SYNTHETIC, SPECTROSCOPIC AND MECHANISTIC STUDIES OF Pd(II)-CARBON BONDING IN CHLORANILATOPALLADIUM(II) COMPLEXES

by

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CHAPTER I
INTRODUCTION

The organometallic chemistry of palladium(II) has slowly built momentum. While the early work focused on coordination of organic molecules to palladium, the evolution of industrial catalytic applications of palladium(II) compounds stimulated a search for reactions mediated by palladium. The growth is reflected in the appearance of several books\textsuperscript{1,2,3} devoted to the chemistry of palladium and about 30 reviews in the last 15 years.

However, the complexities and subtleties of organopalladium chemistry have hampered the understanding and adoption of palladium mediated reactions in organic synthesis. For example, dramatic changes in chemoselectivity, regioselectivity and stereocontrol can frequently be accomplished by minor modifications of experimental conditions, especially choice of ligands. These effects are mainly due to structural and/or kinetic requirements of Pd(II) intermediates involved in the specific reaction. To increase both predictability and applicability of palladium mediated reactions in organic synthesis, it is of great importance to investigate the structural and kinetic natures of Pd(II) intermediates.

General Chemistry of Palladium

Palladium(Pd), a silver-white ductile metal, was first discovered by Wollaston in 1803.\textsuperscript{1} It is a relatively rare metal and occurs in the earth's crust to the extent of about 0.86 ppb, together with the other platinum group metals.

Palladium is a 4d transition metal which shows a very similar chemistry to that of its 5d congener, platinum(Pt), except that Pd is much more labile. Even though Pd complexes
with (0), (I), (II) and (IV) oxidation states are known, almost all the Pd catalysts used in organic synthesis are low-spin d⁸ and diamagnetic Pd(II) complexes.

A wide variety of palladium(II) complexes are known, and Pd(II) prefers to bond to soft donor ligands such as ethylene, phosphine, etc. The great majority of the Pd(II) complexes are square-planar. However, weaker bonds may be formed in the apical sites to give a tetragonally distorted octahedral configuration. There are evidences that these apical positions may be occupied by solvent molecules. Electronic and photoelectron spectra have been interpreted to give the energy ordering of the d-orbitals as $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ in both PdCl₄²⁻ and PtCl₄²⁻. A similar ordering is usually assumed for other square-planar Pd(II) complexes.

**Substitution Reactions in Pd(II) Complexes**

Pd(II) complexes undergo substitution by an associative path via a five-coordinate transition state or intermediate, where the incoming group enters axially along the z-axis and becomes an equatorial ligand in the trigonal-bipyramidal intermediate. Factors between $10³$ and $5 \times 10⁵$ have been reported for the relative reactivities of Pd(II) complexes compared with their Pt(II) analogues. Five-coordinate intermediates are also believed to be involved in the cis-trans isomerization of the complexes [PdL₂X₂]. The tendency for square-planar complexes of Pd(II) to become five coordinate depends on the size of the ligands, being facilitated by smaller ones, and probably also on electronic factors though these remain unquantified. There is, however, some evidence that softer ligands form five-coordinate complexes more readily than harder ones.

**Trans-Influence and Trans-Effect**

Trans-Influence is a ground-state property, detected in crystal structures of complexes (and IR spectra), where it is found that some ligands have the property of selectively lengthening bonds to other groups trans to themselves. This is particularly true for
σ-bonds to hydride and to carbon and trans bond lengthenings of ca 0.1 Å are common.

The following bond length ranges are typical:\(^1\)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Range</th>
<th>Bond</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-C (σ)</td>
<td>2.00-2.05 Å</td>
<td>Pd-F</td>
<td>2.04-2.17 Å</td>
</tr>
<tr>
<td>Pd-C (π)</td>
<td>2.0-2.3 Å</td>
<td>Pd-Cl (terminal)</td>
<td>2.25-2.43 Å</td>
</tr>
<tr>
<td>Pd-N</td>
<td>2.0-2.2 Å</td>
<td>Pd-Cl (bridging)</td>
<td>2.32-2.75 Å</td>
</tr>
<tr>
<td>Pd-P</td>
<td>2.3-2.35 Å</td>
<td>Pd-Br</td>
<td>2.34-2.6 Å</td>
</tr>
<tr>
<td>Pd-As</td>
<td>2.38-2.5 Å</td>
<td>Pd-I</td>
<td>2.59-2.64 Å</td>
</tr>
<tr>
<td>Pd-O</td>
<td>1.98-2.16 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-S</td>
<td>2.23-2.40 Å</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A trans-effect is defined as the impact of a coordinated group upon the rate of substitution of ligands trans to it. This is a property of the activated complex; good trans labilizing ligands act by stabilizing the trigonal-bipyramidal transition state. An approximate order of trans effectiveness is: CO, CN\(^-\), C\(_2\)H\(_4\) > R\(_3\)P > H\(^+\) > CH\(_3\)\(^-\), SC(NH\(_2\))\(_2\) > Ph\(^-\), NO\(_2\)\(^-\), I\(^-\), SCN\(^-\) > Br\(^-\), Cl\(^-\) > pyridine, NH\(_3\), OH\(^-\), H\(_2\)O.\(^1\)

**Palladium(II) Complexes in Organic Synthesis**

The organopalladium chemistry applied to organic synthesis rests on two major types of intermediate, π-allyl systems (\(^1\)) and σ-palladium species (\(^2\)).

