol). This suggests that the barrier to reductive coupling of C-C bonds is strongly coupled to the driving force. Since phosphines stabilize d\textsuperscript{10} relative to s\textsuperscript{1}d\textsuperscript{9}, we would expect the three-coordinate complexes to have a larger barrier for reductive elimination than the four-coordinate complex, which should in turn have a larger barrier than the five-coordinate complex.

The consideration of only the three-coordinate intermediate for systems of class A may be an oversimplification of the real system. Intermolecular paths clearly are important for the decompositon of AuMe\textsubscript{2}L in some solvents [e.g., benzene, decalin, PhCl, n–Bu\textsubscript{2}O, and Tetrahydrofuran (THF)].\textsuperscript{3b} More strongly coordinating solvents [Me\textsubscript{2}SO (DMSO) and dimethylformamide (DMF)] appear to block intermolecular paths, resulting in very little crossover.\textsuperscript{3b} For reductive elimination of ethane from Pd(CH\textsubscript{3})\textsubscript{2}L\textsubscript{2}, crossover experiments show that reductive elimination of ethane is intramolecular only in DMSO or noncoordinating solvents containing dimethylmaleate (DMM).\textsuperscript{6} It has been assumed that DMM serves to trap the PdL\textsubscript{2} product before it can decompose (and thereby affect the decompositon pathway); however, Ozawa et al.\textsuperscript{6d} have shown that variation in concentration of DMM does not affect the rate of decomposition. (They did not report the rate with no added DMM.) This only proves that
DMM is not involved in the rate determining step of reductive elimination (which appears to be loss of a phosphine). The loss of phosphine could also be the rate-determining step in the formation of a four-coordinate intermediate in which one of the phosphines is replaced by DMSO, DMF, or DMM. If reductive elimination is facile from these intermediates then loss of phosphine would be the slow step which would be inhibited by added ligand.

Palladium might be expected to prefer pathways involving loss of phosphine, while other metals of the nickel triad reductively eliminate through four- and five-coordinate pathways since Pd forms weaker bonds to phosphines than Ni and Pt.\textsuperscript{31} Apparently reductive elimination of \( \text{CH}_3\text{CH}=&\text{CHPh} \) from \( \text{Pd(CH=CHPh)(CH}_3)(\text{PPh}_3)_2 \) is not affected by added phosphine because the \( \Delta G^\ddagger \) for elimination from the four coordinate starting complex is lower than the \( \Delta G_r \) of the three coordinate intermediate.

Unfortunately it has not been possible to observe directly the three- or five-coordinate intermediates proposed for class A and C systems. Although EH calculations do support lower barriers for three and five coordinate complexes than four coordinate complexes, these predicted trends in activation energies do not correlate with our observed correlation of \( \Delta E^\ddagger \) and \( \Delta E \). EH calculations are well known\textsuperscript{32} not to give accurate geometries and energetics and should not be considered as proof for the proposed mechanisms. What is needed are \textit{ab initio} calculations of the relative barriers of reductive elimination from three, four and five coordinate intermediates.
B. Reactivity of Metal–Carbon Bonds Involving \( sp^2 \) Hybrids Versus \( sp^3 \) Hybrids

Another trend which has been observed but not explained is the lower stability of \( cis- \)methylphenyl and \( cis- \)biphenyl complexes relative to dimethyl complexes. Reductive elimination from \( cis- \)Ni(CH\(_3\))(C\(_6\)H\(_5\))L\(_2\) is faster than from \( cis- \)Ni(CH\(_3\))\(_2\)L\(_2\) complexes.\(^{28}\) The reaction of PhLi with PdCl\(_2\) (DIPHOS) yields biphenyl directly, whereas MeLi reacts with PdCl\(_2\) (DIPHOS) to give PdMe\(_2\) (DIPHOS) which eliminates ethane slowly.\(^{6a}\) Platinum diphenyl bisphosphine complexes can eliminate biphenyl\(^{11}\) while Pt dimethyl bisphosphine complexes are very stable.\(^{10}\) This trend can be explained by noting that the phenyl group uses a C \( sp^2 \) hybrid orbital to form bonds while the methyl group uses a C \( sp^3 \) hybrid orbital. The increased s character of the \( sp^2 \) hybrids causes this orbital to be less directional than the \( sp^3 \) hybrids. Therefore the \( sp^2 \) hybrid can have more multicentered bonding at the transition state, leading to lower activation energies for CH\(_3\)=CH=CHPh, CH\(_3\)=Ph and Ph-Ph coupling.

It should be noted the Ph–CH\(_3\) and Ph-Ph bond energies are 11.4 kcal/mol\(^{19b}\) and 26 kcal/mol stronger\(^{9c}\) than the H\(_3\)C–CH\(_3\) bond energy (90.4 kcal/mol).\(^{19b}\) Thus, if the Mt–CH\(_3\) and Mt-Ph bond energies were approximately the same, this would lead to a larger driving force for reductive elimination of \( sp^2 \) species. Evans \textit{et al.} have made a thermochemical estimate for the Pt-Ph bond energy of 63.1\(^{33}\) that is 7 kcal/mol stronger than our calculated Pt–CH\(_3\) intrinsic bond energy. This value for the bond energy is, however, strongly dependent on their estimated Pt-Cl bond energy in PtCl\(_2\)(PPh\(_3\))\(_2\) [which was assumed to be the same as the Pt-Cl bond energy in PtCl\(_2\)], which could easily cause errors of ~10 kcal/mol. Therefore, there currently are insufficient data to determine
whether the diphenyl and methylphenyl Pt complexes are less stable thermodynamically than the dimethyl complex.

Thermochemical data\textsuperscript{34} from ThR\textsubscript{2}(Cp\textsuperscript{*})\textsubscript{2} complexes demonstrate that Th-Ph bond energies are 13 kcal/mol stronger than Th-CH\textsubscript{3} bond energies. Therefore it does appear that diphenyl and methylphenyl complexes have approximately the same enthalpy for reductive elimination as dimethyl complexes.

Either of the above interpretations for the increased lability of sp\textsuperscript{2} versus sp\textsuperscript{3} carbons would suggest that alkynyl groups will reductively eliminate faster than phenyl or vinyl groups. Indeed, Ph-C≡C-C≡C-Ph has been indentified in the decomposition products of cis-Pt(C≡C-Ph)\textsubscript{2}L\textsubscript{2}.\textsuperscript{35} A more careful analysis of the decomposition of dialkynyl complexes should help establish the trend of sp hybridization versus rate of reductive elimination.

C. Heat of Formation Of Pt(II) and Pd(II) salts

We have found that the difference in enthalpies [\(\Delta(H)\)] for reductive elimination from the corresponding Pt(II) and Pd(II) compounds is always within 5 kcal/mol of the difference in the s\textsuperscript{1}d\textsuperscript{9} \rightarrow d\textsuperscript{10} splittings for these metals (33 kcal/mol).\textsuperscript{18} Unfortunately, there are no reliable \(\DeltaH^\circ\textsuperscript{0}\)'s for Pt and Pd complexes available in the literature to provide a test of this theoretical trend. However \(\DeltaH^\circ\textsuperscript{0}\) for various Pt(II) and Pd(II) salts are available.\textsuperscript{36} Since Pt and Pd have the same covalent radii and electronegativeties,\textsuperscript{16} we can assume that the lattice energies for the corresponding PtX\textsubscript{2} and PdX\textsubscript{2} salts are the same. Therefore the \(\Delta(H)\) for the reaction Mt(\textsuperscript{13}S)\textsubscript{6} + X\textsubscript{2(g)} \rightarrow MtX\textsubscript{2(g)} should also be approximately equal to 33 kcal/mol. Indeed, as indicated in Table VI, the experimental \(\Delta(H)\) are 33 ± 3 kcal/mol, in excellent agreement with our prediction.
The alternative interpretation based on an ionic model for Mt-C bonds would suggest that the $\Delta(\Delta H)$ is equal to the difference in the sums of the first and second ionization potentials for Pt and Pd. This would predict a $\Delta(\Delta H)$ of 15 kcal/mol instead of 33 kcal/mol. Therefore, our covalent bonding model is far more consistent with the experimentally observed $\Delta H^\circ$ for these salts.

D. Comparison With Other Theoretical Studies

Hoffmann et al. analyzed Extended Hückel (EH) calculations on reductive elimination from complexes of the Ni triad to obtain five conclusions concerning these reactions. The first three of which are relevant to this work since they concern reductive elimination from dimethyl bisphosphine complexes.

1. "The better the $\sigma$-donating capability of the leaving groups, the more readily the elimination reaction proceeds.

2. "Stronger donor ligands that are trans to the leaving groups give a higher barrier for the elimination reaction.

3. "Increased stability of the MA$_2$ b$_2$ orbital [where A indicates modified hydrogens used to model phosphines] facilitates the reductive elimination of D$_2$ [where D is a modified hydrogen used to model CH$_3$ groups]. A lower MA$_2$ b$_2$ energy will be given by a lower metal d orbital energy."

Since we find essentially covalent bonding in Pt and Pd complexes, a better $\sigma$-donor leaving group is equivalent to a leaving group with lower electronegativity. Leaving groups (R) with higher electronegativities would help stabilize the s orbital of the metal atom by increasing the amount of s character in the metal sd hybrid orbital used in the M-R
bond. This will stabilize the $s^1d^9$ configuration of the metal atom and reduce the driving force for reductive elimination. This is in agreement with Hoffmann's first conclusion.

We have not made systematic variations in the ligands; however, the trends in going from no ligands (a very weak donor!) to two $PH_3$ groups are quite suggestive. We find that (due to the overlap between the phosphine lone pairs and the metal s orbital) the sd hybrid orbital used in the M-R bond has to build in p character to stay orthogonal to phosphine lone pairs. This increased p character makes the intrinsic M-R bond strengths slightly stronger, as expected from simple valence bond calculations. The $\sigma$-donating ability of substituted phosphine ligands is directly related to the overlap between the ligand lone pair and metal s orbital. The stronger the donor, the larger the overlap. The larger overlap will lead to stronger M-R bonds which may cause the barriers for reductive elimination to be higher. Therefore, our results are also consistent with the second conclusion of Hoffmann.

However, we believe that Hoffmann's third conclusion, although reasonable, does not present the complete picture. We find that the important issue here is the relative energy of the $s^1d^9$ and $d^{10}$ configurations (VB language) or in MO language the relative energy of the valence s and d orbitals of the metal atom and not just the d orbital energy. The $d^{10}$ configuration is stabilized relative to $s^1d^9$ by destabilizing the the s orbital relative to the d orbital. Stabilization of the $d^{10}$ configuration leads to larger driving forces and lower barriers for reductive elimination. We have shown in an earlier paper that reductive coupling of C-C bonds from PdMe$_2$ is favored over PtMe$_2$, both kinetically and energetically. This dramatic difference arises because relative to Pt, Pd has a 33 kcal/mol
bias for the \( d^{10} \) state. This effect is much more dramatic than the other two and should dominate the stability of the these complexes.

Related trends were also observed in the CNDO calculations of Gritsenko \textit{et al.}\(^{4)}\) where the stability of \( \text{MH}_2(\text{PH}_3)_2 \) complexes (\( \text{Mt} = \text{Pd}, \text{Pt} \)) was correlated with the \( \text{Mt} \) s character of the wavefunction.

Other ab initio theoretical calculations involving square planar complexes of the Ni triad include studies of \( \text{NiMe}_2(\text{H}_2\text{O})_2 \) by Åkermark \textit{et al.}\(^{4e}\) and \( \text{PdH}_2(\text{H}_2\text{O})_2 \) by Siegbahn \textit{et al.}\(^{5e}\). In both of these studies, \( \text{H}_2\text{O} \) was used as a model ligand. Åkermark \textit{et al.}\(^{4e}\) found little change in the \( d \) orbital occupations upon addition of \( \text{H}_2\text{O} \) ligands, and Siegbahn actually found a small stabilization (\( \sim 5 \text{ kcal/mol} \))\(^{38}\) of the \( s^1d^9 \) singlet versus the \( d^{10} \) singlet of \( \text{Pd}(\text{H}_2\text{O})_2 \) relative to the atomic state splittings of Pd. The differences between these previous studies and ours probably results from their use of \( \text{H}_2\text{O} \) ligands rather than \( \text{PH}_3 \). The lone pairs of \( \text{H}_2\text{O} \) are much smaller than the lone pair of \( \text{PH}_3 \). The overlap between the lone pairs of \( \text{H}_2\text{O} \) and the Pd 5s orbital is probably much smaller than for phosphine lone pairs. This would lead to a smaller destabilization of the \( s \) orbital, favoring the \( s^1d^9 \) configuration over \( d^{10} \) (Pd and Pt prefer "softer" ligands such as \( \text{PR}_3 \) over \( \text{H}_2\text{O} \)). The relevant experiments all involve complexes with phosphine ligands, and hence our studies using phosphines are more pertinent for understanding the observed trends in C-C coupling.
IV. Calculational Details

A. Basis Sets and Effective Potentials

The basis sets and relativistic effective potentials used in this study for Pd and Pt are those of Hay et al.\textsuperscript{4b} The basis on carbon is the Dunning double zeta contraction of the Huzinaga (9s5p) basis.\textsuperscript{39} The effective potential for phosphorus is the SHC potential of Rappé et al.\textsuperscript{40} The SHC basis for phosphorus atom\textsuperscript{40} was contracted to a minimum basis set using atomic calculations. Three different basis sets were used on the hydrogen atoms depending on their chemical environment. For hydrogen atoms bound to phosphorus, we used a minimum basis set contraction of the Huzinaga four-gaussian hydrogen basis (no scaling).\textsuperscript{41} Methyl protons were described using a double zeta contraction of the Huzinaga four-gaussian basis scaled by a factor of 1.2.\textsuperscript{39} The active hydrogen bound to the metal atoms in the Pt(H)(Me)(PH\textsubscript{3})\textsubscript{2} and Pt(H)\textsubscript{2}(PH\textsubscript{3})\textsubscript{2} complexes was treated with a triple zeta contraction of the Huzinaga six-gaussian basis.\textsuperscript{41} This was necessary to allow the hydrogen to adjust for optimum bonding to the metal atom in the reactant and optimum bonding to the methyl group or H atom in the products. The chlorine potential was the SHC potential of Rappé et al.\textsuperscript{40} and the double zeta contraction of the SHC basis\textsuperscript{40} was used.

