Theoretical Studies of Oxidative Addition and Reductive Elimination. 3. C–H and C–C Reductive Coupling from Palladium and Platinum Bis(phosphine) Complexes

John J. Low* and William A. Goddard, III*

Abstract: Ab initio calculations were carried out on Pt(CH3)2(Cl)2(PH3)2 and on various M(R)(R)(PH3)2 complexes (where M = 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), Pd(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 the addition of H2 to Pt(0) systems.

I. 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.2,3 Some of the experimental observations are as follows, focusing only on Pd and Pt complexes:

(i) C–C coupling from Pd dialkylbis(phosphines)6

Pt(CH3)2(PR3)2 → Pt(PR3)2 + CH2=CH2

(1)

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

Pt(CH3)2(Cl)2(PR3)2 → Pt(Cl)2(PR3)2 + CH2=CH2

(2)

is intramolecular and consistent with a concerted process. Conversely, (ii) Pt dialkyls tend to decompose through β-hydride elimination if this pathway is available, even though direct C–C reductive coupling is thermodynamically favored (by 11 kcal/mol).9

(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) biphensyls, on the other hand, reductively couple to form C–C bonds.11 (v) In contrast, reductive H–C coupling occurs readily from Pt(II) complexes.12,13

Pt(H)(CH3)2(PR3)2 → Pt(PR3)2 + CH4

(3)

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 observed14 only for

Pt(PR3)2 + H2 → Pt(H)2(PR3)2

(5)

and 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 Pt(CH3)2(PH3)2 (1), Pt(CH3)2(PR3)2 (2), Pt(Cl)(CH3)2(PH3)2 (3), Pt(Cl)(PR3)2 (4), Pt(H)(CH3)2(PH3)2 (5), and Pt(H2)(PH3)2 (6) and for the reductive coupling products

Table 1. Mulliken Populations for the GVB Bond Pairs of M(R)(R)4 populations in GVB bond orbitals

<table>
<thead>
<tr>
<th>M–CH3</th>
<th>M–H or M–Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pt(CH3)2(PH3)2</td>
<td>0.2p^2 + 0.1p^0 + 0.11</td>
</tr>
<tr>
<td>2. Pt(CH3)2(PR3)2</td>
<td>0.1p^2 + 0.1p^0 + 0.11</td>
</tr>
<tr>
<td>3. Pt(Cl)(CH3)2(PH3)2</td>
<td>0.1p^2 + 0.1p^0 + 0.04</td>
</tr>
<tr>
<td>4. Pt(Cl)(PR3)2</td>
<td>0.1p^2 + 0.1p^0 + 0.04</td>
</tr>
<tr>
<td>5. Pt(H)(CH3)(PR3)2</td>
<td>0.1p^2 + 0.1p^0 + 0.04</td>
</tr>
<tr>
<td>6. Pt(H2)(PH3)2</td>
<td>0.1p^2 + 0.1p^0 + 0.04</td>
</tr>
<tr>
<td>7. Pt(H2)(PR3)2</td>
<td>0.1p^2 + 0.1p^0 + 0.04</td>
</tr>
<tr>
<td>8. Pt(H2)(PH3)2</td>
<td>0.1p^2 + 0.1p^0 + 0.04</td>
</tr>
</tbody>
</table>

* 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. 2 Reference 2c.
coupling from \( \text{Mt}(\text{H})_2 \), \( \text{Mt}(\text{H})(\text{CH}_3) \), and \( \text{Mt}(\text{CH}_3)_2 \) complexes (where \( \text{Mt} = \text{Pd} \) or \( \text{Pt} \)) are used to estimate the energetics and

\[
\Delta H_{\text{exo}} = 1.25 \text{ kcal/mol} \quad \text{and} \quad \Delta S_{\text{exo}} = 52.4 \text{ eu} \text{ and ethane} \quad (\Delta H_{\text{exo}} = -20.2 \text{ kcal/mol} \quad \Delta S_{\text{exo}} = 54.9 \text{ eu}) \text{ rather than to reductively eliminate to give \( n \)-butane} \quad (\Delta H_{\text{exo}} = -82.0 \text{ kcal/mol} \quad \Delta S_{\text{exo}} = 74.1 \text{ eu}) \text{ even though } n\text{-propane is the thermodynamically favored product} \quad (\Delta H_{\text{exo}} = -22.5 \text{ kcal/mol} \quad \Delta S_{\text{exo}} = -33.2 \text{ eu} \quad \Delta S_{\text{exo}} = -12.5 \text{ kcal/mol for C}_4\text{H}_8 \to \text{C}_4\text{H}_10). \text{ The } \Delta H_{\text{exo}} \text{ and } \Delta S_{\text{exo}} \text{ were taken from ref 9b. } (\text{Benson}, \text{ S. W. Thermochemical Kinetics}, 2nd ed.; \text{Wiley: New York}, 1976, p 295.)
\]

(10) \text{Chatt, J.; Shaw, B. L. J. Chem. Soc. 1959, 705-716.}


\[
\begin{array}{cccccc}
\text{complex} & \text{M} & \text{sp} & \text{M} & \text{d} & \text{H} & \text{I} & \text{Cl} \\
\hline
1 & \text{Pd}(\text{CH}_3)_2(\text{PH}_3)_2 & 0.73 & 8.89 & 9.13 & 8.06 \\
2 & \text{Pd}(\text{CH}_3)(\text{PH}_3)_2 & 0.33 & 9.09 & 9.20 & 8.10 \\
3 & \text{Pt}(\text{CH}_3)(\text{CH}_3)(\text{PH}_3)_2 & 1.12 & 8.57 & 8.86 & 8.02 & 7.28 \\
4 & \text{Pt}(\text{CH}_3)(\text{PH}_3)_2 & 0.80 & 8.83 & 7.92 & 7.25 \\
5 & \text{Pt}(\text{CH}_3)(\text{CH}_3)(\text{PH}_3)_2 & 0.85 & 8.99 & 9.12 & 0.85 & 7.28 \\
6 & \text{Pt}(\text{CH}_3)(\text{PH}_3)_2 & 0.96 & 9.10 & 0.98 \\
7 & \text{Pt}(\text{PH}_3)_2 & 0.38 & 9.51 & 8.07 \\
8 & \text{Pt}(\text{PH}_3)_2 & 0.19 & 9.63 & 8.09 \\
9 & \text{Pt}(\text{H})(\text{CH}_3)_2 & 1.16 & 9.15 & 0.85 \\
10 & \text{Pt}(\text{H})(\text{PH}_3)_2 & 1.05 & 9.03 & 0.94 & 8.89 \\
11 & \text{Pt}(\text{H})(\text{CH}_3)_2 & 0.97 & 8.91 & 9.06 \\
12 & \text{Pt}(\text{H})(\text{CH}_3)_2 & 0.60 & 9.15 & 9.13
\end{array}
\]