![Diagram](image)

Compounds of the latter type, (\(^2\)), which bear a cis-β-hydrogen have the propensity to eliminate palladium hydride. Palladium hydride is not stable, and typically undergoes a
rapid redox reaction to give Pd(0) and H⁺. Consequently, most known σ-palladium compounds are those of aryl or vinyl derivatives where such cis-β-elimination can not occur.

Generation of type (1) allyl complexes is possible by oxidation of an alkene, metal insertion into C-X bonds (as in allyl alcohol, allyl halides, allylic Grignard reagents or allyl mercury), or transmetallation, as summarized in Eq. (1-1). A comparable series of reactions leading to type (2) alkyl compounds is shown in Eq. (1-2).

\[
\begin{align*}
\text{H} & \xrightarrow{\text{Pd(II)}} \text{Pd(0)} \xrightarrow{\text{Pd(II)}} \text{X} \\
\text{H} & \xrightarrow{\text{Pd(II)}} \text{Pd(0)} \xrightarrow{\text{Pd(II)}} \text{X}
\end{align*}
\]

(1-1) X = leaving group

\[
\begin{align*}
\text{R-H} & \xrightarrow{\text{Pd(II)}} \text{Pd(0)} \xrightarrow{\text{Pd(II)}} \text{R-X} \\
\text{R-metal} & \xrightarrow{\text{Pd(II)}} \text{Pd(0)} \xrightarrow{\text{Pd(II)}} \text{R-X}
\end{align*}
\]

(1-2) X = leaving group

\[\pi\text{-Allylic Palladium(II) Complexes}\]

\[\pi\text{-Allylic palladium(II) complexes provide a versatile synthetic tool due to ease of preparation, high stability and a wide range of reactivity. One can easily obtain a variety of isolable π-allylpalladium(II) complexes or generate these in situ for catalytic use. These complexes serve as a template which not only activates and functionalizes the allyl ligand but also provides a framework for stereochemically controlled reactions. The stereochemistry of the allyl unit can be controlled by two factors:}

(1) The allyl unit usually favors the \textit{syn} geometry (3a), but the steric repulsion between vicinal \textit{syn} substituents may favor the \textit{anti} isomer (3b).13
(2) π-ALLYlpalladium molecules are fluxional. That is, they can undergo a rapid interconversion of their syn and anti stereoisomers (4). This dynamic behavior can be facilitated by phosphine, carboxylate, halide or amine ancillary ligands.¹

By rational manipulation of these variables, conditions may be found where the kinetically produced π-allyl complex reacts quickly on the time scale of syn-anti isomerization.

σ-Alkyl Palladium(II) Complexes

In virtually all well-characterized olefin oxidations by Pd(II), insertion of an alkene coordinated through its π-bonding electron pair into a Pd(II)-ligand bond is an essential step,¹⁴ affording a Pd σ-alkyl complex where the hybridization of the alkene carbon has changed from sp² to sp³. The exceptional stability of the bond between Pd(II) and a saturated carbon center provides ample thermodynamic driving force for the conversion of olefin π-complexes to σ-alkyl forms.¹⁵, ¹⁶, ¹⁷, ¹⁸, ¹⁹ There are two major types of
reactions involving σ-alkyl palladium complexes as intermediates. The former consists of a

cis addition of an alkyl-Pd(II) bond to a coordinated alkene, as exemplified by the Heck

tarylation (Eq. 1-3). The latter involves a nucleophilic trans attack on a coordinated alkene,

as illustrated by the Wacker process (Eq. 1-4).

\[
\begin{align*}
R-Pd-X + \text{Ethylene} & \xrightarrow{\text{Cis-attack}} \begin{array}{c}
\text{R} \\
\text{Pd}
\end{array} \\
\text{OH}^- + \text{PdX}_2 + \text{Ethylene} & \xrightarrow{\text{Trans-attack}} \begin{array}{c}
\text{OH} \\
\text{Pd}
\end{array}
\end{align*}
\]

The overall transformation depends upon the subsequent fate of the Pd-C σ-bond, and a
general rule is that heteroatom nucleophiles prefer a trans addition to an alkene complexed
to Pd(II). Also, carbon monoxide undergoes insertion into Pd-C bonds, accomplished by
coordination to palladium and migration of the alkyl group (Eq. 1-5).