The effective potentials for P, Cl, Pt, and Pd are expected to provide ab initio quality descriptions for these atoms. Good measures for the quality of description for Pd and Pt are the atomic state splittings as indicated in figure 11. For highly accurate calculations, polarization functions (p's on H, d's on C, P and Cl, f's on Pt or Pd) are needed. This will lead to stronger intrinsic bond energies but will probably have little effect on the $\Delta E$ for oxidative addition/reductive elimination reactions.
(since bonds of reactant and product are affected similarly). The major factor in understanding these reactions is that the $s^1d^8-d^{10}$ splitting of the metal atoms be accurately described. Although the level of basis set can certainly be improved, it should be quite adequate for the purposes here, namely, the conceptual description of the differences between Pt(II), Pt(IV), and Pd(II) complexes.

B. Geometries

All geometries of the various complexes were fully optimized at the HF level using analytic energy gradients and the Newton-Raphson procedure. For the calculations on the triplet states of ML$_2$ and MCl$_2$L$_2$, the geometries were frozen at the geometry of the fragment in the corresponding MR$_2$L$_2$ or MR$_2$Cl$_2$L$_2$ complex. This was done so that geometric relaxation energy would not be included in calculating intrinsic bond energies.

C. Wavefunctions

All energetics reported here involve the GVB description of electron correlation for the important valence electrons. For an electron pair that would be described as doubly-occupied in HF theory, the GVB description would allow two orbitals each optimized self-consistently with all other orbitals of the molecules,

$$\psi^{HF}(1,2) = \varphi(1)\varphi(2)(\alpha\beta - \beta\alpha) \rightarrow$$

$$\psi^{GVB}(1,2) = [\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)](\alpha\beta - \beta\alpha).$$

When there are additional electron pairs, each may be correlated as in (41), so that the doubly-occupied orbitals $\varphi_1, \varphi_2, \cdots$ of an HF wavefunction become singly-occupied orbitals [as in (41)], $\varphi_{1a}, \varphi_{1b}, \varphi_{2a}, \varphi_{2b}$ of the GVB wavefunction. Although for HF wavefunctions the doubly-occupied
orbitals can generally be taken as either delocalized (canonical) or localized, the GVB orbitals are uniquely determined and are generally localized (reminiscent of simple valence bond theory). The general form of a GVB wavefunction is

$$\alpha[(\varphi_{1a}\varphi_{1b}\varphi_{2a}\cdots)\chi]$$  \hspace{1cm} (42)

where $$\chi$$ is an appropriate optimized spin function for $$N$$ electrons. However, in calculating the GVB orbitals, it is generally convenient to choose $$\chi$$ as the simple valence bond function (perfect pairing)

$$\chi^{\text{VB}} = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \cdots$$  \hspace{1cm} (43)

In this case the orbitals for different electron pairs are taken as orthogonal, and the resulting orbitals are denoted as GVB-PP to indicate the restricted form of the wavefunction. If five pairs of electrons are so correlated (using ten orbitals), the wavefunction is denoted as GVB-PP(5/10); however, other orbitals of the wavefunction are understood to be calculated self-consistently. (This wavefunction would involve $$2^5 = 32$$ different orbital configurations.) Such wavefunctions quite accurately describe systems where one valence bond structure is adequate (no resonance); however, for transition metal systems, spin couplings other than (43) are often important. These spin coupling effects are usually accurately described using the GVB-PP orbitals but allowing the two electrons of each orbital pair to be either in different orbitals [as in (41)] or in the same orbital [e.g., $$\varphi_a(1)\varphi_a(2)$$]. Allowing a similar description for all correlated pairs leads to the GVB-RCI wavefunction. Since there are three orbital products for each pair of electrons, the GVB-RCI(5/10) wavefunction has $$3^5 = 243$$ orbital products. In addition to an optimized spin coupling, the RCI wavefunction includes important electron correla-
tion effects in which two electrons in one bond pair can respond instantly to the motions of two electrons in another bond pair (interpair correlation). The orbitals of the GVB-RCI wavefunction can be solved self-consistently; however, it is generally adequate to use the orbitals of the GVB-PP wavefunction, and we have found this to be the case for complexes of the type studied in this paper. For cases where resonance of simple valence bond structures would be important, it is often essential to allow readjustments in those bond pairs that would change in the resonance. Thus, for reductive C-C coupling, the two localized M-C pairs change into a C-C bond pair and a metal d pair as the bond is broken, and resonance between these configurations is important. In this case we refine the GVB-RCI(2/4) description of these two pairs by using the GVB-CI(2/4) description, where all four electrons are allowed to occupy all four orbitals in any way (leading to 19 orbital products).

We find (see Figure 11) for Ni, Pd, and Pt that the GVB description (which uses ten optimized orbital for all states) leads to a rather accurate description of the relative energies for the d^{10}, s^1d^9, and s^2d^8 configurations and is particularly accurate for s^1d^9 versus d^{10}, the states relevant for this paper. For the s^2d^8 states the s^2 pair was polarized in the ±Z directions and d_{x^2} and the d_{xy} were singly occupied.

For the various M(R_2)(R_2) complexes, it is necessary to correlate not only the ten metal valence electrons but also the additional electrons involved in the covalent M-R_1 and M-R_2 bonds. Thus, a total of 12 electrons or six electron pairs must be correlated. Consequently, we first carried out GVB-PP(6/12) calculations using 12 orbitals to correlate the motions of these six pairs (12 electrons). (All other orbitals are doubly-occupied but are solved self-consistently.) In order to include the spin-
coupling, interpair correlation, and resonance effects\textsuperscript{2a,c}, the energetics reported here were determined at the GVB-CI(2/4)\times RCI(4/8) level.

In previous studies of the reaction path for reductive coupling, the necessity for simultaneous description of both the reactant (s\textsuperscript{1}d\textsuperscript{9}) and the product (d\textsuperscript{10}) resonance structures in the transition state region required use of three orbitals (rather than two) for each of the two bond pairs that change during the reaction\textsuperscript{2}. Thus, rather than GVB-PP(2/4), these two electron pairs were described with GVB-PP(2/6). In order to allow a full description of resonance effects in the transition state, all occupations of these six orbitals were allowed for all four electrons, denoted as GVB-CI(2/6). The other four pairs of electrons were correlated as usual, leading to a composite wavefunction of the form GVB-CI(2/6)\times RCI(4/8). We also optimized the orbitals at this level. In the current study, the main interest is in overall energy differences between products and reactants, where this resonance is not so important. Consequently, we use only two orbitals for these bond pairs, and the orbitals were optimized at the GVB-PP level. However, as in the previous studies, we carry out a full CI among the (four) orbitals involving those two bond pairs [CI(2/4)]. Thus the wavefunction used in these studies is GVB-CI(2/4)\times RCI(4/8).

Acknowledgments: This work was supported in part by a grant from the National Science Foundation (No. CHE83-18041). One of the authors (J.J.L.) wishes to acknowledge financial support in the form of fellowships from Exxon and ARCO.
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(9) (a) PtEt₂(PEt₃)₂ is known to β-hydride eliminate to give ethylene $(\Delta H^{\circ}_{298} = 12.5 \text{ kcal/mol}, S_{298} = 52.4 \text{ e.u.})$ and ethane $(\Delta H^{\circ}_{298} = -20.2 \text{ kcal/mol}, S_{298} = 54.9 \text{ e.u.})$ rather than to reductively eliminate to give n-butane $(\Delta H^{\circ}_{298} = -30.2 \text{ kcal/mol}, S_{298} = 74.1 \text{ e.u.})$ even though n-propane is the thermodynamically favored product $(\Delta H_{298} = -22.5 \text{ kcal/mol}, \Delta S_{298} = -33.2 \text{ e.u., } \Delta G_{298} = -12.5 \text{ kcal/mol for } C_2H_4 + C_2H_6 + n-C_4H_{10}).$ The $\Delta H^{\circ}_{298}$ and $S^{\circ}_{298}$ were taken from ref 9b.


(b) ibid. 1976, 1310-1314;
(c) ibid. 1977, 1892-1897.


(19) The $D_{298}^{\text{HH}}$ used in these calculations are $D_{298}^{\text{HH}}(\text{H-H}) = 104.2$ kcal/mol $D_{298}^{\text{HH}}(\text{H-CH}_3) = 105.1$ kcal/mol and $D_{298}^{\text{HH}}(\text{H}_3\text{C-CH}_3) = 90.4$ kcal/mol. These bond energies were derived from spectroscopic measurements of $\text{H}_2$ and the reported $D_{298}^{\text{HH}}$ for $\text{H}_3\text{C-CH}_3$ and $\text{H-CH}_3$.
(20) $D_{298}^{sp}$ [cyclopropyl-H] = 106.3 kcal/mol$^{16b}$; $D_{298}^{sp}$ [H-CH(CH$_3$)$_2$] = 95.1 kcal/mol.$^{16b}$


(22) $D_{298}$ [H$_2$C=CH$_2$] = 172.2 ± 2.07 kcal/mol and $D_{298}$ [F$_2$C=CF$_2$] = 69.3 ± 2.7 were derived from the following enthalpies:

$\Delta H_f$(C$_2$F$_4$) = -157.7 ± 0.7 kcal/mol and $\Delta H_f$(C$_2$H$_4$) = 12.54 ± 0.07 kcal/mol [see Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables," 2nd ed.; National Bureau of Standards: Washington, DC, June 1971; NSRDS-NBS 37].


(37) The last two conclusions concern the three-coordinate intermediates resulting from loss of phosphine from the square planar complexes.

(38) This stabilization energy was derived from the results of Siegbahn *et al.* by summing the energy needed to bend the O-Pd-O angle in Pd(OH₂)₂ from its equilibrium value of 180° to 90° (15 kcal/mol) and the diabatic d¹⁰ → s¹d⁹ singlet splitting for Pd(OH₂)₂ (20
kcal/mol), at a 90° O-Pd-O angle to give an adiabatic splitting of 35 kcal/mol. This splitting is 5 kcal/mol smaller than their calculated $d^{10} \rightarrow s^1d^9$ splitting for Pd atom of 40 kcal/mol.


(42) All of the geometry optimizations were obtained by using an analytic gradient program (GVBGRAD). This program was based on subroutines from (a) the GVB2P5 program [Bobrowicz, F. W.; Goddard III, W. A. In "Modern Theoretical Chemistry: Methods of Electronic Structure Theory," Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4, pp 79-127] to evaluate density matrices for restricted HF and GVB-PP wavefunctions, (b) the HONDO program [Dupuis, M.; King, H. F. J. Chem. Phys. 1978, 68, 3998-4004] to calculate derivatives of the ab initio terms in the energy expression, and (c) routines from the GAUSS 80 program [Binkely, J. W.; Whitesides, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. "Gauss 80," Department of Chemistry, Carnegie-Mellon University: Pittsburgh, PA, 1980] to calculate the effective potential terms of the derivative. To determine the step size taken each iteration, we used a relatively simple Newton-Raphson technique in which the second derivative matrix is updated after every gradient calculation (except for the starting geometry) [Low, J. J.; Goddard III, W. A.,
manuscript in preparation].
Table 1. Mulliken Populations for the GVB Bond Pairs of $M_1(M_2)$. For each bond there are two listings, the top one is the metal-like GVB orbital and the bottom one is the ligand-like orbital.