\( ^4 \text{This is the average occupation of the PH}_3 \text{ groups in this complex. The PH}_3 \text{ group trans to CH}_3 \text{ has 8.04 e}^\circ \text{ and the PH}_3 \text{ group trans to H has 8.06 e}^\circ. \text{ Reference c.} \)


(14) \text{Parensa, R. S.; Trogler, W. C. J. Am. Chem. Soc. 1982, 104, 1138-1140.}
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1. Pt(II) Systems. The Pt–CH₃ bond orbitals (from GVB calculations) of 1–3 and 5 are shown in Figures 1–4, the Pt–Cl orbital 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 Pt–CH₃ bonds are covalent, with one electron in an sp³ hybrid orbital on the CH₃ and one electron in an spd hybrid orbital (60–75% d) mainly on the metal.

2. The Pt–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 Pt–Cl bonds are partially ionic, with one electron in a CI pz orbital and the other electron in an orbital that is partly on the CI and partly on the metal (spd hybrid with 30–50% d character).

4. There are generally about 10 electrons on the metal with character corresponding to either (i) the atomic d⁰ configuration for 7 and 8 (generally denoted as Mt(0)), (ii) the atomic s¹d⁹ configuration for 1, 2, and 4–6 (generally denoted as Mt(I)), or (iii) the atomic s²d⁸ configuration for 3 (generally denoted as Mt(IV)).

This focus on the 10-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. The methyl orbital of the Pt–CH₃ bond pair is 89% on the C atom (18% s and 71% p or s¹p⁴). The HCH bond angles (108°, 108°, and 110°) are very close to the tetrahedral bond angles expected for the 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 105°, 109°, and 110°. 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.

The major effect of the phosphines here is to decrease the Pt d character (69–60%) and Pt s character (30% to 28%), to increase the Pt p character (1–12%), and to increase the charge transfer to the methyl (0.06–0.13 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 d⁰ configuration.

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 (Pt¹H⁻))...
by an amount corresponding to a transfer of 0.26 e\textsuperscript{−} to H, whereas
the Mulliken population indicates a positive charge on H of 0.1 e\textsuperscript{−}.\textsuperscript{16} 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\textsuperscript{−} total charge). The total populations on the Pt for 1 lead to (sp)\textsuperscript{0.71}(d)\textsuperscript{0.29}, reasonably consistent with the characterization as s\textsuperscript{1}d\textsuperscript{9}. The description of the two M–C bonds as covalent is in reasonable agreement with the Pauling electronegativities\textsuperscript{16} (2.2 for Pt and 2.5 for C).

Changing the metal atom from Pt in 1 to Pd in 2 leads to a small increase in charge transfer to CH\textsubscript{3} (0.13 vs. 0.20 e\textsuperscript{−}) and to PH\textsubscript{3} (0.06 vs. 0.10 e\textsuperscript{−}), to a decrease in sp population (0.73 vs. 0.33 e\textsuperscript{−}), and to a slight increase in d population (8.89 vs. 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 the 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, when 1 (Pt) and 2 (Pd) are compared, the metal part of the M–CH\textsubscript{3} bond orbital has 0.17 vs. 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 analyze the differences between Pt–CH\textsubscript{3} and Pt–Cl bonds. The net effect of replacing both CH\textsubscript{3}s 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 (vs. 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%).

In summary all complexes that would be described as Mt(II) in the normal oxidation state formalism are unoxidized and have s\textsuperscript{1}d\textsuperscript{9} 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° 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}) capable 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\textsuperscript{1}d\textsuperscript{8} state of Pt (as well as Ni and Pd). In the d\textsuperscript{10} state of Pt, the Hartree–Fock (HF) description has give 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., dxz) 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\textsuperscript{10} in terms of 10 orbitals for the 10 electrons, while HF uses 5 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\textsuperscript{10} state as if there were five doubly occupied orbitals.

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(16) Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell
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 as 10 orbitals for the 10 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^1d^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 10 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 CH_3), leading to a 180° bond angle. Indeed, the triplet state of PtH_3, Pt(CH_3)_2, and PtCl_3 should be linear, being formed by bonding to these sp hybrids, leaving a d^9 configuration (probably 3A). (For Ni there should also be similar strongly bound triplet states; however, for Pd the very high energy of the s^1d^9 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 s^1d^9. Electronegative ligands favor bonding to the sp hybrid orbitals since the ionization potential of the s orbital is 2.79 eV lower (leading to Pt^+ s^1d^9) than the d orbital (leading to Pt^+ s^1d^8). Thus, in 3 we expect the Pt–Cl bonding to favor Pt sp, while Pt–CH_3 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 CH_3 groups as cis.) Comparing the M–Cl bonds in 4 and 3, we see an increase in ionic character for 3 (for the metal–ligand the number of electrons on the Cl increases from 0.27 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 → 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 metal orbital decreases from 0.89 to 0.78 e). Simultaneously, the d character in the metal part of the bond pair increases dramatically (60–74%), 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^1d^7 configuration, having two sp hybrid pairs as in Mg, Al, and Si.

This state is the only one that can allow the Pt atom to form four covalent bonds: two bonds to singly occupied d orbitals and two bonds to the pair of sp lobe orbitals. The Mulliken populations for 3 are ambiguous in assigning the electronic configuration of the 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 (0.28 e^-) make the Pt atom appear intermediate between s^1d^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 sp orbitals, we obtain a charge of 1.68 for sp and 8.05 for d, reasonably close to s^1d^8. The bonding in this Pt(IV) complex is essentially covalent, which should not be too surprising since the Pauling electronegativities for Pt is 2.2 vs. 3.0 for Cl and 2.5 for carbon.