\[
\begin{align*}
& \begin{array}{c}
\text{R} \\
\text{Pd}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{R} \\
\text{Pd}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{Pd} \\
\text{C} \\
\text{O}
\end{array}
\end{align*}
\]

Although there have been many successful applications using Pd-C σ-alkyl complexes
as catalysts, detailed understanding of the elementary processes is not well established for
the following reasons:20

(1) Isolation of Pd σ-alkyl complexes is difficult, even in the presence of stabilizing
ligands such as tertiary phosphines, because Pd-C σ-bonds are readily susceptible to
thermolysis or reductive elimination reactions.
(2) It is difficult to study the mechanisms for the making and breaking of Pd-C \( \sigma \)-bonds because:

a) The formation reactions are usually non-stoichiometric.

b) The stability of Pd-C \( \sigma \)-complexes is hindered by decay pathways, such as thermolysis, reductive elimination and cis-trans isomerization (for \( R_2\text{PdL}_2 \)).

The development of new applications for organopalladium compounds depends upon the understanding of pathways followed in a simpler systems where Pd-C bonds are made or broken with an accompanying hybridization change at the ligated carbon atom.

**Chemistry of Chloranilic Acid**

Quinones and quinoid molecules occupy a special position in the areas of organic and biochemistry. Certain activated quinones can convert alcohols into the corresponding carbonyl compounds.\(^{21}\) Benzoquinones with electron-withdrawing substituents, such as chloranil (tetrachloro-1,4-benzoquinone), are versatile two-electron oxidants in organic synthesis\(^ {22}\) and the catalytic potential of benzoquinones is considerably enriched through the coordination of these ligands to transition-metal ions.\(^ {23}\) For example, a study on the oxidation of ethanol by chloranilic acid (H\(_2\)CA, 2,5-dihydroxy-3,6-dichlorobenzoquinone) catalyzed by chromium(III) showed that a binuclear complex of the form \( \text{Cr}_2(\text{CA})^{4+} \) (\( \text{CA}^{2-} = 2,5\)-dioxo-3,6-dichloro-1,4-benzoquinone) is the most reactive catalyst species.\(^ {24}\)

Various para-quinones form stable complexes with Pd(0), but not with Pd(II). Infrared and \(^{13}\)C NMR studies suggest an unusual equilibrium between olefinic and di-olefinic structural types, as shown below.\(^ {25}\)

However, the X-ray crystal structure\(^ {26}\) of \( \text{K}_2[\text{Pd}(\text{CA})\text{Cl}_2] \cdot 4\text{H}_2\text{O} \) shows both the remarkable affinity of Pd(II) for sp\(^3\)-hybridized carbon and the unusual stability of the Pd-C \( \sigma \)-bond. Thus, instead of forming a conventional adduct\(^ {23, 27}\) through olefinic \( \pi \) or phenolate oxygen electron pairs, the \( \text{CA}^{2-} \) moiety ligates Pd(II) as a bidentate.
bis(carbanion) donor in which negative charges are localized on sp$^3$-hybridized carbon atoms bonded to both Pd(II) and Cl substituents (Figure 1). The bend angle of this non-quinonoid, boat conformation of coordinated chloranilate is 46.0° and the two Pd-C bond lengths are 2.02 and 2.07 Å, respectively. Bis(carbanion), para-quinone, and ortho-quinone resonance forms of the CA$^{2-}$ moiety (Figure 2) suggest at least three possibilities for linkage isomerization in Pd(II)-CA$^{2-}$ complexes.

One would expect that the electron-releasing, dicarbanion resonance form (C-CA$^{2-}$) will be preferred in the presence of π-accepting or weakly σ-donating ligands. Conversely, the π-accepting capability of chloranilate bonded through diene electron pairs in its π-quinone resonance form (π-CA$^{2-}$), shown below, should effectively complement good σ donors towards the soft Pd(II) metal center.

**Objectives**

The goals of our research are the following:

(1) The CA$^{2-}$ moiety, acting as a "reporter group," should reflect the bonding mode dictated by other ligands. We wish to test an important hypothesis that the C-CA$^{2-}$ form will be favored in the presence of weak σ-donors or good π-acceptors and isomerization to a π-CA$^{2-}$ form will be facilitated by the presence of good σ-donor ligands. For this reason, we will study an extensive family of compounds containing
the Pd(CA) core unit with a variety of donor and acceptor types to test this hypothesis thoroughly.