<table>
<thead>
<tr>
<th></th>
<th>Populations in GVB Bond Orbitals</th>
<th>M-CH$_3$</th>
<th>M-H or M-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M-CH$_3$</td>
<td>M-H or M-Cl</td>
</tr>
<tr>
<td>1</td>
<td>$\text{Pt(CH$_3)$_2(PH$_3$_2)}$</td>
<td>$s^{0.23},p^{0.10},d^{0.49},C^{0.17}$</td>
<td>($sp$)$^{0.03},d^{0.13},C^{0.18},p^{0.71}$</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Pd(CH$_3)$_2(PH$_3$_2)}$</td>
<td>$s^{0.17},p^{0.07},d^{0.48},C^{0.24}$</td>
<td>($sp$)$^{0.02},d^{0.15},C^{0.18},p^{0.56}$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Pt(CH$_3$_2(Cl)$_2(PH$_3$_2}$}</td>
<td>$s^{0.17},p^{0.07},d^{0.68},C^{0.04}$</td>
<td>$s^{0.18},p^{0.25},d^{0.21},C^{0.37}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($sp$)$^{0.00},d^{0.18},C^{0.11},p^{0.67}$</td>
<td>($sp$)$^{0.06},d^{0.07},C^{0.03},p^{0.43}$</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Pt(Cl)$_2(PH$_3$_2}$}</td>
<td>$s^{0.21},p^{0.14},d^{0.57},C^{0.27}$</td>
<td>($sp$)$^{0.03},d^{0.06},C^{0.01},p^{0.05}$</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Pt(H)(CH$_3$_2(PH$_3$_2}$}</td>
<td>$s^{0.24},p^{0.11},d^{0.46},C^{0.15}$</td>
<td>$s^{0.27},p^{0.13},d^{0.51},H^{0.09}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($sp$)$^{0.04},d^{0.15},C^{0.18},p^{0.72}$</td>
<td>($sp$)$^{0.02},d^{0.16},C^{0.01},P^{0.85}$</td>
</tr>
<tr>
<td></td>
<td>$\text{Pt(H)$_2$}$</td>
<td>$s^{0.28},p^{0.02},d^{0.63},H^{0.07}$</td>
<td>($sp$)$^{0.02},d^{0.16},H^{0.80}$</td>
</tr>
<tr>
<td></td>
<td>$\text{Pt(H)(CH$_3$_2}$</td>
<td>$s^{0.26},p^{0.01},d^{0.54},C^{0.09}$</td>
<td>$s^{0.30},p^{0.02},d^{0.60},H^{0.08}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($sp$)$^{0.01},d^{0.16},C^{0.12},p^{0.70}$</td>
<td>($sp$)$^{0.01},d^{0.16},H^{0.80}$</td>
</tr>
<tr>
<td></td>
<td>$\text{Pt(CH$_3$_2}$</td>
<td>$s^{0.27},p^{0.01},d^{0.62},C^{0.10}$</td>
<td>($sp$)$^{0.00},d^{0.15},C^{0.14},p^{0.70}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($sp$)$^{0.00},d^{0.20},C^{0.28},p^{0.52}$</td>
<td>($sp$)$^{0.00},d^{0.20},C^{0.28},p^{0.52}$</td>
</tr>
</tbody>
</table>

$^a$ Reference 2c.
Table II. Mulliken Populations for Pt and Pd bisphosphine complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M sp</th>
<th>M d</th>
<th>CH₃</th>
<th>H</th>
<th>PH₃</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(CH₃)₂(PH₃)₂</td>
<td>0.73</td>
<td>8.89</td>
<td>9.13</td>
<td>8.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(CH₃)₂(PH₃)₂</td>
<td>0.33</td>
<td>9.09</td>
<td>9.20</td>
<td>8.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(CH₃)₂(Cl)₂(PH₃)₂</td>
<td>1.12</td>
<td>8.57</td>
<td>8.86</td>
<td>8.02</td>
<td>7.28</td>
<td></td>
</tr>
<tr>
<td>Pt(Cl)₂(PH₃)₂</td>
<td>0.80</td>
<td>8.83</td>
<td>7.92</td>
<td>7.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(H)(CH₃)(PH₃)₂</td>
<td>0.85</td>
<td>8.99</td>
<td>9.12</td>
<td>0.93</td>
<td>8.05(^a)</td>
<td></td>
</tr>
<tr>
<td>Pt(H)₂(PH₃)₂</td>
<td>0.96</td>
<td>9.10</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(PH₃)₂</td>
<td>0.38</td>
<td>9.51</td>
<td></td>
<td>8.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(PH₃)₂</td>
<td>0.19</td>
<td>9.83</td>
<td></td>
<td>8.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(H)₂(^b)</td>
<td>1.16</td>
<td>9.15</td>
<td></td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(H)(CH₃)₂(^b)</td>
<td>1.05</td>
<td>9.03</td>
<td>9.04</td>
<td>0.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(CH₃)₂(^b)</td>
<td>0.97</td>
<td>8.91</td>
<td>9.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(CH₃)₂(^b)</td>
<td>0.60</td>
<td>9.15</td>
<td>9.13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) This is the average occupation of the PH₃ groups in this complex. The PH₃ group trans to CH₃ has 8.04 e⁻ and the PH₃ group trans to H has 8.06 e⁻.

\(^b\) Reference 2c.
### Table III: Calculated and predicted energetics for reductive coupling processes.

All energies are in kcal/mol. $\Delta H_{298}$ is the reaction enthalpy at 298 K, which is obtained from the calculated energy difference ($\Delta E$) by adding in estimated zero point energy and temperature corrections. $\Delta H^\ddagger$ is the calculated energy barrier for reductive coupling and $\Delta H^\ddagger$ is the predicted activation barrier at 298 K. Parentheses indicate the level of approximation in obtaining an estimated value. Each level of parenthesis probably adds an additional uncertainty of ± 5 kcal/mol.

<table>
<thead>
<tr>
<th></th>
<th>$M(H)_2 \rightarrow M + H_2$</th>
<th>$M(H)(CH_3) \rightarrow M + CH_4$</th>
<th>$M(CH_3)_2 \rightarrow M + C_2H_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E$</td>
<td>$\Delta H_{298}$</td>
<td>$\Delta H^\ddagger$</td>
</tr>
<tr>
<td>a) $M = Pt$</td>
<td>33.8</td>
<td>33.3</td>
<td>-- a)</td>
</tr>
<tr>
<td>$M = Pt(PH_3)_3$</td>
<td>15.9</td>
<td>12.3</td>
<td>18.1</td>
</tr>
<tr>
<td>$PH_3$ destabilization</td>
<td>17.7</td>
<td>20.9</td>
<td></td>
</tr>
<tr>
<td>b) $M = Pd$</td>
<td>-3.6</td>
<td>-4.0</td>
<td>1.6</td>
</tr>
<tr>
<td>$M = Pd(PH_3)_3$</td>
<td>(-21.5)</td>
<td>(-25.1)</td>
<td>((7.4)b)</td>
</tr>
<tr>
<td>$PH_3$ destabilization</td>
<td>(17.9)</td>
<td>(21.1)</td>
<td>((8.0))</td>
</tr>
<tr>
<td>c) $M = Pt(Cl)(PH_3)_3$</td>
<td>(7.7)</td>
<td>(3.5)</td>
<td>(17.4)</td>
</tr>
<tr>
<td>Cl destabilization</td>
<td>(9.2)</td>
<td>(8.1)</td>
<td>((14.1))</td>
</tr>
<tr>
<td>d) $M = Pd(Cl)(PH_3)_3$</td>
<td>((-17.1)c)</td>
<td>((-15.5)b)</td>
<td>(((15.9))</td>
</tr>
<tr>
<td>Cl destabilization</td>
<td>((18.2))</td>
<td>((18.1))</td>
<td></td>
</tr>
</tbody>
</table>

**a)** No barrier is found for oxidative addition.

**b)** No barrier is found for reductive coupling. The negative values indicate the estimated energy (relative to the product) at the geometry corresponding to the transition state for $M(H)(H) = M + H_2$.

**c)** Based on correcting the $M = Pt(Cl)(PH_3)_3$ case using $\Delta E = 45.4$ kcal/mol [$Pd(d^9\rightarrow d^8) = 16.2$ kcal/mol and $Pd(d^9\rightarrow d^8) = 63.0$ kcal/mol].
Table IV. Average bond energies for $M(R)_2$ complexes (kcal/mol).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Excitation Energy</th>
<th>$D_{200}$</th>
<th>$D_I$</th>
<th>$D_{200}$</th>
<th>$D_I$</th>
<th>$D_{200}$ and $D_I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M = $ Pt</td>
<td>-12.3</td>
<td>68.7</td>
<td>62.6</td>
<td>53.0</td>
<td>46.9</td>
<td>15.7</td>
</tr>
<tr>
<td>$M = $ Pd</td>
<td>+19.6</td>
<td>50.1</td>
<td>59.9</td>
<td>35.8</td>
<td>45.7</td>
<td>14.2</td>
</tr>
<tr>
<td>$M = $ Pt(PH$_3$)$_2$</td>
<td>+32.1$^a$</td>
<td>58.3</td>
<td>74.4</td>
<td>39.6</td>
<td>55.7</td>
<td>18.7</td>
</tr>
<tr>
<td>$M = $ Pd(PH$_3$)$_2$</td>
<td>+57.2$^a$</td>
<td>39.6</td>
<td>68.2</td>
<td>22.3</td>
<td>50.9</td>
<td>17.3</td>
</tr>
<tr>
<td>$M = $ Pt(Cl)$_2$(PH$_3$)$_2$</td>
<td>38.6$^a$</td>
<td>(53.4)</td>
<td>(72.7)</td>
<td>31.7</td>
<td>51.0</td>
<td>(21.7)</td>
</tr>
<tr>
<td>$M = $ Pd(Cl)$_2$(PH$_3$)$_2$</td>
<td>(64.0)$^b$</td>
<td>((33.3))</td>
<td>((75.3))</td>
<td>(10.0)</td>
<td>(52.0)</td>
<td>((23.3))</td>
</tr>
</tbody>
</table>

$^a$ Based on the geometry of the $M(CH_3)_2$ complex.

$^b$ Based on $\Delta E = 38.6$ kcal for Pt complex plus the differential $d^8s^1$ to $d^8s^2$ energy (45.4 kcal).
Table V. Geometric parameters around metal atom in Pt and Pd complexes (all distances are in Å and all angles are in degrees).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>M-P distance</th>
<th>M-C distance</th>
<th>misc. distance</th>
<th>P-M-P angle</th>
<th>C-M-C angle</th>
<th>misc. angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pt(CH₃)₂(PH₃)₂</td>
<td>2.46</td>
<td>2.06</td>
<td>-</td>
<td>101</td>
<td>89</td>
<td>-</td>
</tr>
<tr>
<td>2 Pd(CH₃)₂(PH₃)₂</td>
<td>2.50</td>
<td>2.02</td>
<td>-</td>
<td>98</td>
<td>81</td>
<td>-</td>
</tr>
<tr>
<td>3 PtCl₆(CH₃)₂(PH₃)₂</td>
<td>2.44</td>
<td>2.03</td>
<td>M-Cl(2.38)</td>
<td>95</td>
<td>90</td>
<td>Cl-M-Cl(177)</td>
</tr>
<tr>
<td>4 PtCl₆(PH₃)₂</td>
<td>2.44</td>
<td>-</td>
<td>M-Cl(2.35)</td>
<td>102</td>
<td>-</td>
<td>Cl-M-Cl(97)</td>
</tr>
<tr>
<td>5 Pt(H)(CH₃)(PH₃)₂</td>
<td>2.46</td>
<td>2.06</td>
<td>M-H(1.50)</td>
<td>101</td>
<td>-</td>
<td>H-Pt-C(84)</td>
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<tr>
<td>6 PtH₆(PH₃)₂</td>
<td>2.45</td>
<td>-</td>
<td>M-H(1.50)</td>
<td>100</td>
<td>-</td>
<td>H-Pt-H(79)</td>
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<tr>
<td>7 Pt(PH₃)₂</td>
<td>2.32</td>
<td>-</td>
<td>-</td>
<td>180</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8 Pd(PH₃)₂</td>
<td>2.41</td>
<td>-</td>
<td>-</td>
<td>180</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt(CH₃)₂</td>
<td>-</td>
<td>1.97</td>
<td>-</td>
<td>98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt(H)(CH₃)²</td>
<td>-</td>
<td>1.96</td>
<td>M-H(1.48)</td>
<td>-</td>
<td>-</td>
<td>H-Pt-C(98)</td>
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<td>-</td>
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a) This geometry was not optimized but was estimated from the geometries (1) and (6). The geometries of the Pt(CH₃)(PH₃) fragment were taken frozen at the geometry of (1), and the C-Pt-H angle was chosen to be the average of the C-Pt-C angle of (1) and the H-Pt-H angle of (6).

b) Reference 2a.

c) Reference 2c.
Table VI. Enthalpies (kcal/mol at 298°K) for Pt(II) and Pd(II) salts. All $\Delta H_f$ are from ref 36, except as noted.

<table>
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<tr>
<th>Compound</th>
<th>$\Delta H_f^{0}$[PtX$_2$(s)]</th>
<th>$\Delta H_f^{0}$[PdX$_2$(s)]</th>
<th>$\Delta H_f^{0}$[Pt$_2$(g) + X$_2$(g) → PtX$_2$(s)]</th>
<th>$\Delta H_f^{0}$[Pd$_2$(g) + X$_2$(g) → PdX$_2$(s)]</th>
<th>$\Delta (\Delta H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt(OH)$_2$  a)</td>
<td>-84</td>
<td>-88</td>
<td>-184  a)</td>
<td>-148</td>
<td>36</td>
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<td>MtCl$_2$</td>
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<td>MtBr$_2$</td>
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<td>-148</td>
<td>-118</td>
<td>30</td>
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b) $\Delta H_{sub}$(Pt) = 121.6 kcal/mol at 25°C, 36 $\Delta E(3D - ^1S) = 11.0$ kcal/mol; 18 consequently, $\Delta H_f^0([^1S]Pt) = 121.6 + 11.0 = 132.6$ kcal/mol.

c) $\Delta H_{sub}$(Pd) = 92.96 kcal/mol. 36 The ground state of Pd is $^1S$; therefore, $\Delta H_{sub}$(Pd) = $\Delta H_f^0[Pd_g(^1S)]$. 
Supplementary Material.  -140-

The following seven tables contain the cartesian coordinates of the optimized geometries for the molecules studied in this paper. The eighth table contains the internal coordinates of the phosphine and methyl groups for the geometries tabulated in tables SI-SVII.
Table S.1. Cartesian Coordinates for Pt(CH₃)₂(PH₃)₂ (Å)

<table>
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<th>Z</th>
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<th>Level of Wavefunction</th>
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<th>Total Energies at Dissociated Limit (hartrees)</th>
<th>ΔE (kcal/mol)</th>
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Table S.II. Cartesian Coordinates for Pd(CH₃)₂(PH₂)₂ (Å)

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Table S.III. Cartesian Coordinates for PtCl$_2$(CH$_3$)$_2$(PH$_3$)$_2$ (Å)

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<th>Total Energies at Dissociated Limit (hartrees)</th>
<th>ΔE (kcal/mol)</th>
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Table S.IV. Cartesian Coordinates for PtCl₂(PH₃)₂ (Å)