3. Mt(0) Systems. The ground state of Pd(0) is s^1d^10, with the (triplet) s^1d^9 configuration 21.9 kcal/mol higher^{18} (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^{18} (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 Pt than for Pd by 21.9 + 11.0 = 32.9 kcal/mol (calculated value 31.9 kcal).

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

\[ \text{Pt}(R_1)(R_2) \rightarrow \text{Pt} + R_1R_2 \]

is d^10 in both cases. Adding two phosphines stabilizes d^10 with respect to s^1d^9 so that the ground state of Mt(PH_3)_2 is the linear d^10 singlet for both Mt = 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 Mt(PH_3)_2 is about 20–25 kcal/mol more exothermic for both Mt = 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 the 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^1d^8 configuration, forming four covalent bonds. We will find this view to be quite useful in rationalizing the relative reaction energetics of Pt(II) vs. Pd(II) and of Pt(II) vs. 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 wave functions (which give accurate s^1d^8-d^10 state splittings) at geometries optimized for HF wave functions (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

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

\[ \Delta H_f = -11.3 \text{ kcal/mol} \]

(18) Moore, C. E. Atomic Energy Levels; National Bureau of Standards: Washington, DC, 1971; Vol. III. (These state splittings were averaged over J states to cancel out spin–orbit coupling.)
which can be compared to
\[ \text{Pt}(\text{CH}_3)_2 \rightarrow \text{Pt} + \text{C}_2\text{H}_6 \] (8)
\[ \Delta H_8 = 15.5 \text{ kcal/mol} \]

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'd^9 configuration for the reactant side of (7) and (8) but a d^10 configuration for the product side. As discussed in section II.A.3, phosphines stabilize d^0 relative to s'd^9, leading to a more exothermic reaction.

Consider next the analogous reactions with Pd,
\[ \text{Pd}(\text{CH}_3)_2(\text{PH}_3)_2 \rightarrow \text{Pd}(\text{PH}_3)_2 + \text{C}_2\text{H}_6 \] (9)
\[ \Delta H_9 = -45.8 \text{ kcal/mol} \]

which can be compared to
\[ \text{Pd}(\text{CH}_3)_2 \rightarrow \text{Pd} + \text{C}_2\text{H}_6 \] (10)
\[ \Delta H_{10} = -18.8 \text{ kcal/mol} \]

The reaction enthalpies differ dramatically from those of Pt; however, these differences are easily explained. All four reactions involve converting the metal from s'd^9 to d^10, but using d^0 as the reference Pt favors s'd^9 by 12.3 kcal/mol, whereas Pd disfavors s'd^9 by 19.6 kcal/mol. Thus, relative to Pt, Pd has a bias against s'd^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 bis(phosphine) and 34.3 kcal/mol for the unsubstituted metal.

These results for Mt(II) can be compared to the Mt(IV) reaction,
\[ \text{Pt}(\text{CH}_3)_2(\text{Cl})_2(\text{PH}_3)_2 \rightarrow \text{Pt}(\text{Cl})(\text{PH}_3)_2 + \text{C}_2\text{H}_6 \] (11)
\[ \Delta H_{11} = -27.0 \text{ kcal/mol} \]

Here the metal changes from s'd^9 to s'd^8, which for the free atom is exothermic by 17.2 kcal/mol. Comparing to (7) which involves s'd^9 to d^10, which is endothermic in the atom by 12.3 kcal/mol, we would expect from atomic considerations that (11) should be 29.5 kcal/mol more exothermic than (7). Of course the four-coordinate Pt(II) and six-coordinate Pt(IV) also differ in other respects; however, we find that (11) is 16 kcal/mol more exothermic than (7), so that the atomic change of configuration effects dominate.

On the basis of differential atomic excitation energies, the Pd analogue of (11) 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 Pt(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'd^9, d^10, and s'd^8 configurations.

2. Calculated Energetics for C-H Reductive Coupling. We calculate that
\[ \text{Pt}(\text{H})(\text{CH}_3)(\text{PH}_3)_2 \rightarrow \text{Pt}(\text{PH}_3)_2 + \text{CH}_4 \] (12)
\[ \Delta H_{12} = -5.8 \text{ kcal/mol} \]

whereas
\[ \text{Pt}(\text{H})(\text{CH}_3) \rightarrow \text{Pt} + \text{CH}_4 \] (13)
\[ \Delta H_{13} = 19.0 \text{ kcal/mol} \]

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
\[ \text{Pd}(\text{H})(\text{CH}_3) \rightarrow \text{Pd} + \text{CH}_4 \] (14)
\[ \Delta H_{14} = -17.2 \text{ kcal/mol} \]
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Table IV. Average Bond Energies for M(R2) Complexes (kcal/mol)

<table>
<thead>
<tr>
<th>M-H</th>
<th>M-CH3</th>
<th>difference in M-H and M-CH3 bond energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = Pt</td>
<td>-12.3</td>
<td>53.0</td>
</tr>
<tr>
<td>M = Pd</td>
<td>+19.0</td>
<td>35.8</td>
</tr>
<tr>
<td>M = Pt(PH3)2</td>
<td>+32.1*</td>
<td>39.6</td>
</tr>
<tr>
<td>M = Pd(PH3)2</td>
<td>+57.2*</td>
<td>22.3</td>
</tr>
<tr>
<td>M = Pt(Cl2)(PH3)2</td>
<td>38.6*</td>
<td>31.7</td>
</tr>
<tr>
<td>M = Pd(Cl2)(PH3)2</td>
<td>(84.0)*</td>
<td>(10.0)</td>
</tr>
</tbody>
</table>

*Based on the geometry of the M(CH3)2 complex. Based on ΔE = 38.6 kcal for the Pt complex plus the differential d5s1 to d6s1 energy (45.4 kcal).

but did not calculate the H-C coupling from the bis(phosphine). However, the above results suggest that for Pd the bis(phosphine) would promote H-C reductive coupling by ~25.0 kcal/mol, leading to

\[ \text{Pd(H)(CH3)(PH3)2} \rightarrow \text{Pd(PH3)2} + \text{CH4} \] (15)

\[ \Delta H_{15} \approx -42.2 \text{ kcal/mol} \]

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 suggest that

\[ \text{Pt(H)(CH3)2(Cl)(PH3)2} \rightarrow \text{Pt(Cl)(PH3)2} + \text{CH4} \] (16)

\[ \Delta H_{16} \approx -19.5 \text{ kcal/mol} \]

while the analogous Pd complex would not be stable.

