of Bz'C(=O)Mn(CO)S was much lower (S56). Such additional trapping often show different chemistry. As one example, reductive coupling of C-C bonds from Pd(II) systems led us to pursue the present experimental and theoretical studies in correlation with metrical information with reactivity, we undertook an X-ray structural study of the complexes cis-(CH3)2P(CH2)3CH2M, where M = Pd or Pt. Prior to this study, no structural comparisons of Pt and Pd allyl complexes had been made. In fact, the literature contains only two reports6 of structures with Pd–Me bonds. The present complexes were chosen because of their relative stability and simplicity, cis-M(CH3)2P(CH2)3CH2M, M = Pd or Pt, are strictly isosstructural.

Geometrical Characteristics from Experiment and Theory of Isosstructural Complexes Involving Palladium– and Platinum–Methyl Bonds

Jean M. Wisner, Tadeusz J. Bartczak, and James A. Ibers*

Department of Chemistry, Northwestern University Evanston, Illinois 60201

John J. Low and William A. Goddard III*

Contribution No. 7169, Division of Chemical Engineering, California Institute of Technology Pasadena, California 91125

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Oxidative addition and reductive elimination reactions play a critical role in some of the most important processes in organometallic chemistry.1 In such reactions, Pd(II) and Pt(II) systems often show different chemistry. As one example, reductive coupling of C–C bonds from Pd(II)2

Pd(CH3)2(PPh3)2 → Pd(PPh3)2 + CH3H

Table I. Experimental and Theoretical Bond Distances (Å) in (CH3)2P(Pr)2 Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Exp B</th>
<th>Exp A</th>
<th>Th B</th>
<th>Th A</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pr–C)</td>
<td>2.120</td>
<td>2.090</td>
<td>2.06</td>
<td>2.02</td>
</tr>
<tr>
<td>(Pd–C)</td>
<td>2.090</td>
<td>2.070</td>
<td>2.02</td>
<td>2.02</td>
</tr>
<tr>
<td>(Pt–Pr)</td>
<td>2.254</td>
<td>2.254</td>
<td>2.46</td>
<td>2.46</td>
</tr>
<tr>
<td>(Pd–P)</td>
<td>2.332</td>
<td>2.322</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>(Pt–Pt)</td>
<td>-0.039</td>
<td>-0.019</td>
<td>-0.04</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

Figure 1. Coordination sphere around the metal in cis-(CH3)2P(CH2)3CH2M, M = Pd, Pt. Bond distances and angles for the Pd complex are in smaller type. Thermal ellipsoids at the 50% probability level are shown.
so a comparison of metrical parameters in these two complexes is not complicated by solid-state effects. The theoretical studies examined M(R1)2(R2)3(PH3)2 complexes, M = Pd, Pt; R1, R2 = H, CH3.

These theoretical and experimental studies were completed simultaneously and independently (Table I). Of particular interest are the differences in bond lengths, \( \Delta_C = (\text{Pt} - \text{C}) - (\text{Pd} - \text{C}) \) and \( \Delta_P = (\text{Pt} - \text{P}) - (\text{Pd} - \text{P}) \), which are of opposite sign.\(^9\) Figure 1 illustrates the inner coordination sphere in these complexes and presents pertinent bond distances and angles. Coordination about the central metal in both complexes is essentially square-planar with a very slight tetrahedral distortion. Chemically equivalent ligands, such as alkyls and halides, tend to show longer bonds to third-row transition metals than to their second-row analogues, whereas the opposite is true for "soft" or \( \pi \)-bonding ligands, such as phosphines.

We will now use the wavefunctions from theory to analyze more precisely the origin of geometric changes from Pd to Pt.