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Table S.V. Cartesian Coordinates for Pt(H)(CH₃)(PH₃)₂ (Å)

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<th>ΔE (kcal/mol)</th>
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Table S.VI. Cartesian Coordinates for Pt(PH$_3$)$_2$ (Å)

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Table S.VII. Cartesian Coordinates for Pd(PH₃)$_2$ (Å)

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Figure 1. The CVB orbitals for 1 [from the CVB(5/10)-PP wavefunction]. Nuclei in the plane are indicated by asterisks. Positive contours are solid, negative contours are dotted, and nodal lines are long dashes. The spacing between contours is 0.05 a.u. Analysis of each CVB orbital in terms of a Mulliken population is shown.
Figure 2. The GVB orbitals for the Pt-C bonds of 2.
Figure 3. The GVB orbitals for the Pt-C bonds of 3.
Figure 4. The GVB orbitals for the Pt-H and Pt-C bonds of 5.
Figure 5. The GVB orbitals for the Pt-Cl bond of 3.
Figure 6. The GVB orbitals for the Pt-Cl bond of 4.
Figure 7. The GVB orbitals for the $s^2$ pair of the $d^8s^2$ state of Pt.
Figure 8. Estimated energetics for R₁–R₂ reductive coupling of (PH₃)₂Mt(R₁)(R₂) complexes. All quantities are enthalpies at 298°K.
Figure 9. ORTEP plot of 1 and 2.
Figure 11. Atomic excitation energies for Ni, Pd, and Pt. All quantities in kcal/mol.
CHAPTER 4

Theoretical Studies of $\text{CH}_x$ and $\text{NH}_x$

Species Chemisorbed on Ni Clusters
I. Introduction

The chemisorption of small molecules on metal surfaces has been the subject of many experimental\textsuperscript{1} and theoretical\textsuperscript{2} studies. The low index surfaces of metals have been used to model many catalytic reactions including methanation\textsuperscript{3} and ammonia decomposition on metal surfaces.\textsuperscript{4} The problem with experimental studies is that critical intermediates are often very unstable and cannot be observed under typical experimental conditions. The advantage theory has is that a theorist can perform calculations on the various proposed intermediates and compare their relative energetics to see whether the proposed mechanism is reasonable or not.\textsuperscript{5} The problem that a theorist has is that the system to be modelled is very large, which forces him to make various approximations in his calculations. These approximations affect the results in various ways that should be accounted for when attempting to relate theory to experiment.

In this paper we examine theoretically cluster models for the various intermediates important for methanation and ammonia decomposition on Ni surfaces. We have used the one-electron modified effective potential (MEP) of Upton and Goddard (UG)\textsuperscript{6} to simulate the Ni atoms of the cluster. This approximation involves replacing the Ar core and 3d\textsuperscript{9} shell of Ni by the MEP. Only the Ni 4s electrons are treated explicitly. This method allows the use of large clusters (13-20 atoms) to model the metal surface for chemisorption. The method has been used with considerable success in modelling chemisorption of H, O, S, Cl,\textsuperscript{6} and CO\textsuperscript{7} on Ni surfaces.

We have used the four-coordinate site of the Ni\textsubscript{13} cluster (see Figure 1) to model chemisorption of small molecules on the Ni(100) surface. This site allows the singly-occupied orbitals of the radical to have the largest overlap with the conduction band orbitals. This should lead to radical
species forming the strongest bonds on high coordination sites. Carbon has been observed to bond to a similar site in various carbido carbonyl clusters\(^8\) (i.e., \(\text{Fe}_n\text{C(CO)}_{13}\)). Akylidyne have been observed to be coordinated to three metal atoms in various metal cluster compounds.\(^9\) Since such a site is not available on the Ni(100) cluster, methylidyne and carbon should both prefer the four-coordinate site. Methylene, on the other hand, has only been observed to bind to metal clusters at two-coordinate bridge sites.\(^10\) In this work we intend a first pass at the relative energetics for these chemisorbed intermediates. For these purposes the four-coordinate site of \(\text{Ni}_{13}\) is quite adequate. We have used the \(\text{Ni}_{14}\) (see figure 2) cluster to model chemisorption of closed shell molecules (i.e., \(\text{NH}_3\) and \(\text{CO}\)) where the bonding is dominated by lewis acid/base interactions. More quantitative results would require larger clusters and perhaps higher levels of theory. This work is intended to provide a qualitative understanding of the nature of the surface chemical bond and to help organize further theoretical study in this area.
II. Results

A. Qualitative Description of Bonding

The $^4T_{1g}$ ($1a_{1g}^2t_{1u}^6t_{2g}^4e_{g}^1$) excited state of the Ni$_{13}$ cluster was chosen to model the bulk for the four-coordinate site of Ni(100). This state is 5.6 kcal/mol above the $^2T_{1g}$ ($1a_{1g}^2t_{1u}^6t_{2g}^5$) ground state. This state was chosen because it had orbitals available for forming $\sigma$ and $\pi$ bonds to the various intermediates studied here. The $^2T_{1g}$ ground state only had a singly-occupied orbital of $\pi$ symmetry available for forming bonds. In the ground state of all the CH$_x$ and NH$_x$ complexes studied here, the Ni$_{13}$ cluster was in its $^4T_{1g}$ electronic state. (For more details about the low lying states of the Ni$_{13}$ cluster see Appendix A.) The $^1A_{1g}$ ground state of Ni$_{14}$ cluster$^7$ was chosen to model the bulk for the one-coordinate site of Ni(100). The calculated geometries, vibrational frequencies and energetics are shown in Table I.

The GVB orbitals for methylidyne (CH), methylene (CH$_2$), and methyl (CH$_3$) are shown in Figures 3-5. In general, the bonding of these species can be characterized as forming a high-overlap ionic $\sigma$-bond and low-overlap covalent $\pi$ bonds. The surface bonds for methylidyne, methylene, and methyl are best described as triple (1$\sigma$ and 2$\pi$), double (1$\sigma$ and 1$\pi$), and single (1$\sigma$) bonds, respectively. The carbon-surface $\pi$ bonds in these systems are quite strong. This causes the decomposition of chemisorbed CH$_x$ to chemisorbed CH$_{x-1}$ and chemisorbed H to be about 14 kcal/mol downhill for x=(2 and 3).

\[ \text{CH}_3(a) \rightarrow \text{CH}_2(a) + \text{H}(a) \quad \Delta H^\circ = -12.7 \text{ kcal/mol} \]

\[ \text{CH}_2(a) \rightarrow \text{CH}(a) + \text{H}(a) \quad \Delta H^\circ = -15.0 \text{ kcal/mol} \]
By assuming a C-H bond strength of 98 kcal/mol\textsuperscript{11} and a surface-H bond strength of 63 kcal/mol,\textsuperscript{12} we estimate a surface-carbon \pi bond strength of 49 kcal/mol. This is only 5 kcal/mol stronger than our calculated surface-carbon \sigma bond strength of 43.6 kcal/mol for chemisorbed methyl. The surface-carbon \pi bond strength is close to the difference in the C-H bond strength (98 kcal/mol) and half of the H-H bond strength (52.1 kcal/mol)\textsuperscript{13} which causes the dehydrogenation of chemisorbed methyl or methylene to give dihydrogen and chemisorbed methylene or methyldyne to be essentially isoenergetic processes.

\[
\text{CH}_3(\text{a}) \rightarrow \text{CH}_2(\text{a}) + \frac{1}{2}\text{H}_2(\text{g}) \quad \Delta H_f^0 = -1.2 \text{ kcal/mol}
\]

\[
\text{CH}_2(\text{a}) \rightarrow \text{CH}(\text{a}) + \frac{1}{2}\text{H}_2(\text{g}) \quad \Delta H_f^0 = -3.5 \text{ kcal/mol}
\]

Carbon atom bonds to the surface in a very different manner (see the GVB orbitals in Figure 6). The chemisorbed carbon atom is best described as a C\textsuperscript{−}, which has formed two covalent \pi bonds to the surface. An electron from the cluster has moved to the C 2p\textsubscript{z} orbital. This implies that the maximum number of bonds that a CH\textsubscript{x} species can form to the surface is three. When the last C-H bond is broken in chemisorbed methyldyne to yield chemisorbed carbon, the carbon electron involved in the C-H bond is not able to form another bond to the surface. Thus the chemisorbed carbon ends up having significant radical character. Therefore it is uphill energetically to dissociate methyldyne to carbon and hydrogen atoms on our clusters. This will have a significant impact on the surface chemistry of carbon, which will be discussed in the next section.
\[ \text{CH}(a) \rightarrow \text{C}(a) + \text{H}(a) \quad \Delta H_f^\circ = 25.7 \text{ kcal/mol} \]

\[ \text{CH}(a) \rightarrow \text{C}(a) + \frac{1}{2}\text{H}_2 \quad \Delta H_f^\circ = 37.2 \text{ kcal/mol} \]

The GVB orbitals for imidogen (NH), amidogen (NH$_2$), and ammonia (NH$_3$) are shown in Figures 7-9. In general, these species make \( \sigma \) bonds that can be characterized as donor-acceptor bonds and covalent \( \pi \) bonds. The bonds that imidogen, amidogen, and ammonia make to the surface are triple, double, and single bonds, respectively. Nitrogen atom (see GVB orbitals in Figure 10) forms a triple bond to the surface. The three bonds consist of an ionic \( \sigma \) bond and two covalent \( \pi \) bonds to the surface that are similar to the methyllidyne surface bonds.

Just like the CH$_x$ species, the NH$_x$ species also makes fairly strong \( \pi \) bonds to the surface. This causes the decomposition of NH$_x(a)$ to NH$_{x-1}(a)$ and H$_x(a)$ to be downhill by about 18 kcal/mol for x=(2 and 3). Assuming a N-H bond strength of 106 kcal/mol,$^{14}$ we can estimate a surface-N \( \pi \) bond energy of 61 kcal/mol.

\[ \text{NH}_3(a) \rightarrow \text{NH}_2(a) + \text{H}(a) \quad \Delta H_f^\circ = -17.1 \text{ kcal/mol} \]

\[ \text{NH}_2(a) \rightarrow \text{NH}(a) + \text{H}(a) \quad \Delta H_f^\circ = -18.7 \text{ kcal/mol} \]

When chemisorbed imidogen decomposes to chemisorbed nitrogen and hydrogen, the lewis acid/base surface-N bond and N-H bond are replaced by a surface-N ionic bond and surface-H bond. The difference between these two bond energies is apparently very close to difference in energy between a N-H (106 kcal/mol) and a surface-hydrogen bond (63
kcal/mol) which causes the decomposition of chemisorbed imidogen to chemisorbed nitrogen and hydrogen to be essentially isoenergetic.

\[ \text{NH}(a) \rightarrow \text{N}(a) + \text{H}(a) \quad \Delta H_f = -0.9 \text{ kcal/mol} \]

The bond that ammonia makes to the four-coordinate site of Ni_{13} is very weak (2.04 kcal/mol). In fact, when the zero point energy is added, it is unbound by 1.6 kcal/mol. Ammonia is bound by 10 kcal/mol to the one-coordinate site of the Ni_{14} cluster. This shows that the donor/acceptor bond of ammonia is stronger when bound to the one-coordinate site than to higher coordination sites. The lone pair of ammonia favors the on-top site because it can form a lewis acid/base bond to the metal center, without disrupting metal-metal bonding in the cluster. Even though the lone pair of ammonia would be stabilized by more metal centers at a higher coordination site through lewis acid/base interactons, it would also have higher overlap with the occupied orbitals of the conduction band (4s) electrons. We therefore believe that ammonia prefers sites where it is coordinated to only a single metal center.

We find that the surface-carbon and surface-nitrogen π bonds are very important in the nature of the surface chemical bond. In general, we find that these π bonds are slightly stronger than the corresponding σ bonds for CH\_x species. This is also true for NH\_x species, because we have found that these species prefer to bind oriented perpendicular to the surface where it can make a π bond and a lewis acid/base σ bond.
rather than to bend over where it can only make a $\sigma$ bond.

We find that oxygen atom binds to the surface by making an ionic $\sigma$ bond and a covalent $\pi$ bond (see figures 11 and 12). This state is very similar to the oxide state found on Ni$_{20}$ by UG.$^6$

**B. Quantitative Discussion**

The parameters calculated for chemisorbed species discussed above are shown in Table I. In general, in going from single to double to triple bonds, the bond energy increases. The calculated bond energies for the multiple surface bonds appear to be systematically high. The worst case is for the surface oxygen bond of 157 kcal/mol, which is much higher than the experimental estimates of 94-135 kcal/mol.$^{15}$ The calculated bond energy for H on Ni$_{13}$ (66 kcal/mol) is fortuitously close to the experimental value for hydrogen bound to Ni surfaces (63 kcal/mol).$^{12}$ If we examine the process
we calculate a $\Delta H^\circ$ for this reaction of -23.3 kcal/mol compared to experimental $\Delta H^\circ$ of -40.1 kcal/mol. This means that the calculated $D_0$ for the chemisorbed hydrogen is 16.8 kcal/mol too strong, assuming that the correlation error is the same for the surface H bond as it is for the H-H bond. This error can arise from either the small cluster size or the tendency of the MEP to have systematically large bond energies.\textsuperscript{16}

In order to account for this bias toward stronger bond strengths, we have used the error in the Ni-H bond to account for the errors made in carbon-surface and nitrogen-surface bonds. The procedure we have used is essentially an equibondedness approach,\textsuperscript{17} in which the total number of bonds and the number of bonds to the surface were held fixed (see Calculational Details). All of the bonds made through donor-acceptor bonds to the surface have been assumed to have no correlation error. This appears to be reasonable in light of the bond strength (10.9 kcal/mol) of NH$_3$ to Ni$_{14}$, which compares well to the experimental chemisorption energy of NH$_3$ to nickel surfaces (\textsim 12 kcal/mol)\textsuperscript{5}. The reactions used to calculate enthalpies of formation at 0ºK are shown in Table II. The enthalpies for any particular intermediate are predicted from the change in the calculated energies and from enthalpies known either from experiment (see Table III) or previous equibondedness reactions. We have used the experimental enthalpies of methane, ammonia, chemisorbed H and chemisorbed CO\textsuperscript{18} as references. The $\Delta H^\circ$ calculated in this manner along with experimental $\Delta H^\circ$ (see table III and IV) can then be used to calculate the corrected $D_0$ shown in Table I and to compare the relative enthalpies of various intermediates.
A good test of these energetics is to compare them to two simple reactions which are known to proceed on Ni surfaces.\textsuperscript{19} Our calculated enthalpy for the disproportionation reaction of CO (the Boudouard Reaction)\textsuperscript{19a}

\[ 2\text{CO} \rightarrow \text{C}(a) + \text{CO}_2 \quad \Delta H^o_f = -14.8 \text{ kcal/mol} \]

indicates that our carbon-surface bond strength is reasonable, but we calculate the reduction of chemisorbed oxygen\textsuperscript{19b}

\[ \text{H}_2 + \text{O}(a) \rightarrow \text{H}_2\text{O} \quad \Delta H^o_f = 35.2 \text{ kcal/mol} \]

to be uphill energetically, indicating that our corrected oxygen-surface bond strength is still too high.