3. Calculated Energetics for H-H Reductive Coupling. We calculate that

\[ \text{Pt(H2)(PH3)2} \rightarrow \text{Pt(PH3)2} + \text{H}_2 \] (17)

\[ \Delta H_{17} = 12.3 \text{ kcal/mol} \]

whereas

\[ \text{Pt(H2)} \rightarrow \text{Pt + H}_2 \] (18)

\[ \Delta H_{18} = 33.2 \text{ kcal/mol} \]

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

\[ \text{Pd(H2)} \rightarrow \text{Pd + H}_2 \] (19)

\[ \Delta H_{19} = -4.0 \text{ kcal/mol} \]

but did not calculate the reductive H-H coupling from the bis(phosphine). However, the above results suggest that the phosphines would promote H-H coupling on Pd by about 21.1 kcal/mol, leading to

\[ \text{Pd(H2)(PH3)2} \rightarrow \text{Pd(PH3)2} + \text{H}_2 \] (20)

\[ \Delta H_{20} \approx -25 \text{ kcal/mol} \]

We did not calculate the energetics of H-H coupling from Pt(IV) or Pd(IV) complexes; however, we estimate that

\[ \text{Pt(H2)(Cl)(PH3)2} \rightarrow \text{Pt(Cl)(PH3)2} + \text{H}_2 \] (21)

\[ \Delta H_{21} \approx 25 \text{ kcal/mol} \]

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,19 the exothermicity of 11.3 kcal/mol for (7) leads to an average Pt-C bond energy of

\[ D_{298}([PH3]_2Pt-CH3) = 39.6 \text{ kcal/mol} \] (22)

Similarly, since the H-H bond energy is 104.2 kcal/mol,19a the energetics in (17) correspond to an average Pt-H bond energy of

\[ D_{298}([PH3]_2Pt-H) = 58.3 \text{ kcal/mol} \] (23)

As a check upon the utility of such average bond energies, we can use (22) and (23) plus the C-H bond energy in CH4 (105.1 kcal/mol)\(^{19b}\) to predict

\[ \Delta H_{12} = 39.6 + 58.3 - 105.1 = -7.2 \text{ kcal/mol} \]

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

The average bond energies for the bare metal are obtained from (8) and (18) as

\[ D_{298}(Pt-CH3) = 53.0 \text{ kcal/mol} \] (24)

\[ D_{298}(Pt-H) = 68.7 \text{ kcal/mol} \] (25)

which leads to a prediction of

\[ \Delta H_{13} = 53.0 + 68.9 - 105.2 = +16.5 \text{ kcal/mol} \]

in reasonable agreement with the calculated value of ΔH13 = 19.0 kcal/mol.

The average bond energies for Pt complexes are calculated to be about 18 kcal/mol lower (see Table IV) because of the propensity for Pt to form d10 configurations.

Averaging the results for Pt and Pd, we find that M-H bonds are 18 kcal/mol stronger than M-CH3 bonds for the bis(phosphine) and 15 kcal/mol stronger for the bare metal. Thus, the phosphines lead to a relative weakening of M-CH3 vs. 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,

\[ D_{298}([Cl2](PH3)2Pt-CH3) = 31.7 \text{ kcal/mol} \] (26)

As discussed above, this 8 kcal/mol decrease from the value for Pt(II) is dominated by the preference of Pt convert from s4d0 to s5d1.

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 \( D_{298} \). Thus, for example, the C-H bond energy of cyclopropane is 11 kcal/mol stronger\(^{20}\) than for H-CH(CH3), 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 \( \pi \) orbital on each carbon corresponding to the \( \beta \) 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/mol\(^{20}\) is electronically diabatic (it involves a small amount of

\[ \Delta E = 38.6 \text{ kcal for the Pt complex plus the differential d5s1 to d6s1 energy (45.4 kcal).} \]

\[^{19} \text{The ΔE used in these calculations are ΔE}_{298}(H-H) = 104.2 \text{ kcal/mol, ΔE}_{298}(H-C) = 105.1 \text{ kcal/mol, and ΔE}_{298}(H-C-H) = 90.4 \text{ kcal/mol. These bond energies were derived from spectroscopic measurements of H,}^{19a} \text{and the reported D}_{298}^{19b} \text{ for H2-C2H and H2-CH3.} \]

\[^{19a} \text{Huber, K. P.; Herzberg, G. Constants of Diatomic Molecules; Van Nostrand: New York, 1979.} \]


\[^{20} \text{D}_{298}(\text{cyclopropyl-H}) = 106.3 \text{ kcal/mol,}^{19a} \text{D}_{298}(\text{H-C(H2)C-H}) = 195.1 \text{ kcal/mol.}^{19b}\]

but the Pt atom no doubt retains s^d^d character. Thus, the exo-
thermicity of (28) 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^d^d. 
Thus, the theory and experiment are in reasonable agreement.

C. Barriers and Rates. In previous studies of

\[ DI = \frac{1}{2}[\Delta H(MR_2 \rightarrow M + R_3) + bE(M \rightarrow M) + D_{298}[R-R]] \]  

(27)

where \( bE(M \rightarrow M) \) is the singlet–triplet excitation energy 
described above, \( M \) is the singlet metal complex product in its 
ground-state geometry, and \( M \) 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^d^d and d^10 states and 
of bent vs. linear phosphines. Comparing the intrinsic Mt–R bond 
strengths of bis(phosphine) complexes (e.g., 56 kcal/mol for 
Pt(CH_2)(PH_3)_2) and the corresponding MR_2 complexes (e.g., 
47 kcal/mol for PtMe_2), it 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, increasing the intrinsic 
barrier strength. On the other hand, the phosphines lead to a 
decrease in the adiabatic bond energies (from 53 kcal/mol for 
Pt(CH_2)(PH_3)_2 to 40 kcal/mol for Pt(CH_2)(PH_3)). This is probably 
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^III–C 
bond in bis(phosphine) complexes. This is probably because the 
Pt 6s character of the Pt^IV–C bond 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 (~60% d and 40% sp) that is available in the 
platinum(II) bis(phosphine) complex.