In fact, detailed comparisons of the electronic structure for Pd–C vs. Pt–C bonds do not provide an explanation of the short Pd–C bond length relative to Pt–C. Thus, calculations on M(CH3)2(PH3)2, where \( M = \text{Pt} \text{ or Pd} \), yield M–C = 1.96 Å and Pt–C = 1.98 Å, which can be compared with 2.06 Å, 2.02 Å, 89°, and 81° calculated for M(CH3)2(PH3)2. All four complexes involve M–C bonds that are essentially covalent on one electron in a \( \text{sp} \) orbital and the other in an M spd hybrid. Thus, calculations on M(CH3)2(PH3)2 yield M–C = 1.96 Å and Pt–C = 1.98 Å, whereas the opposite is true for "soft" or \( \pi \)-bonding ligands, such as phosphines. We will now use the wavefunctions from theory to analyze more precisely the origin of geometric changes from Pd to Pt.

Because of the large increase in relativistic effects from Pd to Pt, the valence s electrons on Pt are greatly stabilized with respect to valence d electrons, leading to a d\(^3\) ground state for Pt (with d\(^{10}\) higher by 11.0 kcal/mol),\(^10\) whereas Pd has a d\(^{10}\) ground state (with d\(^{9}\) higher by 21.9 kcal/mol).\(^10\) Similarly, the electron affinity\(^1\) of Pt(d\(^{9}\)) is 2 eV greater than for Pd(d\(^{10}\)). Since Pt has a d\(^{10}\) formal charge as compared to Pd, this makes Pt more stable than Pd. This is consistent with the fact that the respective P–CH3 bond distances are of the same value in Pt(1.56 Å) and Pd(1.53 Å).

The mechanism of hydrolysis of phosphate monoesters remains uncertain in spite of intensive study in a number of laboratories.\(^1\) On the basis of pH–rate profiles, the involvement of a hypothetical metaphosphate ion intermediate, at least not in protic media. The mechanism of hydrolysis of substituted phenyl phosphates at a number of pH values. Subsequent medium and product studies uncovered evidence of free metaphosphate ion in aprotic media, and its direct observation in the gas phase by negative ion mass spectrometry was reported shortly thereafter.\(^2\) Recent investigations, on the other hand, have tended to emphasize that these reactions cannot generate a completely free metaphosphate ion intermediate, at least not in protic media. The hydrolysis of esters chiral at phosphorus by \( \text{H}_{3}O^{+} \), \( \text{O}^{-} \), and \( \text{H}_{2}O \) substitution proceeded with inversion of configuration.\(^3\) Transfer of a phosphoryl residue from a pyridinium\(^4\) or quinolinium\(^5\) to the ground state of the respective P–CH3. Additional structural studies of comparable accuracy would be valuable in ascertaining the generality of this explanation in terms of both electronic and steric effects.

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**On the Freeeness of the Metaphosphate Anion in Aqueous Solution**

F. Ramirez, J. Marecek, J. Minore, S. Srivastava, and W. le Noble*  

*Department of Chemistry  
State University of New York  
Stony Brook, New York 11794

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The mechanism of hydrolysis of phosphate monoesters remains uncertain in spite of intensive study in a number of laboratories.\(^1\) On the basis of pH–rate profiles, the involvement of a hypothetical metaphosphate ion in the aqueous solvolysis of these compounds was first proposed 3 decades ago by Westheimer\(^1\) and by Bunton.\(^2\) Further support for this mechanism was provided by studies on the hydrolysis of substituted phenyl phosphates at a number of pH values. Subsequent medium and product studies uncovered evidence of free metaphosphate ion in aprotic media,\(^3\) and its direct observation in the gas phase by negative ion mass spectrometry was reported shortly thereafter.\(^4\) Recent investigations, on the other hand, have tended to emphasize that these reactions cannot generate a completely free metaphosphate ion intermediate, at least not in protic media. The hydrolysis of esters chiral at phosphorus by \( \text{H}_{3}O^{+} \), \( \text{O}^{-} \), and \( \text{H}_{2}O \) substitution proceeded with inversion of configuration.\(^5\) Transfer of a phosphoryl residue from a pyridinium\(^6\) or quinolinium\(^7\) to the ground state of the respective P–CH3. Additional structural studies of comparable accuracy would be valuable in ascertaining the generality of this explanation in terms of both electronic and steric effects.

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