The enthalpies of formation at 0° K for NH\textsubscript{x} intermediates are shown in Figure 13. The enthalpy changes for the steps shown in figure 13 are tabulated in table V. Chemisorbed imidogen is calculated to be the most stable NH\textsubscript{x} intermediate. Decomposition of ammonia has been observed to occur at low temperature (200° K) in an electron beam on Ni(111) surfaces\textsuperscript{20} and the decomposition product was tentatively assigned to chemisorbed imidogen by ultraviolet photoelectron spectroscopy. Ammonia also decomposes on Ni(110) at temperatures above 150° K to some unidentified NH\textsubscript{x} intermediate.\textsuperscript{21,22} Hütttinger and Kippers\textsuperscript{23} have performed thermal desorption spectroscopy (TDS) experiments suggesting that chemisorbed amidogen is formed by exposing ammonia to Ni(110) at temperatures below 350° K. This species decomposes at 410° K to give H\textsubscript{2} and chemisorbed nitrogen atom. Exposure of ammonia to Ni(110) at 400° K yields chemisorbed imidogen which decomposes at \textasciitilde800° K to give N\textsubscript{2} and H\textsubscript{2}. Ammonia gas also been observed to decompose when exposed to Ni(100) at room temperature.\textsuperscript{24} The intermediates were assigned to a
imidogen and amidogen intermediates by X-ray Photoelectron Spectroscopy. Unfortunately, all of the experimental work for ammonia decomposition only really shows that chemisorbed amidogen and imidogen are kinetically stable and not necessarily energetically stable. The experimental work does indicate that it is energetically favorable to dissociate ammonia on Ni surfaces, which is in agreement with our results, but the activation energy for dissociative chemisorption is higher than that for desorption of NH$_3$ molecules.

The relative enthalpies at 0° K for the various intermediates relevant for methanation are shown in Figure 14. The enthalpy changes for the steps shown in figure 14 are tabulated in table VI. These enthalpies imply that methylidyne is the most stable CH$_x$ intermediate on Ni. Experimentally it is known that both acetylene and ethylene will decompose to chemisorbed methylidyne on Ni(100)$^{25}$ and Ni(111)$^{27}$ suggesting that methylidyne is the most stable CH$_x$ intermediate on Ni. Kinetic experiments$^{28}$ suggest that the most abundant species on supported Ni catalysts during methanation is chemisorbed carbon and chemisorbed methylidyne. Both of these experiments are consistent with our calculated energetics and proposal that methylidyne is the most stable CH$_x$ intermediate on Ni surfaces.

The first step in dissociation of CO to chemisorbed carbon and oxygen is calculated to be downhill by 10.3 kcal/mol. Experimentally it is known that the dissociative chemisorption of CO does not occur for the low index faces of Ni[(111) and (100)]$^{29,30}$ for temperatures below 450° K, at this temperature CO will have desorbed under ultra high vacuum conditions. This implies that the activation barrier for CO decomposition is larger than for molecular desorption. Dissociative chemisorption of CO takes
place at low temperatures (180° K) on Ni(110) surfaces and on stepped surfaces of Ni. This is most probably caused by a lower activation energy at steps on these surfaces. This experimental evidence supports favorable energetics for CO dissociation.

Unfortunately the removal of chemisorbed oxygen by hydrogen molecule or chemisorbed hydrogen (reactions 3 and 9 in figure 14) is calculated to be extremely endothermic (35.1 kcal/mol and 58.1 kcal/mol). These enthalpies do not appear to be reasonable in light of kinetic experiments which give an activation barrier of 24.7 kcal/mol for the methanation reaction. Water was a principle product under the conditions under which these experiments were carried out. Although the observations of the chemistry of chemisorbed oxygen do not agree with our estimates, the relative energetics of the various chemisorbed CHx and NHx intermediates appear to be reasonable and consistent with experimental results.

There has been considerable controversy regarding the geometry of O on Ni(100). UG have carried out calculations on Ni20 to model this system and found two low lying electronic states: an "oxide" state with a surface-oxygen distance of 0.55 Å and vibrational frequency of 218 cm⁻¹ and a "radical" state with a surface-oxygen distance of 0.88 Å and vibrational frequency of 371 cm⁻¹. In order to model higher coverages UG carried out calculations on Ni20O⁺ and obtained a R₂=0.26 Å and a vibrational frequency of 266 cm⁻¹. These results provided an explanation for why the metal-oxygen stretching frequency (310 cm⁻¹) in the c(2x2) O overlayer was lower than in the p(2x2) O overlayer (430 cm⁻¹) on Ni(100). Parameters derived from these calculations were used in detailed calculations of the low frequency phonon spectrum which agreed
well with experiment.\textsuperscript{33} This led to the conclusion that the c(2x2) O overlayer had chemisorbed oxygen atoms in the "oxide" state with an $R_d = 0.26$ Å and the p(2x2) O overlayer contained chemisorbed oxygen atoms in the "radical" with an $R_d = 0.88$ Å state. However, many experiments have been performed since then which find a longer surface-oxygen distance of 0.8 to 0.9 Å for the c(2x2) overlayer,\textsuperscript{34} although some experiments do support the shorter Ni-O bond distance.\textsuperscript{34c,d,35} Bauschlicher \textit{et al.}\textsuperscript{36} have performed calculations on the Ni$_{13}$O cluster in which they found that the inclusion of Ni 4p functions to the double-$\zeta$ basis of UG$^6$ increased the surface-oxygen distance from 0.57 Å to 0.68 Å for the oxide state at the HF level. Their final surface-oxygen distance of 0.74 Å and vibrational frequency of 320 cm$^{-1}$ was calculated at the singles and doubles CI level. In our GVB-CI calculations we have used a basis of the same quality as Bauschlicher \textit{et al.} (see appendix) and find a surface-oxygen distance of 0.712 Å and vibrational frequency of 380 cm$^{-1}$ for Ni$_{13}$O. We have also carried out calculations on Ni$_{20}$O with the same cluster basis and found an $R_d$ of 0.647 Å and a vibrational frequency of 358 cm$^{-1}$ at the GVB-CI level. The results are in good agreement with the Ni$_{13}$O calculations and fair agreement with the experimental geometries of 0.8-0.9 Å.

Our calculated geometry for H chemisorbed at the four fold site of Ni$_{13}$ ($R_d = 0.74$ Å) is also substantially longer than that calculated by UG$^6$ at the same site ($R_d = 0.30$ Å). A recent experimental determination of geometry for deuterium on Ni(100) by transmission tunneling gives a value of $R_d = 0.5 \pm 0.1$ Å$^{37}$. Helium diffraction experiments\textsuperscript{38} gave a geometry for chemisorbed hydrogen on Ni(100) with an $R_d$ of 0.9-1.0 Å. Our calculated value of 0.74 Å lies in between the two experimental results, which does support the longer $R_d$ we are finding with a more com-
plete cluster basis. However, our calculated vibrational frequency of 845 cm\(^{-1}\) for the surface-hydrogen stretch does not agree as well with the experimental\(^{39}\) frequency of 596 cm\(^{-1}\) as that calculated by UG\(^{6}\) (589 cm\(^{-1}\)).

The experimental determination of the geometry of carbon on Ni(100) has been hampered by significant reconstruction of the substrate.\(^{40}\) The LEED data has been shown to be consistent with two structures. In one structure the carbon atoms are 0.9 Å from the surface and in the other structure the carbon atoms are 0.1 Å from the surface. The best fit was found for the second structure and helium diffraction experiments\(^{38}\) also support the shorter R\(_1\). However, we calculate a surface-carbon distance of 0.858 Å which is in better agreement with the R\(_1\) =0.9 Å structure. Since we have held the Ni atoms in our cluster fixed we cannot rule out the shorter surface-C distance, which could be favored if the Ni atoms were allowed to relax.
III. Calculational details

In all of the calculations presented here the Ni atoms were described by the MEP of UG. The double-$\zeta$ basis of UG plus bond functions (DZB) at octahedral and tetrahedral interstitials with exponents of 0.208 and 0.310 respectively was used to describe the Ni cluster. In the appendix we compare the DZB basis with a cluster basis in which the double-$\zeta$ basis is augmented by a single-$\zeta$ Ni 4p function with an exponent of 0.14. The exponents for the bond functions and single-$\zeta$ Ni 4p function were optimized for an averaged field wavefunction of Ni$_{13}$, in which one-third of an electron was placed in the 2a$_{1g}$ and 1e$_{g}$ orbitals, four-thirds of an electron was placed in the 1t$_{2g}$ orbitals, and the 1a$_{1g}$ and 1t$_{1u}$ orbitals were doubly occupied. This wavefunction corresponds to an average of all electronic states in which one electron occupies a 1e$_{g}$ or 1a$_{1g}$ orbital and four electrons with triplet spin occupy the t$_{2g}$ set of orbitals. This average field wavefunction includes many of the low lying states of the Ni$_{13}$ cluster and should give a basis which is unbiased toward any particular state of the cluster. Dunning's valence double-$\zeta$ contraction (9S5P|3S2P) augmented by polarization functions (D exponents 0.75, 0.80, 0.85) was used for carbon, nitrogen, and oxygen. Hunzina's four gaussian basis contracted double zeta and scaled by a factor of 1.2 was used for hydrogens bound to nitrogen, carbon and oxygen. Hydrogen bound directly to the cluster was described by a double zeta contraction of Hunzina's four gaussian basis unscaled.

The internal coordinates and orientation relative to the surface of each chemisorbed species were optimized with the Ni$_{13}$ cluster described by the double zeta basis (DZ) without bond functions at the Hartree-Fock level. Every CH$_x$ and NH$_x$ intermediate was found to have its axis of sym-
metry oriented perpendicular to the surface. The calculated internal coordinates of each chemisorbed molecule is listed in table VII. The distance of each molecule from the surface \((R_d)\) was reoptimized with the double zeta plus bond functions basis at the GVB-CI level, while holding the internal coordinates fixed. The nearest neighbor distance between Ni atoms in the clusters was fixed at 2.487 Å.\(^6\)

The GVB-CI wavefunction is a full configuration interaction (CI) calculation in which the orbitals were optimized at the GVB perfect-pairing (GVBPP) level.\(^{43}\) For every complex studied here, except Ni\(_{13}C\), we have used a GVBPP wavefunction where only the electrons in absorbate valence orbitals and metal-surface bonds were correlated. This generally corresponded to wavefunctions which contained four GVB pairs described by two orbitals each \([\text{GVB}(4/8)]\). The GVB-CI wavefunction for nitrogen on Ni\(_{13}\), which has zero spin, contains 331 configurations and 492 spin eigenfunctions. The chemisorbed carbon atom is an exception in that only seven electrons were localized on the carbon and in surface-carbon bonds. The wavefunction used to described this complex was a full CI in the orbitals described by three GVB pairs and the singly occupied \(C_2p^e\) orbital.

In appendix A we show results from RCI wavefunctions. This CI wavefunction involves single and double excitations within each pair times single and double excitations in all other pairs. Excitations between pairs are not allowed. This calculation was felt to be a good test of basis set effects. The RCI wavefunction for nitrogen on Ni\(_{13}\) contains 81 configurations and 150 spin eigenfunctions.

The equibondedness reactions used to cancel correlation errors are shown in Table II. The total energies, zero point energies and enthalpies
used to calculated the enthalpies of Table I are tabulated in Table I, II and III. The $\Delta H^o_f$ for these reactions represent the difference in total energies from our calculations and estimated zero point energies. In each of this reactions the number of bonds to the surface and the total number of H-H, C-H and N-H bonds were held constant. Chemisorbed carbon did not fit well into this scheme because it appears to make between two and three bonds to the surface (two metal-carbon $\pi$ bonds and a one-electron ionic $\sigma$ bond). Two reactions are shown to predict the $\Delta H^o_f$ of chemisorbed carbon. The second reaction ($\text{Ni}_{13}\text{CH} + \text{Ni}_{13}\text{H} \rightarrow \text{Ni}_{13}\text{C} + \text{H}_2 + \text{Ni}_{13}$) was not considered a fair cancellation of errors because in order for this reaction to be considered an equibondedness reaction chemisorbed carbon would have to make four bonds to the surface, which it is not able to do. We felt that using singlet methylene in the first reaction ($2\text{Ni}_{13}\text{H} + (^{1}\text{A}_1)\text{CH}_2 \rightarrow \text{Ni}_{13}\text{C} + 2\text{H}_2 + \text{Ni}_{13}$) to cancel correlation errors was better because methylene is divalent and has a doubly occupied 2s orbital, like chemisorbed carbon atom which has two surface $\pi$ bonds and a doubly occupied 2s orbital. Unfortunately carbon has also picked up an extra electron from the cluster, which we have not accounted for in our equibondedness scheme. This will cause larger errors in our corrected surface-carbon enthalpy estimate.