Few bond strengths are known experimentally for Pt–C or 
Pd–C. From studies of the decomposition of PtMe_2Cp, an 
experimental Pt–CH_3 bond energy of 39 ± 5 kcal/mol has been 
determined. This is an adiabatic bond energy, 

\[ PtMe_2Cp \rightarrow *Me^+ + PtMeCp \]  

(28)

but the Pt atom no doubt retains s^d^d character. Thus, the exo-
thermicity of (28) 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^d^d. 
Thus, the theory and experiment are in reasonable agreement.

Consequently, at the transition state the CH_3 group has an 
intermediate orientation which is less favorable for both 10 and 11, 
leading to a significant barrier. If R_1 = R_2 = 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^d^d, making reductive coupling about 23 kcal/mol more exo-
thermic (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 equal
part of the d^{10} and s^d 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 1 and Figure 8.

Particularly clean experiments have been carried out for H-C coupling from Pt(II), for which we estimate \( \Delta H^\ddagger = 15.7 \) kcal/mol. This can be compared to cis-Pt(H)(CH2CF3)(PPh3) → Pt(PPh3)2 + CH3CF3 (30) where in benzene solvents \( \Delta H^\ddagger = 24.6 \pm 0.6 \) and \( \Delta S^\ddagger = 4.9 \pm 2.0 \), and to cis-Pt(H)(CH2)(PPh3)2 → Pt(PPh3)2 + CH4 (31) where (in toluene at \(-25^\circ C\)) \( \Delta G^\ddagger = 18.2 \). Assuming \( \Delta S^\ddagger = 5 \), this latter value leads to \( \Delta H^\ddagger = 17.0 \) kcal/mol, in good agreement with our predictions.

Other relevant activation energies have been measured by Moravskiy and Stille for reductive elimination of ethane from cis-Pd(CH3)(PPh3)2. They find activation energies (\( E_\ddagger \)) of 6-11 kcal/mol in polar-coordinating solvents (Me2SO-d6, Me2CO-d6, and CD3CN) and 25-28 kcal/mol in aromatic solvents (C6D6 and C6D5CH3). It is uncertain how to compare these numbers with our calculations since it is likely that reductive elimination does not proceed directly from the bis(phosphine) complex (see section III.A). However, we estimate \( \Delta H^\ddagger = 10.4 \) kcal/mol (at 300 K), and hence the estimated barrier (at 300 K) is \( E_\ddagger = \Delta H^\ddagger + RT = 10.7 \) kcal/mol, surprisingly close to the \( E_\ddagger \) measured in coordinating solvents.

On the other hand, our estimates lead to \( \Delta H^\ddagger = 41 \) kcal/mol for C-C coupling on Pt(II), certainly consistent with the lack of observation of this reaction.

The calculated endothermicity (\( \Delta H^\ddagger = 12.3 \) kcal/mol) and barrier (\( \Delta H^\ddagger = 14.0 \) kcal/mol) for H-H coupling from Pt(II) are consistent with the equilibrium observed in such systems by Troger. On the other hand, our calculations suggest that cis-Pd(H)(CH3)(PPh3)2 and cis-Pd(H)(CH2)(PPh3)2 would have no barrier for decomposition and hence should not be stable.

The estimated barriers for Mt(IV) complexes are much more uncertain since barriers were not calculated even for complexes without phosphines. In this case we have assumed that half of the addition exothermicity relative to Mt(II) goes into the transition state.

Brown et al. have measured \( E_\ddagger \) for the reductive elimination of ethane from various Pt(IV) trimethyl complexes. They find \( E_\ddagger = 27.7 \pm 1.2 \) for reductive elimination from PtCl(CH3)3, (PMe3Ph)2 at 353 K. Our estimate is \( E_\ddagger = 34.9 \) kcal/mol (\( \Delta H^\ddagger = 34.2 \) kcal/mol) for elimination from PtCl2(CH3)3, (PMe3Ph)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 \( \Delta H^\ddagger = 9 \) 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
Table V. Geometric Parameters around the Metal Atom in Pt and Pd Complexes (All Distances Are in Å and All Angles Are in deg)

<table>
<thead>
<tr>
<th>molecule</th>
<th>distances</th>
<th>angles</th>
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</thead>
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<tr>
<td></td>
<td>M-P</td>
<td>M-C</td>
</tr>
<tr>
<td>1, Pt(CH3)2(PH3)2</td>
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<td>2.06</td>
</tr>
<tr>
<td>2, Pd(CH3)2(PH3)2</td>
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<td>2.02</td>
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<td>2.03</td>
</tr>
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<td>4, PtCl2(PH3)2</td>
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<tr>
<td>5, Pt(H)(CH3)(PH3)2</td>
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</tr>
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<td></td>
</tr>
<tr>
<td>7, Pt(PH3)2</td>
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<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>Pt(H)(CH3)(PH3)2</td>
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<td></td>
</tr>
<tr>
<td>Pt(H)2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(CH3)2</td>
<td>1.96</td>
<td></td>
</tr>
</tbody>
</table>

*This geometry was not optimized but was estimated from the geometries 1 and 6. The geometries of the Pt(CH3)(PH3)2 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. *Reference 2a. *Reference 2c.

Figure 9: ORTEP plot of 1 and 2.

Figure 10: ORTEP plot of 3.

coupling facile for Pd(II) and unobserved for Pt(II). In addition, it is known that Pt(IV) dimethyl, trimethyl, and tetramethyl complexes will reductively eliminate ethane, while Pt(II) dimethyl complexes do not. 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 vs. C-H vs. H-H coupling. Given the results for one metal, these ideas may be used to predict the results on other metals by using only atomic data.

D. Geometries. The geometries for all molecules studied in this work have been optimized for the HF wave functions by using analytic gradient techniques. The fully optimized HF geometries of I (Pt(Me)2(PH3)2), 2 (Pd(Me)2(PH3)2), and 3 (Pt(Me2)2Cl2(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 supplementary material. 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 (Pt–C sp3) 2.09 Å and is in the range observed in X-ray structures of Pt(II) dialkyl complexes, an average of 2.05 Å in PtMe4 (μ-dppm)22c (dppm = Ph3PCH2PPh3); 2.18 and 2.15 Å in PtMe2 (tripod) (tripod = 1,1,1-tris(diphenylphosphinomethyl)ethane);24a and 2.05 and 2.12 Å in Pt(C4H8(PPh3))2.25

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 structures of Pt2Me6(μ-dppm)2 (81.6°) and Pt(C4H8(PPh3))2 (80.9°).25 This difference is most likely due to the PPh3 ligands having less steric bulk than substituted phosphines.