As a test of the accuracy of the equibondedness schemes we have calculated the enthalpy change for hydrogen abstraction from various gas phase CH$_x$ and NH$_x$ species. The results of these calculations are tabulated in Table VIII and give C-H and N-H bonds energies which agree with the experimental enthalpies to within $\pm$ 6 kcal/mol, which justifies its use in these cluster calculations.

Our calculated surface-O bond energy (157.2 kcal/mol) in Ni$_{13}$O is
disturbingly large. This is much larger than the experimental values (94-134 kcal/mol)\textsuperscript{15} but the experimental estimates are very uncertain since chemisorbed oxygen will tend to form oxides at higher temperatures. The fact that we calculate the reduction of oxygen to be uphill is disturbing and means that we must be overestimating the surface-oxygen bond strength by as much as 30 kcal/mol. This is most likely due to the small size of the cluster. We have calculated a surface-oxygen bond energy of 142.6 kcal/mol in Ni\textsubscript{20}O at the same level of electronic correlation and basis set.\textsuperscript{44} We can use this difference in bond energies to estimate a \textquote{cluster effect} of 15 kcal/mol. This correction applied to the Ni\textsubscript{13}O results derived from the equibondedness analysis gives a bond energy of 136 kcal/mol for oxygen chemisorption on Ni. This is in the range of bond energies found for oxygen on Ni polycrystalline films which range from 94 to 134 kcal/mol.\textsuperscript{14}
IV. Conclusions

These results are at best qualitative estimates of the heat of formation for various chemisorbed intermediates on Ni(100). Each step of the equibondedness procedure gives errors of approximately ±7 kcal/mol. The Ni$_{13}$ cluster appears to give bond strengths which are too large; an attempt to correct this bias yields reasonable energetics for NH$_x$ (x = 0-3) and CH$_x$ (x = 1-3). The energetics for carbon and oxygen chemisorption appear to have larger errors which are most likely due to cluster effects. Our results do indicate that it is energetically favorable to decompose NH$_3$ on Ni, that imidogen is the most stable NH$_x$ intermediate, and that methylidyne is the most stable CH$_x$ intermediate on Ni, all of which are consistent with experiment.

We find that nitrogen-surface and carbon-surface $\pi$ bonds are slightly stronger than the corresponding $\sigma$ bonds. This causes both CH$_x$ and NH$_x$ species to be oriented perpendicular to the surface and favors species which are multiply bonded to the surface. We feel that this is a general trend and can be extrapolated to the surface of bulk metals.
Appendix A.

A. Introduction

Upton and Goddard (UG)\textsuperscript{6} have developed the basic approximations used in this work and applied them to large clusters of Ni atoms (up to 87 atoms).\textsuperscript{45} The heart of this method involves simulating the Ni atoms by a modified effective potential (MEP) in which the Ar core and d\textsuperscript{9} shell of electrons are included in the MEP. Only the 4s electrons of the Ni atoms are treated explicitly.

UG made several tests of the frozen d\textsuperscript{9} shell approximation, both for the electronic structure of the Ni\textsubscript{13} cluster\textsuperscript{46} and for chemisorption of hydrogen on Ni\textsubscript{20}.\textsuperscript{6,46} These tests showed that the frozen d\textsuperscript{9} shell was a good approximation for large clusters of Ni atoms and for chemisorption on them.

UG\textsuperscript{46} felt that large clusters of atoms (20-87 atoms) were needed to simulate the bulk for chemisorption. This was only made feasible by using an unpolarized basis that contained a double zeta (DZ) 4s function for each Ni atom. In spite of the relatively large differences in the ionization potential (IP) (1.42, 2.46, and 1.63 eV for 13-, 19-, and 20-atom clusters), electron affinity (EA) (1.34, 1.89, and 1.47 eV), and cohesive energy (0.62 and 0.48 eV/atom) for the 13- and 19-atom clusters between the polarized and unpolarized basis sets,\textsuperscript{45-47} UG felt that in order to mimic the bulk for chemisorption, it was more important to use large clusters approximately than to do highly accurate calculations on small clusters. This approximation appeared to be justified in that the IP and EA of large clusters approached those of the bulk metal as the clusters grew larger.\textsuperscript{45} This result implied that the effect of polarization functions was less important for large clusters than small ones.
Siegbahn et al.\textsuperscript{48} have also done tests on the effects of including Ni 3d electrons explicitly in cluster models of hydrogen chemisorption. These results basically confirm the conclusions of UG in that the replacement of d electrons by the MEP did not significantly affect the equilibrium properties of chemisorbed hydrogen atom. However, Siegbahn et al.\textsuperscript{48} did find that the addition of polarization functions significantly altered the energetics (\(\sim 10\) kcal/mol per H atom) calculated for hydrogen chemisorption.

Siegbahn et al.\textsuperscript{48} found that freezing the Ni d orbitals significantly affected their calculated barriers for the dissociative chemisorption of \(\text{H}_2\). They found a barrier of 4.4 kcal/mol in calculations which include d orbitals, while they find a barrier of 48 kcal/mol for calculations in which the d orbitals were included in the MEP. These results indicate that the d orbitals played an important role in the barrier for activation of dihydrogen but not for the equilibrium structure of hydrogen chemisorption. Upton\textsuperscript{49} has presented arguments based on the orbital phase continuity principle\textsuperscript{50} that suggest that low barriers for \(\text{H}_2\) dissociation on Ni can be obtained by just considering the s and p bands of the bulk. Although he did not completely optimize the transition state \(\text{H}_2\) dissociation, the lowest barrier he finds is 10 kcal/mol. This result directly contradicts the results of Siegbahn et al. We believe that Upton's barrier is more reliable since the wavefunction he used allowed the electrons in the conduction band of the cluster to have the optimum spin coupling at the transition state. Since dissociative chemisorption of \(\text{H}_2\) on Ni surface is known to be an unactivated process, the barrier height calculated by various methods should be a good test of their validity. Upton's results show that the frozen d\textsuperscript{9} shell approximation is valid for this process as well.
Bauschlicher et al.\textsuperscript{36} have carried out calculations on chemisorption of oxygen atoms on a small Ni cluster (five atoms) to test the effect of Ni polarization functions on the calculated parameters for oxygen chemisorption. They found that polarization functions caused an increase in the distance of the oxygen atom from the surface (0.11 Å) and a small increase in the vibrational frequencies (39 cm\textsuperscript{-1} out of 290 cm\textsuperscript{-1}). Bauschlicher and co-workers have also tested the importance of d electrons for oxygen chemisorption on Ni(100)\textsuperscript{51} and for CO chemisorption on Ni(100).\textsuperscript{52} In both cases MEP Ni atoms were replaced by all-electron Ni atoms at the Hartree-Fock level (AEHF). The differences in these calculations are not surprising in light of the fact that AEHF Ni atoms have a 28.7 kcal/mol bias\textsuperscript{53} favoring the \(^3\text{F}(s^2d^8)\) versus \(^3\text{D}(s^1d^9)\) state of Ni atom, while the 10 e\textsuperscript{-} MEP\textsuperscript{54} was constructed to match the experimental state splitting (0.07 kcal/mol).\textsuperscript{55} It is very likely that the Ni atoms in these studies have a significant amount of d\textsuperscript{8} character that would have increased the 4s population of their wavefunction. This could very likely explain the long oxygen-surface distance (1.05 Å AE versus 0.68 Å MEP) for Ni\(_2\)O. It is well known that errors in the state splittings for Ni atom at the AEHF level can cause significant errors in description of the electronic structure of molecules containing Ni. For example, AEHF predicts the ground state for NiCO to be \(^3\Delta\) while good quality CI calculations predict the ground state to be \(^1\Sigma\).\textsuperscript{56} Thus all tests of the d\textsuperscript{8} frozen shell approximation carried out with the 10 e\textsuperscript{-} MEP have shown that this approximation is valid. The AEHF tests conducted so far have given different results because of their bias towards the \(s^2d^8\) configuration and are therefore not fair tests. Until it becomes possible to do all electron CI calculations for Ni clusters in which the \(^3\text{F}-^3\text{D}\) state splitting is well
described, the MEP is a necessary and reasonable approximation for describing Ni clusters.

In this appendix we demonstrate that for a large number of cases, the double-\(\zeta\) cluster basis is not an adequate basis set for modelling chemisorption. Clusters described at the double-\(\zeta\) level have basis set deficiencies which cause errors in geometries, vibration frequencies and bond energies. It is shown that augmenting the double-\(\zeta\) cluster basis with s gaussians placed at the tetrahedral and octahedral interstitials of the cluster (bond functions) give results as good as those in the basis set included p polarization functions.
B. Results and Discussion

The results of Siegbahn et al., Bauschlicher et al., and the results presented in this appendix show that polarization functions are necessary for accurate cluster chemisorption studies. Test calculations for hydrogen (see Table AI) and nitrogen (see Table AII) chemisorption on Ni₁₃ show that clusters described by the DZ basis of UG are basis set deficient. In chemisorption studies, this basis set deficiency causes the cluster to compensate by using the basis set of the adsorbate, leading to bond energies that are too large and bond distances that are too short.

Polarization functions also affect the ordering of electronic states in the cluster (see Table AIII). Basically, the lack of polarization functions favors high spin states because of weaker bonds between Ni atoms in the cluster. The major disadvantage of using p functions to polarize the basis set is that the size of the polarized basis is factor 3.5 times that of the DZ basis. For Ni₁₃, the DZ basis contains 26 basis functions, while the DZ plus single-ξ p functions basis (DZP) contains 85 basis functions. The larger basis set will increase the computational effort by a factor of approximately 39 (= 2.5⁴). The high computational cost of the DZP basis will make the study of the chemisorption of polyatomic molecules (i.e., CH₄ or NH₃) unpractical with the technology currently available to quantum chemists. An intermediate basis that corrects the basis set deficiency of clusters described with the DZ basis is one that uses bond functions at the octahedral and tetrahedral interstitials of the metal cluster. This basis set was found to mimic quite well the DZP results for hydrogen and nitrogen chemisorption (see Tables AI and AII) and the ordering of electronic states for the Ni₁₃ cluster (see Table AIII). The advantage of bond functions is that the improvement in the basis set is concentrated where
it is most needed, inside the cluster. This improvement is accomplished
with smaller basis sets and considerable savings in cost. For Ni\textsubscript{13}, the DZ
plus bond functions (DZB) basis, which contains 40 functions (26 Ni 4s
functions plus one bond function each at six octahedral and eight
tetrahedral interstitial sites), yielded a savings of 25 functions and 85\% \[1
- \left(\frac{40}{65}\right)^4\] of the computation effort over the DZP basis. The DZB basis
should not be as flexible as the DZP basis in calculating geometries or
cohesive energies of the clusters themselves. However, since we are hold-
ing the geometry of the cluster fixed in these studies, the use of bond
functions is an appropriate way to correct the artifacts due to the basis
set deficiencies of clusters described by the DZ basis. A comparison of
the results for various CH\textsubscript{x} and NH\textsubscript{x} species is shown in Table AIV for clus-
ters described by the DZ and DZB basis sets.

In general, the DZ basis results have shorter surface adsorbate dis-
tances (R\textsubscript{d}) and larger dissociation energies than the DZB results. For
larger R\textsubscript{d}, this basis set error gets smaller. This is consistent with the
cluster using adsorbate basis functions at the DZ level, in that the effect
appears to get smaller as the adsorbate moves farther away from the
cluster.

It is strongly recommended that all future calculations are per-
formed either with the DZB or DZP basis sets. Although the other approx-
imations made in this work may affect the accuracy of these calculations,
correcting the basis set deficiency makes the method self-consistent in
that larger basis sets should not affect the results to a significant extent.
Because of the large number of atoms and the complicated nature of
transition metals, a highly accurate method that would include all of the
valence electrons and the differential electronic correlation effects of
large clusters is not yet feasible.
References


York, 1970.


(14) The N-H bond strength was assumed to be the same as that in NH₃, which was derived from the experimental enthalpies in Tables V and VII.


(22) Jacobi, K.; Hensen, E. S.; Rhodin, T. N.; Merrill, R. P. Surf. Sci. 1981, 


324.


1472.

(34) (a) Norman, D.; Stöhr, J.; Jaeger, R.; Durham, P.J.; Pendry, J.B. 
142-146;
(c) Demuth, J.E.; Dinardo, N.J.; Cargill III, G.S. Phys. Rev. Lett. 
1983, 50, 1373-1376. In this paper the authors propose a structure 
for the c(2x2) O overlayer in which the oxygen atom has moved 0.3 
Å along the <110> direction. This results in two shorter Ni-O
distances of 1.74 Å and two longer distances of 2.14 Å. The shorter distance is in agreement with the Ni-O distance calculated by UG\textsuperscript{6} of 1.78 Å.

(d) Tong, S.Y.; Lau, K.H. Phys. Rev. B \textbf{1982}, 25, 7382-7387. The analysis of the LEED data in this paper was shown to be consistent with a surface-oxygen distance of either less than 0.1 Å or 0.9 Å.