The calculated Pt-CI bond distance in 4 of 2.35 Å and the Cl-Pt-CI bond angle of 91° match very well with the observed Pt-CI distances (2.368 and 2.377 Å) observed in the X-ray structure of cis-Pt(PMe3)2Cl2.26

The calculated Pt-P bond distances are 0.1–0.2 Å longer than experiment (Pt–P = 2.23 and 2.24 Å in PtCl2(PMe3),26 vs. 2.44 Å calculated for (4); 2.279 and 2.285 Å in Pt(C4H8(PPh3))227 vs. 2.46 Å calculated in (1)). This is systematic for Pt–P bonds at this level of calculation26 and may be partially due to the effect of substituted phosphines vs. PPh3. 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 vs. 98.9° in Pt(C4H8(PPh3))2 and 102° in 9 vs. 96.2° in PtCl2(PMe3))26.

Noell and Hay46 were the first to show that HF wave functions yield geometries of Pt and Pd complexes which compare well with X-ray structures, indicating that HF is a reasonable level of wave function with which to optimize geometries.


III. Discussion

A. 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 PdMe₂L₆,⁶ and AuMe₂L₁₀,¹¹²³ experiment shows that reductive elimination of ethane is retarded by added phosphine. This led Hoffman et al.¹⁴ 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

\[ \text{Pd}(\text{CH₃})₂(\text{CH}=\text{CHPh})(\text{PH₃})₂ \rightarrow \text{CH₃CH}=\text{CHPH} + \text{P}(\text{PH₃})₂ \] (32)

\[ \text{Ni}(\text{CH₃})₂(\text{DIPHOS}) \rightarrow \text{Ni}(\text{DIPHOS}) + \text{CH₃H₄} \] (33)

(DIPHOS = PH₃(CH₂)₂PH₃), where the addition of phosphine does not affect 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 cis-NiP(C₆H₅)(CH₃)DPE (14) and cis-Pt(C₆H₅Me₂-4)(P₂H₂)₃ (15), where reductive coupling of C−C bonds is promoted by the addition of phosphines.³⁰,³¹ This led Braterian and Cross¹⁰ to propose a mechanism by which reductive elimination proceeds through a five-coordinate intermediate, a mechanism that was also supported by EH calculations of Tsutsumi et al.³²,³³

Our calculations on reductive elimination of ethane from PdR₂ and PtR₂ show that reductive elimination is favored energetically from PdR₂ because Pd prefers the d¹⁰ configuration.²⁴ It is interesting to note that the difference in ΔH° for elimination of CH₃H₄ from Pd(CH₃)₂ and Pt(CH₃)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 reductive elimination of C−C bonds is strongly coupled to the driving force. Since phosphines stabilize d¹⁰ relative to d⁸, we 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 decomposition of AuMe₃L. In some solvents (e.g., benzene, decalin, PhCl, n-Bu₂0, and tetrahydrofuran (THF)),²⁶ More strongly coordinating solvents (Me₂SO and dimethylformamide (DMF)) appear to block intermolecular paths, resulting in very little driving force for reductive elimination.

For reductive elimination of ethane from Pd(CH₃)₂L₂, crossover experiments show that reductive elimination of ethane is intramolecular only in Me₂SO or noncoordinating solvents containing dimethyl maleate (DMM).⁴ It has been assumed that DMM serves to trap the PdL₃ product before it can decompose (and thereby affect the decomposition pathway); however, Ozawa et al.⁴¹ have shown that variation in the 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 a rate-determining step in the formation of the four-coordinate intermediate in which one of the phosphines is replaced by Me₂SO, 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.³¹ Apparently reductive elimination of CH₃CH₂=CHPH from Pd(CH₃CH₂=CHPH)(P₂H₂)₃ is not affected by added phosphine because the ΔG° for elimination from the four-coordinate starting complex is lower than the ΔG° 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 relative to four-coordinate complexes, these predicted trends in activation energies do not correlate with our observed correlation of ΔG° and ΔE. EH calculations are well-known to not give accurate geometries and energetics and should not be considered as proof for the proposed mechanisms. What is needed are ab initio calculations of the relative barriers of reductive elimination from three-, four-, and five-coordinate intermediates.

B. Reactivity of Metal−Carbon Bonds Involving sp² Hybrids vs. sp³ 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(CH₃)(C₆H₅)L₂ is faster than from cis-Ni(CH₃)₂L₂ complexes.²⁸ The reaction of PhLi with PdCl₂(DIPHOS) yields biphosphine directly, whereas MeLi reacts with PdCl₂(DIPHOS) to give PdMe₂(DIPHOS) which eliminates ethane slowly.²⁸ Platinum diphosphinylbis(phosphine) complexes can eliminate biphosphine,³¹ while platinum dimethyl complexes cannot. Although this trend can be explained by noting that the phenyl group uses a C sp³ hybrid orbital to form bonds, while the methyl group uses a C sp² hybrid orbital. The increased s character of the sp³ hybrids causes this orbital to be less directional than the sp² hybrids. Therefore, the sp³ hybrid can have more multicentered bonding at the transition state, leading to lower activation energies for CH₃CH₂=CHPH, CH₃CH₂=CHPH, and PhCH₂Ph coupling. It should be noted that Th-Ph bond energies are 11.4⁶⁺ and 26 kcal/mol stronger than the H₃C=CH₂ bond energy (90.4 kcal/mol).²⁸ Thus, if the Mt−CH₃ and Mt−Ph bond energies were approximately the same, this would lead to a larger driving force for reductive elimination of sp² species. Evans et al. have made a thermochemical estimate for the Pt−Ph bond energy of 63.1³⁴ that is 7 kcal/mol stronger than our calculated Pt−CH₂ intrinsic bond energy. This value for the bond energy is, however, strongly dependent on their estimated Pt−Cl bond energy in PtCl₂(P₂H₂)₃ (which was assumed to be the same as the Pt−Cl bond energy in PtCl₂), 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 from Th₃R₂(Cp³)₂ complexes demonstrate that Th−Ph bond energies are 13 kcal/mol stronger than Th−CH₂ bond energies. Therefore, it does appear that diphenyl and methylphenyl complexes have approximately the same thermodynamic stability for reductive elimination as dimethyl complexes.

Either of the above interpretations for the increased lability of sp² vs. sp³ carbons would suggest that alkylnyl groups will reductively eliminate faster than phenyl or vinyl groups. Indeed, Pt−CC≡C−C≡C−Ph has been indentified in the decomposition products of cis-Pt−(C≡C−C≡C−Ph)₂Cl₂. (35) The decomposition of dialkynyl complexes should help establish the trend of sp hybridization vs. rate of reductive elimination.

C. Heat of Formation of Pt(II) and Pt(II) Salts.

We have found that the difference in enthalpies (ΔH°) for reductive elimination from the corresponding Pt(II) and Pt(II) compounds

Table VI. Enthalpies (kcal/mol at 298 K) for Pt(II) and Pd(II) Salts

<table>
<thead>
<tr>
<th>compd</th>
<th>$\Delta H^\circ [\text{PtX}_2(s)]$</th>
<th>$\Delta H^\circ [\text{PtX}_2(\text{aq})]$</th>
<th>$\Delta H^\circ [\text{Pt}(\text{S}) + \text{X}_2(g) \rightarrow \text{PtX}_2(s)]$</th>
<th>$\Delta H^\circ [\text{Pd}(\text{S}) + \text{X}_2(g) \rightarrow \text{PdX}_2(\text{aq})]$</th>
<th>$\Delta (\Delta H)$</th>
</tr>
</thead>
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<td>MtCl$_2$</td>
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<td>MtBr$_2$</td>
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</tbody>
</table>

All $\Delta H$ are from ref 36, except as noted. $^b \Delta H^\circ_{\text{Me}(\text{H}_2\text{O})_2} = -32.53$ kcal/mol: Stull, D. R.; Prophet, H. JANAF Thermochemical Tables, 2nd ed.; National Bureau of Standards: Washington, DC, June 1971; NSRDS-NBS 37. $\Delta H^\circ_{\text{Pd}(\text{S})} = 121.6$ kcal/mol at 25°C. $\Delta H^\circ_{\text{Pd}(\text{S}) + \text{O}_2(g) \rightarrow \text{PdO}(\text{S})}$ is 11.0 kcal/mol: consequently, $\Delta H^\circ_{\text{Pt}(\text{S}) + \text{O}_2(g) \rightarrow \text{PtO}(\text{S})}$ is 121.6 kcal/mol at 25°C. $\Delta H^\circ_{\text{Pd}(\text{S}) + \text{X}_2(g) \rightarrow \text{PdX}_2(\text{aq})}$ is 92.96 kcal/mol. The ground state of Pd is 1S; therefore, $\Delta H^\circ_{\text{Pd}(\text{S}) + \text{X}_2(g) \rightarrow \text{PdX}_2(\text{aq})}$ is 92.96 kcal/mol.  

is always within 5 kcal/mol of the difference in the $s^d$ $\rightarrow d^{10}$ splittings for these metals (33 kcal/mol). Unfortunately, there are no reliable atomic state splittings for these metals. Consequently, $\Delta H^\circ_{\text{Pt}(\text{S}) + \text{X}_2(g) \rightarrow \text{PtX}_2(s)}$ for Pt and Pd complexes available in the literature to provide a test of this theoretical trend. However, $\Delta H^\circ_{\text{Pt}(\text{S})}$s for various Pt(II) and Pd(II) salts are available.$^b$ Since Pt and Pd have the same covalent radii and electronegativities,$^b$ we can assume that the lattice energies for the corresponding PtX$_2$ and PdX$_2$ salts are the same. Therefore, the experimental $\Delta (\Delta H)$s are 3 $\pm$ 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 $\Delta H^\circ_{\text{Pt}(\text{S})}$s for these salts. D. Comparison with Other Theoretical Studies. Hoffmann et al.$^b$ 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 dimethylbis(phosphine) complexes.$^b$ Hoffman et al. stated three rules to be the following:

1. Stronger donor ligands that are trans to the leaving groups give a higher barrier for the elimination reaction.
2. Increased stability of the M$_2$A$_2$ orbital [where A indicates modified hydrogen 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 energy for the b$_2$ orbital of M$_2$A$_2$ results from a more stable metal d hybrid orbital used in the M-R bond. This will stabilize the $s^d$ 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 in the metal sd hybrid orbital used in the M-R bond. This will stabilize the $s^d$ configuration of the metal atom and reduce the driving force for reductive elimination. This is in agreement with Hoffman's first conclusion.

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scribed by using a double-\( \zeta \) contraction of the Huzinaga four-Gaussian basis scaled by a factor of 1.2. The active hydrogen bound to the metal atoms in the \( \text{Pt(H)(Me)(PH}_3 \) and \( \text{Pt(H)}_2 \text{(PH}_3 \) complexes was treated with a triple-\( \zeta \) contraction of the Huzinaga six-Gaussian basis. This was necessary to allow the hydrogen to adjust for optimum bonding to the metal atom in the restricted and optimum bonding to the methyl group or H atom in the product. The chlorine potential was the SHC potential of Rapp et al., and the double-\( \zeta \) contraction of the SHC basis was used for the metal atoms in the reactant and optimum bonding to the methyl group or H atom in the product. The chlorine potential was the SHC potential of Rapp et al., and the double-\( \zeta \) contraction of the SHC basis 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 \( \Delta \varepsilon \) 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\(^2\)d\(^2\) splitting of the metal atoms be accurately described. Although the level of basis can certainly be improved, it should be quite adequate for the purposes here, namely, the conceptual description of the differences between \( \text{Pt}(\text{II}), \text{Pt}(\text{IV}), \) and \( \text{Pd}(\text{II}) \) 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 the HONDO program (Dupuis, M.; King, H. F. 1978, 68, 3998–4004) to calculate derivatives of the ab initio terms in the energy expression, and (c) routines from the GAUSSIAN 86 program (Binkley, J. W.; Whitesides, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. 1980, 3998–4004) 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, W. A., III, unpublished results).