(44) The same Ni\textsubscript{20} cluster was used by UG\textsuperscript{6} to model the bulk for chemisorption.


(55) Moore, C. E. "Atomic Energy Levels," National Bureau of Standards: Washington, DC, 1971; Vol. II. (These state splittings were averaged over j states to cancel out spin-orbit coupling.)

Table I.
GVB-CI Parameters for Chemisorption on Four-Coordinate (100) Site of Ni13.

<table>
<thead>
<tr>
<th>Chemisorbed Species</th>
<th>R(Ni-X) (Å)</th>
<th>R_j (Å)</th>
<th>ω_j (cm⁻¹)</th>
<th>D_e (kcal/mol)</th>
<th>Total Energy (a.u.)</th>
<th>Corrected D_0 (kcal/mol)</th>
<th>Corrected AHF (kcal/mol)</th>
<th>Ground State</th>
<th>Zero Point Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.957</td>
<td>0.858</td>
<td>390</td>
<td>142.1</td>
<td>-42.1654</td>
<td>144.8</td>
<td>24.8</td>
<td>^2A_1</td>
<td>1.7</td>
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<td>CH</td>
<td>1.991</td>
<td>0.634</td>
<td>457</td>
<td>175.5</td>
<td>-42.6130</td>
<td>153.6</td>
<td>-12.4</td>
<td>^1A_1</td>
<td>8.5</td>
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<td>CH₂</td>
<td>2.051</td>
<td>1.056</td>
<td>430</td>
<td>111.8</td>
<td>-43.3735</td>
<td>101.1</td>
<td>-8.9</td>
<td>^3B_2</td>
<td>15.6</td>
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<td>CH₃</td>
<td>2.223</td>
<td>1.360</td>
<td>341</td>
<td>53.4</td>
<td>-43.9383</td>
<td>43.6</td>
<td>-7.7</td>
<td>^3A'</td>
<td>22.9</td>
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<td>N</td>
<td>1.848</td>
<td>0.569</td>
<td>347</td>
<td>141.3</td>
<td>-58.8561</td>
<td>134.6</td>
<td>-22.1</td>
<td>^1A_1</td>
<td>1.5</td>
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<td>NH</td>
<td>1.980</td>
<td>0.910</td>
<td>482</td>
<td>129.4</td>
<td>-59.4426</td>
<td>117.0</td>
<td>-32.7</td>
<td>^1A_1</td>
<td>9.2</td>
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<td>NH₂</td>
<td>2.102</td>
<td>1.152</td>
<td>424</td>
<td>81.3</td>
<td>-59.9987</td>
<td>70.6</td>
<td>-25.5</td>
<td>^3B_2</td>
<td>17.2</td>
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<td>NH₃</td>
<td>2.702</td>
<td>2.052</td>
<td>129</td>
<td>2.04</td>
<td>-60.5369</td>
<td>-1.6</td>
<td>-7.7</td>
<td>^4A'</td>
<td>24.6</td>
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<tr>
<td>NH₃,a)</td>
<td>2.092</td>
<td>2.092</td>
<td>354</td>
<td>15.0</td>
<td>-61.0079</td>
<td>10.0</td>
<td>-19.3</td>
<td>^1A'</td>
<td>26.0</td>
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<td>CO,b)</td>
<td>2.017</td>
<td>2.017</td>
<td>330</td>
<td>17.5</td>
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<td>30.0</td>
<td>-57.2</td>
<td>^1A_1</td>
<td>a)</td>
</tr>
<tr>
<td>O</td>
<td>1.897</td>
<td>0.712</td>
<td>380</td>
<td>157.2</td>
<td>-79.3137</td>
<td>151.3</td>
<td>-92.3</td>
<td>^3E</td>
<td>1.6</td>
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<tr>
<td>H</td>
<td>1.908</td>
<td>0.740</td>
<td>845</td>
<td>65.6</td>
<td>-4.8394</td>
<td>63.1</td>
<td>-11.5</td>
<td>^3A_2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

a) The reduced mass used to calculate vibrational frequencies was the same as a diatomic in which one atom had a mass equal to the mass of four Ni atoms and the other atom had the mass of the chemisorbed species.

b) The zero point energies were based on ω_j, frequencies from calculations with the DZ cluster basis and estimated frequencies.

c) Relative to 4Σ⁻ methyldyne dissociated limit (Total energy of 4Σ⁻ methyldyne is -38.2976 hartrees.)

d) Geometry optimized at the GVB-perfect pairing level.

e) Chemisorption on one-coordinate site of Ni₁₄.

f) Experimental value for D_0 (M-CO). (see ref. 18)

g) Not evaluated since not used in equibondedness reactions (see table II).

h) Experimental value for D_0 (M-H) (see ref. 11)
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ$</th>
<th>Calculated Quantity</th>
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</thead>
<tbody>
<tr>
<td>$\text{CH}<em>4 + \text{Ni}</em>{13}\text{H} \rightarrow \text{Ni}_{13}\text{CH}_3 + \text{H}_2$</td>
<td>19.6</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{CH}_3) = -7.7$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{13}\text{CH}<em>3 + \text{Ni}</em>{13}\text{H} \rightarrow \text{Ni}</em>{13}\text{CH}_2 + \text{H}<em>2 + \text{Ni}</em>{13}$</td>
<td>10.5</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{CH}_2) = -8.9$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{13}\text{CH}<em>2 + \text{Ni}</em>{13}\text{H} \rightarrow \text{Ni}</em>{13}\text{CH} + \text{H}<em>2 + \text{Ni}</em>{13}$</td>
<td>8.0</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{CH}) = -12.4$</td>
</tr>
<tr>
<td>$2[\text{Ni}_{13}\text{H}] + (^1\text{A}_1)\text{CH}<em>2 \rightarrow \text{Ni}</em>{13}\text{C} + 2\text{H}<em>2 + \text{Ni}</em>{13}$</td>
<td>-53.5</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{C}) = 24.8$</td>
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<tr>
<td>$\text{Ni}<em>{13}\text{C} - \text{H} + \text{Ni}</em>{13} - \text{H} \rightarrow \text{Ni}_{13}\text{C} + \text{H}<em>2 + \text{Ni}</em>{13}$</td>
<td>62.9</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{C}) = 39.0$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{13}\text{NH}<em>3 + \text{Ni}</em>{13}\text{H} \rightarrow \text{Ni}</em>{13}\text{NH}_2 + \text{H}_2$</td>
<td>-6.3</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{NH}_2) = -25.5$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{13}\text{NH}<em>2 + \text{Ni}</em>{13}\text{H} \rightarrow \text{Ni}</em>{13}\text{NH} + \text{H}_2$</td>
<td>4.3</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{NH}) = -32.7$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{13}\text{NH} + \text{Ni}</em>{13}\text{H} \rightarrow \text{Ni}_{13}\text{N} + \text{H}_2$</td>
<td>22.1</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{N}) = -22.1$</td>
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<tr>
<td>$2[\text{Ni}_{13}\text{H}] + \text{H}<em>2\text{O} \rightarrow \text{Ni}</em>{13}\text{O} + 2\text{H}<em>2 + \text{Ni}</em>{13}$</td>
<td>-12.2</td>
<td>$\Delta H^\circ(\text{Ni}_{13}\text{O}) = -92.3$</td>
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# Table III.

Total Energies, Zero Point Energies, and ΔH_f

for Molecules Used in Table II.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Total Energy^a) (GVB-Cl, hartrees)</th>
<th>Zero Point^b) (kcal/mol)</th>
<th>ΔH_f^c) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>-1.1445</td>
<td>6.3</td>
<td>0.0</td>
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<tr>
<td>CH₄</td>
<td>-40.2771</td>
<td>27.1</td>
<td>-16.0</td>
</tr>
<tr>
<td>NH₃</td>
<td>-56.2979</td>
<td>21.0</td>
<td>-9.3</td>
</tr>
<tr>
<td>H₂O</td>
<td>-76.1495</td>
<td>12.9</td>
<td>-57.1</td>
</tr>
<tr>
<td>CO</td>
<td>-112.9192</td>
<td>3.1</td>
<td>-27.2</td>
</tr>
<tr>
<td>(1A₁) CH₂</td>
<td>-38.9396</td>
<td>15.6</td>
<td>101.3^d)</td>
</tr>
<tr>
<td>(4T₁g) Ni₁₃^e)</td>
<td>-4.2357</td>
<td>-</td>
<td>0.0</td>
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<tr>
<td>(1A₁₄) Ni₁₄^e)</td>
<td>-4.6861</td>
<td>-</td>
<td>0.0</td>
</tr>
</tbody>
</table>

^a) Calculated at experimental geometry; (ref. 13)

^b) Calculated with experimental vibrational frequencies (ref. 13).


^e) We have assumed that the heat of formation of the Ni cluster is the same as the bulk and that the zero point energy of the cluster is essentially constant during the reactions studied here. The geometries of the Ni₁₃ and Ni₁₄ clusters are described in the text.
Table IV.

Calculated Total Energies, Zero Point Energies and Experimental Enthalpies at 0°K for Various Radicals Used in This Paper.\(^{a)}\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Total Energy (\text{GVB-Cl (hartrees)})</th>
<th>Zero Point energy (\text{(kcal/mol)})</th>
<th>(\Delta H_f^\circ) (\text{(kcal/mol)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-0.4993</td>
<td>0.0</td>
<td>51.6</td>
</tr>
<tr>
<td>C</td>
<td>-37.7033</td>
<td>0.0</td>
<td>169.6</td>
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<tr>
<td>CH</td>
<td>-38.3100</td>
<td>4.1</td>
<td>141.2</td>
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<tr>
<td>CH(_2)</td>
<td>-38.9597</td>
<td>10.4</td>
<td>92.2(^{b)})</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>-39.6176</td>
<td>18.2</td>
<td>35.9(^{c)})</td>
</tr>
<tr>
<td>N</td>
<td>-54.3972</td>
<td>0.0</td>
<td>112.5</td>
</tr>
<tr>
<td>NH</td>
<td>-55.0008</td>
<td>4.7</td>
<td>84.3(^{d)})</td>
</tr>
<tr>
<td>NH(_2)</td>
<td>-55.6335</td>
<td>11.2</td>
<td>45.1(^{e)})</td>
</tr>
<tr>
<td>O</td>
<td>-74.8274</td>
<td>0.0</td>
<td>59.0</td>
</tr>
</tbody>
</table>

\(^{a)}\) Values are from JANAF [footnote (c), Table V] unless otherwise specified. Geometries and vibrational frequencies are those of reference 13.

\(^{b)}\) McMillen, D. F.; Golden, D. M., Ann. Rev. Phys. Chem., 33, 493-532 (1982). This value was extrapolated to 0° K from \(\Delta H_{298}^\circ = 35.1 \text{ kcal/mol}\).


Table V.

Reactions for Ammonia Decomposition.
(see figure 13)

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>ΔH° (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH₃(₉) → NH₃(ₐ)</td>
<td>-10.0</td>
</tr>
<tr>
<td>2</td>
<td>NH₃(ₐ) → NH₂(ₐ) + ½H₂(₉)</td>
<td>-6.2</td>
</tr>
<tr>
<td>3</td>
<td>NH₂(ₐ) → NH(ₐ) + ½H₂(₉)</td>
<td>-7.2</td>
</tr>
<tr>
<td>4</td>
<td>NH(ₐ) → N(ₐ) + ½H₂(₉)</td>
<td>10.6</td>
</tr>
<tr>
<td>5</td>
<td>N(ₐ) → ½N₂(₉)</td>
<td>22.1</td>
</tr>
<tr>
<td>6</td>
<td>NH₃(ₐ) → NH₂(ₐ) + H(ₐ)</td>
<td>-17.7</td>
</tr>
<tr>
<td>7</td>
<td>NH₂(ₐ) → NH(ₐ) + H(ₐ)</td>
<td>-18.7</td>
</tr>
<tr>
<td>8</td>
<td>NH(ₐ) → N(ₐ) + H(ₐ)</td>
<td>-0.9</td>
</tr>
<tr>
<td>Reaction</td>
<td>ΔH\textsuperscript{o} \text{ (kcal/mol)}</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------------------</td>
<td></td>
</tr>
<tr>
<td>1 CO\textsubscript{(g)} → CO\textsubscript{(a)}</td>
<td>-30.0</td>
<td></td>
</tr>
<tr>
<td>2 CO\textsubscript{(a)} → C\textsubscript{(a)} + O\textsubscript{(a)}</td>
<td>-10.3</td>
<td></td>
</tr>
<tr>
<td>3 O\textsubscript{(a)} + H\textsubscript{2(g)} → H\textsubscript{2}O\textsubscript{(g)}</td>
<td>35.2</td>
<td></td>
</tr>
<tr>
<td>4 C\textsubscript{(a)} + \frac{1}{2} H\textsubscript{2(g)} → CH\textsubscript{(a)}</td>
<td>-37.2</td>
<td></td>
</tr>
<tr>
<td>5 CH\textsubscript{(a)} + \frac{1}{2} H\textsubscript{2(g)} → CH\textsubscript{2(a)}</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>6 CH\textsubscript{2(a)} + \frac{1}{2} H\textsubscript{2(g)} → CH\textsubscript{3(a)}</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>7 CH\textsubscript{3(a)} + \frac{1}{2} H\textsubscript{2(g)} → CH\textsubscript{4(g)}</td>
<td>-8.3</td>
<td></td>
</tr>
<tr>
<td>8 same as 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 O\textsubscript{(a)} + 2H\textsubscript{(a)} → H\textsubscript{2}O\textsubscript{(g)}</td>
<td>58.2</td>
<td></td>
</tr>
<tr>
<td>10 C\textsubscript{(a)} + H\textsubscript{(a)} → CH\textsubscript{(a)}</td>
<td>-25.7</td>
<td></td>
</tr>
<tr>
<td>11 CH\textsubscript{(a)} + H\textsubscript{(a)} → CH\textsubscript{2(a)}</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>12 CH\textsubscript{2(a)} + H\textsubscript{(a)} → CH\textsubscript{3(a)}</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>13 CH\textsubscript{3(a)} + H\textsubscript{(a)} → CH\textsubscript{4(g)}</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>
Table VII. Internal coordinates of $\text{AH}_x$ (where $A = \text{N}$ or $\text{C}$) used in this study.