**C. Wave Functions.** 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

\[
\phi^{HF}(1, 2) = \psi(1)\psi(2)(n^2 - \beta a) \rightarrow \phi^{GVB}(1, 2) = \psi(1)\psi(2) + \psi(1)\psi(2)(n^2 - \beta a) \quad (34)
\]

When there are additional electron pairs, each may be correlated as in (34) so that the doubly occupied orbitals \( \psi_1, \psi_2, \text{etc.} \), of an HF wave function become singly occupied orbitals (as in (34)), \( \psi_1, \psi_2, \psi_3, \psi_4 \) of the GVB wave function. Although for HF wave functions 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 wave function is

\[
\alpha(\psi_1, \psi_2, \psi_3, \psi_4) = \chi \quad \chi = \alpha(\psi_1) \psi_2(\psi_3) \psi_4(\psi_5) \chi \quad (35)
\]

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 wave function. If 5 pairs of electrons are so correlated (using 10 orbitals), the wave function is denoted as GVB-PP(5/10); however, other orbitals of the wave function are understood to be calculated self-consistently. (This wave function would involve \( 5^2 = 25 \) different orbital configurations.) Such wave functions quite accurately describe systems where one valence bond structure is adequate (no resonance); however, for transition-metal systems, spin couplings other than (36) 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 (34)) or in the same orbital (e.g., \( \psi(1)\psi(2) \)). Allowing a similar description for all correlated pairs leads to the GVB-RCI wave function. Since there are three orbitals for each pair of electrons, the GVB-RCI(5/10) wave function has \( 3^5 = 243 \) orbital products. In addition to an optimized spin coupling, the RCI wave function includes important electron correlation effects in which two electrons in one bond pair can respond instantaneously to the motions of two electrons in another bond pair (interpair correlation). The orbitals of the GVB-RCI wave function can be solved self-consistently; however, it is generally adequate to use the orbitals of the GVB-PP wave function, 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

\[
\phi^{GVB-PP}(1, 2) = \psi(1)\psi(2)(n^2 - \beta a) \quad (34)
\]

where \( \chi \) is an optimized appropriate spin function for \( N \) electrons. However, when the GVB orbitals are calculated, it is generally convenient to choose \( \chi \) as the simple valence bond function (perfect pairing)
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-C1(2/4) description. Thus, 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 10 optimized orbitals for all states) leads to a rather accurate description of the relative energies for the d^6, d^5, and d^6 configurations and is particularly accurate for the d^5 vs. d^6, the states relevant for this paper. For the d^5 the state the s^2 pairs was correlated in the ax directions, and d^5 and the d^6 were singly occupied.

For the various M(R,R')(R') complexes, it is necessary to correlate not only the 10 metal valence electrons but also the additional electrons involved in the covalent M-R and M-R bonds. Thus, a total of 12 electrons or 6 electron pairs must be correlated. Consequently, we first carried out GVB-PP(6/12) calculations using 12 orbitals to correlate the motions of these 6 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,28 the energetics reported here were determined at the GVB-C1(2/4) × RCI(4/8) level.

In previous studies of the reaction path for reductive coupling, the necessity for the simultaneous description of both the reactant (s^2d^5) and the product (d^9) resonance structures in the transition-state region required the use of three orbitals (rather than two) for each of the two bond pairs that change during the reaction.29 Thus, rather than GVB(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-C1(2/6). The other four pairs of electrons were correlated as usual, leading to a composite wave function of the form GVB-C1(2/6) × 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 these two bond pairs (C1(2/4)). Thus, the wave function used in these studies is GVB-C1(2/4) × RCI(4/8).

Acknowledgment. This work was supported in part by a grant from the National Science Foundation (No. CHE83-18041). J.J.L. acknowledges financial support in the form of fellowships from Exxon and ARCO.

Registry No. 1, 79232-18-1; 2, 79218-06-7; 3, 103191-78-2; 4, 79239-16-1; 5, 79222-17-0; 6, 76832-29-6; 7, 76830-85-8; 8, 78452-79-6.

Supplementary Material Available: Cartesian coordinates for Pt- and Pd(CH3)2(PH3)2, PtC12(CH3)2(PH3)2, PtC12(PH3)2, Pt(H(CH3)2)(PH3)2, and Pt- and Pd(PH3)2 and internal coordinates of methyls and phosphines (8 pages). Ordering information given on any current masthead page.

Ribose Puckering: Structure, Dynamics, Energetics, and the Pseudorotation Cycle

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Abstract: We have examined the pucker dependence of ribose structure and ribose conformational energy in a set of 4800 configurations generated during a 304-K, 24-ps, in vacuo molecular dynamics simulation of phenylalanine transfer RNA. This data set spans all of the thermodynamically accessible regions of the northern (N), eastern (E), and southern (S) quadrants of the traditional polar representation of sugar puckering conformational space. Spontaneous repuckering, with passage between the minimum energy configurations at C2'-endo (S) and C3'-endo (N), occurs for riboses in single-stranded and loop regions with an observed frequency of about 1 ns⁻¹, and the lowest energy barrier is observed at O4'-endo, so repuckering is via the N-E-S pathway, as expected. The pseudorotational description of sugar puckers is found to be reasonably accurate, although we find a small dependence of puckering amplitude (δw) on puckering phase angle (P), and there are substantial fluctuations in δw at any given value of P. The three pseudorotation formalisms (Altona-Sundaralingam, Rao-Westhof-Sundaralingam, and Cremer-Pople) give only small differences when characterizing a given configuration, and we discuss relationships for interconverting between the formalisms. On examining our potential energy function, we find that the most important contributions to the shape of the conformational energy curve arise from the torsional energy terms. For examining questions of structure and for comparing different potential energy functions, molecular dynamics is a useful complement to energy minimization, because of the very large number of configurations that are generated, and because these configurations represent all thermally accessible states.

The central role of the furanose ring in the conformation of nucleic acids has long been recognized. The global conformation of the molecule is affected by sugar conformation in two ways. First, the backbone which connects successive phosphate atoms passes through the furanose ring. Second, the base is covalently bonded to the C1' atom in the ring. Thus, the geometry of the sugar (ribose in RNAs, deoxyribose in DNAs) is one of the critical determinants of the entire molecule. A number of methods to mathematically describe the deviation of closed cyclic rings from planarity have been given.1-4 Although their methods differ (see Methods), they all describe the ring conformation in terms of a puckering phase angle, P, identifying which part of the ring is farthest from planarity, and an amplitude, measuring the magnitude of the deviation from planarity. Amplitude is denoted by δw if puckering is defined in terms of ring torsion


0002-7863/86/1508-6128$01.50/0 © 1986 American Chemical Society