<table>
<thead>
<tr>
<th>Chemisorbed Species</th>
<th>Internal Coordinate of Fragment</th>
<th>A-H distance (Å)</th>
<th>H-A-H angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td></td>
<td>1.013</td>
<td></td>
</tr>
<tr>
<td>NH$_2$</td>
<td></td>
<td>1.017</td>
<td>97.7</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>1.003</td>
<td>105.1</td>
</tr>
<tr>
<td>CH</td>
<td></td>
<td>1.095</td>
<td></td>
</tr>
<tr>
<td>CH$_2$</td>
<td></td>
<td>1.107</td>
<td>100.4</td>
</tr>
<tr>
<td>CH$_3$</td>
<td></td>
<td>1.094</td>
<td>104.1</td>
</tr>
</tbody>
</table>
Table VIII. Test of Equibondedness Reactions (in kcal/mol).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_f^\circ$ (exp)</th>
<th>$\Delta H_f^\circ$ (GVB-Cl)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + H$_2$ → CH + H</td>
<td>23.2</td>
<td>21.9</td>
<td>-1.3</td>
</tr>
<tr>
<td>CH + H$_2$ → CH$_2$ + H</td>
<td>2.6</td>
<td>-2.8</td>
<td>-5.4</td>
</tr>
<tr>
<td>CH$_2$ + H$_2$ → CH$_3$ + H</td>
<td>-5.0</td>
<td>-6.5</td>
<td>1.5</td>
</tr>
<tr>
<td>CH$_3$ + H$_2$ → CH$_4$ + H</td>
<td>-0.3</td>
<td>-6.4</td>
<td>-6.1</td>
</tr>
<tr>
<td>N + H$_2$ → NH + H</td>
<td>23.4</td>
<td>24.5</td>
<td>1.2</td>
</tr>
<tr>
<td>NH + H$_2$ → NH$_2$ + H</td>
<td>12.4</td>
<td>7.6</td>
<td>-4.8</td>
</tr>
<tr>
<td>NH$_2$ + H$_2$ → NH$_3$ + H</td>
<td>-2.8</td>
<td>-8.5</td>
<td>-5.7</td>
</tr>
</tbody>
</table>
Table AI.  
Basis Set Effects on Hydrogen Chemisorption on Ni$_{13}$. a)

<table>
<thead>
<tr>
<th>Level of Calculation</th>
<th>Basis Set</th>
<th>$R_\perp$ (Å)</th>
<th>$\omega_\perp$ b) (cm$^{-1}$)</th>
<th>Bond Energy (kcal/mol)</th>
<th>Total Energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>DZ</td>
<td>0.355</td>
<td>637</td>
<td>60.0</td>
<td>-4.6190</td>
</tr>
<tr>
<td>GVB(1/2)</td>
<td>DZ</td>
<td>0.385</td>
<td>659</td>
<td>67.1</td>
<td>-4.6301</td>
</tr>
<tr>
<td>RCI(1/2)</td>
<td>DZ</td>
<td>0.388</td>
<td>661</td>
<td>67.3</td>
<td>-4.6304</td>
</tr>
<tr>
<td>HF</td>
<td>DZP</td>
<td>0.690</td>
<td>828</td>
<td>58.6</td>
<td>-4.9125</td>
</tr>
<tr>
<td>GVB(1/2)</td>
<td>DZP</td>
<td>0.726</td>
<td>814</td>
<td>66.7</td>
<td>-4.9254</td>
</tr>
<tr>
<td>RCI(1/2)</td>
<td>DZP</td>
<td>0.724</td>
<td>804</td>
<td>66.9</td>
<td>-4.9258</td>
</tr>
<tr>
<td>HF</td>
<td>DZB</td>
<td>0.730</td>
<td>891</td>
<td>57.2</td>
<td>-4.8266</td>
</tr>
<tr>
<td>GVB(1/2)</td>
<td>DZB</td>
<td>0.764</td>
<td>871</td>
<td>65.4</td>
<td>-4.8393</td>
</tr>
<tr>
<td>RCI(1/2)</td>
<td>DZB</td>
<td>0.740</td>
<td>845</td>
<td>65.6</td>
<td>-4.8394</td>
</tr>
</tbody>
</table>

a) The bond lengths ($R_\perp$), vibrational ($\omega_\perp$), bond energies, and total energies are extrapolated from spline fits to calculated values.
b) The vibrational frequencies were calculated using the reduced mass for a hydrogen atom and a particle four times the mass of a nickel atom; $\mu = 1.0035$ atomic mass units.
Table All.  
Basis Set Effects on  
Nitrogen Chemisorption on Ni₁₃. a)

<table>
<thead>
<tr>
<th>Level of Calculation</th>
<th>Basis Set</th>
<th>R_l (Å)</th>
<th>( \omega_l ) b) (cm(^{-1}))</th>
<th>Bond Energy (kcal/mol)</th>
<th>Total Energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>DZ</td>
<td>0.157</td>
<td>410</td>
<td>71.5</td>
<td>-58.4584</td>
</tr>
<tr>
<td>GVB(4/8)</td>
<td>DZ</td>
<td>0.205</td>
<td>387</td>
<td>106.6</td>
<td>-58.5173</td>
</tr>
<tr>
<td>RCI(4/8)</td>
<td>DZ</td>
<td>0.232</td>
<td>352</td>
<td>146.2</td>
<td>-58.5804</td>
</tr>
<tr>
<td>HF</td>
<td>DZP</td>
<td>0.442</td>
<td>325</td>
<td>52.7</td>
<td>-58.7239</td>
</tr>
<tr>
<td>GVB(4/8)</td>
<td>DZP</td>
<td>0.550</td>
<td>308</td>
<td>93.4</td>
<td>-58.7917</td>
</tr>
<tr>
<td>RCI(4/8)</td>
<td>DZP</td>
<td>0.511</td>
<td>332</td>
<td>133.5</td>
<td>-58.8556</td>
</tr>
<tr>
<td>HF</td>
<td>DZB</td>
<td>0.487</td>
<td>325</td>
<td>50.7</td>
<td>-58.6370</td>
</tr>
<tr>
<td>GVB(4/8)</td>
<td>DZB</td>
<td>0.612</td>
<td>320</td>
<td>91.8</td>
<td>-58.7055</td>
</tr>
<tr>
<td>RCI(4/8)</td>
<td>DZB</td>
<td>0.550</td>
<td>320</td>
<td>130.7</td>
<td>-58.7675</td>
</tr>
</tbody>
</table>

a) The bond lengths (R_l), vibrational (\( \omega_l \)), bond energies, and total energies are extrapolated from spline fits to calculated values. The Nitrogen basis used for these calculations was a double-\( \xi \) contraction of Rappé's "fours" basis (see table AV).

b) The vibrational frequencies were calculated using the reduced mass for a nitrogen atom four times the mass of a nickel atom; \( \mu = 13.2084 \).
<table>
<thead>
<tr>
<th>State</th>
<th>Configuration&lt;sup&gt;a&lt;/sup&gt;</th>
<th>State Splittings (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t&lt;sub&gt;2g&lt;/sub&gt; (xy)</td>
<td>t&lt;sub&gt;2g&lt;/sub&gt; (xz)</td>
</tr>
<tr>
<td>(2T_{2g})</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(4T_{2g})</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>(4T_{1g})</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>(4T_{1g})</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>(6A_{1g})</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(6E_{g})</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

<sup>a</sup> The 1a<sub>1g</sub> and 1t<sub>1u</sub> orbitals which are doubly occupied for all of these states are not shown.

<sup>b</sup> The total energy for Ni<sub>13</sub> in the DZ basis is ~4.0206 h.

<sup>c</sup> The total energy for Ni<sub>13</sub> in the DZP basis is ~4.3324 h.

<sup>d</sup> The total energy for Ni<sub>13</sub> in the DZB basis is ~4.244628 h.

<sup>e</sup> Only the lowest energy \(4T_{1g}\) state was solved for in the DZP and DZB basis sets.
Table AIV. Effects of Bond Functions on \( \text{AH}_n \) (where \( A = \text{N or C} \)) on the
Four-Coordinate Site of Ni\(_{13}\).\(^a\)

<table>
<thead>
<tr>
<th>Ground State</th>
<th>Chemisorbed</th>
<th>( R_j ) (Å)</th>
<th>( \omega_j ) (cm(^{-1}))</th>
<th>( D_e ) (kcal/mol)</th>
<th>Total Energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DZ</td>
<td>DZB</td>
<td>DZ</td>
<td>DZB</td>
</tr>
<tr>
<td>( ^1A_1 )</td>
<td>N</td>
<td>0.232</td>
<td>0.551</td>
<td>352</td>
<td>337</td>
</tr>
<tr>
<td>( ^2A_1 )</td>
<td>NH</td>
<td>0.807</td>
<td>0.908</td>
<td>476</td>
<td>484</td>
</tr>
<tr>
<td>( ^3B_2 )</td>
<td>NH(_2)</td>
<td>1.088</td>
<td>1.15</td>
<td>462</td>
<td>426</td>
</tr>
<tr>
<td>( ^4A'' )</td>
<td>NH(_3)</td>
<td>1.57</td>
<td>2.05</td>
<td>292</td>
<td>129</td>
</tr>
<tr>
<td>( ^2A_1 )</td>
<td>C</td>
<td>0.355</td>
<td>0.833</td>
<td>333</td>
<td>413</td>
</tr>
<tr>
<td>( ^1A_1 )</td>
<td>CH</td>
<td>0.742</td>
<td>0.934</td>
<td>484</td>
<td>457</td>
</tr>
<tr>
<td>( ^2B_2 )</td>
<td>CH(_2)</td>
<td>0.895</td>
<td>1.057</td>
<td>401</td>
<td>430</td>
</tr>
<tr>
<td>( ^3A'' )</td>
<td>CH(_3)</td>
<td>1.282</td>
<td>1.36</td>
<td>375</td>
<td>341</td>
</tr>
</tbody>
</table>

\(^a\) These calculations were all performed at the RCI(4/6) level.

\(^b\) The nitrogen basis for DZ calculations was a double-\( \xi \) contraction of Rappé's "Fours" basis (set table AV).
Table AV.

The (7s4p|3s2p) Contraction of Rappé's "Fours" Nitrogen basis set$^a$)

<table>
<thead>
<tr>
<th>Component</th>
<th>Type</th>
<th>Exponent</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S</td>
<td>588.790042</td>
<td>0.0207721952</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>88.7013675</td>
<td>0.142129065</td>
</tr>
<tr>
<td>3</td>
<td>S</td>
<td>19.8226575</td>
<td>0.479025723</td>
</tr>
<tr>
<td>4</td>
<td>S</td>
<td>5.26862757</td>
<td>0.500943653</td>
</tr>
<tr>
<td>1</td>
<td>S</td>
<td>7.003173828</td>
<td>-0.195396724</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>0.767161436</td>
<td>1.07488985</td>
</tr>
<tr>
<td>1</td>
<td>S</td>
<td>0.231739294</td>
<td>1.00000000</td>
</tr>
<tr>
<td>1</td>
<td>P</td>
<td>13.5561742</td>
<td>0.0589506223</td>
</tr>
<tr>
<td>2</td>
<td>P</td>
<td>2.92431073</td>
<td>0.320281888</td>
</tr>
<tr>
<td>3</td>
<td>P</td>
<td>0.799357604</td>
<td>0.753138039</td>
</tr>
<tr>
<td>1</td>
<td>P</td>
<td>0.219198754</td>
<td>1.00000000</td>
</tr>
</tbody>
</table>

$^a$) Rappé, A.K.; Goddard, W.A., III, unpublished results
Figure 1. The Ni$_5$ cluster. The arrow marks the four-coordinate site.
Figure 2. The Ni$_{14}$ cluster. The arrow marks the one-coordinate site.
Figure 3. The GVB orbitals for Ni$_{13}$CH [from the GVB(4/8)-PP wavefunction]. Nuclei in the plane are indicated by asterisks. Positive contours are solid, negative contours are dotted, and nodal lines are long dashes. The spacing between contours is 0.02 a.u.
Figure 4. The GVB orbitals for the Ni$_{13}$CH$_2$ cluster.
Figure 5. The GVB orbitals for the Ni$_{13}$CH$_3$ cluster.
Figure 6. The GVB orbitals for the Ni$_{13}$C cluster.
Figure 7. The GVB orbitals for the Ni$_{13}$NH cluster.
Figure 8. The GVB orbitals for the Ni$_{13}$NH$_2$ cluster.
Figure 9. The GVB orbitals for the Ni$_{13}$NH$_3$ cluster.
Figure 10. The GVB orbitals for the Ni$_{13}$N cluster.
Figure 11. The GVB orbitals for the $\sigma$ orbitals of the Ni$_{13}$O cluster.
Figure 12. The GVB orbitals for the $\pi$ orbitals of the Ni$_{13}$O cluster.
Figure 13. Enthalpies (kcal/mol) for Intermediates Relevant for Ammonia Decomposition.
Figure 14. Enthalpies (kcal/mol) for Intermediates Relevant for Methanation.