(2) To understand the thermodynamic and kinetic basis for reactions involving Pd-C σ-bond making and cleavage. As an experimentally feasible approach to achieve this goal, we have chosen coordination isomerization in the Pd-CA$^{2-}$ core unit because:

a) Reductive elimination of the carbon-donating ligand, often encountered in the simple dialkyl systems, can be avoided.

b) Chloranilic acid is highly resistant to ring-opening or fragmentation reactions, and contains no β-hydrogen which could lead to a Pd(II)H species.

c) It is easy to detect coordination isomerization of the CA$^{2-}$ moiety spectrophotometrically because the characteristic UV-visible spectra of the several bonding modes are markedly different.

(3) To define the mechanism of Pd-C σ-bond breaking. We will examine both electronic and steric influences through substituent effects of entering ligands which cause an isomerization reaction of the CA$^{2-}$ moiety. Correlation of rates with ground state properties will be carried out to determine the degree of Pd-C σ-bond breaking and Pd-L bond making in the activated complex, where L is the entering group.
Figure 1

Boat Conformation of Carbon-bonded Chloranilate in $\text{K}_2\text{Pd}(_2\text{CA})\text{Cl}_2\cdot\text{H}_2\text{O}$
Dicarbanion Resonance Form (C-CA)

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \] 

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \] 

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \] 

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \]

p-Quinone Resonance Form

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \] 

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \] 

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \] 

\[ \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} \]

o-Quinone Resonance Form

Figure 2

Resonance Forms of the Chloranilate Dianion
CHAPTER II
EXPERIMENTAL

Materials

Reagent grade chemicals were used without further purification. Palladium chloride (PdCl₂), 2,4-pentanedione, 1,5-cyclooctadiene, bipyridine, ethylenediamine and 7,7,8,8-tetracyanoquinodimethane were supplied by Aldrich. Triphenylarsine, triphenylantimony and all the phosphines were obtained from Strem Chemicals except tris(3-methoxyphenyl) phosphine (Alfa) and 1,2-bis(diphenylphosphino)ethane (Aldrich). 2,5-Dihydroxy-3,6-dichloro-p-benzoquinone (chloranilic acid, H₂CA) was from Sigma, and the dipotassium salt of 2,5-dioxo-3,6-dichloro-p-benzoquinone (K₂CA) was obtained by neutralizing chloranilic acid with 2 equivalents of KOH. Acetonitrile (certified A.C.S. grade from Fisher) dried over molecular sieves and triply distilled water were used throughout, and various other solvents were used after simple distillation. Nitrogen gas was passed through 2 aqueous chromous scrubbing towers to remove oxidizing impurities and at least 2 solvent towers to saturate the stream with various solvents employed in syntheses and kinetic measurements. All the elemental analysis data reported were obtained from Desert Analytics (Tucson, Arizona).

Syntheses

Precursor Complexes

K₂Pd(CA)Cl₂·1/2H₂O (5)

The synthetic method for (5) was adapted from that of Krasochka et al.²⁶ Palladium(II) chloride (PdCl₂, 5.11 g, 28.8 mmole), 4.73 g of KCl (63.4 mmole) and 1 ml of concentrated HCl were mixed in 150 ml of hot water (60 °C). The mixture was stirred
until all solids were completely dissolved (1 hour) and then filtered. Upon cooling the supernatant in an ice bath, greenish-brown needle type crystals of K₂PdCl₄ formed, which were collected by filtration, and washed with methanol and ether. The yield was 96% (8.99 g, 27.5 mmole) after vacuum drying.

Potassium tetrachloropalladate (8.99 g, 27.5 mmole) was dissolved in 200 ml of water and 5.75 g of H₂CA (27.5 mmole) was added with stirring. A green insoluble intermediate that formed immediately gradually converted to yellow needle type crystals in about 10 hours upon continuous stirring. The solid was collected on a sintered glass filter, and a second crop was obtained after evaporating the supernatant to 10 ml. Both were washed with cold water, methanol and ether, and vacuum dried. Yield: 97% (12.60 g, 26.6 mmole). Anal. Calcd. for K₂Pd(CA)Cl₂·1/2H₂O: C, 15.29; H, 0.21; Cl, 30.08; K, 16.59. Found: C, 15.12; H, 0.43; Cl, 29.94; K, 16.71. IR (KBr pellet): 3580(s,br), 3490(s,br), 1694(s), 1661(s), 1628(s), 1275(w), 1214(m), 1180(m), 1161(m), 982(w), 865(s), 638(s). UV/VIS (H₂O, pH = 3.68 (HClO₄), [Cl⁻] = 1 X 10⁻² M); λₘₐₓ 236.0 nm (ε 2.17 X 10⁴ M⁻¹cm⁻¹), 263.6 (1.79 X 10⁴), 312.4 (1.461 X 10⁴). ¹³C NMR (D₂O): δ 99.5. 169.4 ppm.

Anal. Found for green intermediate: C, 16.98; H, 0.42. IR (KBr pellet): 3610(s,br), 3500(s,br), 1720(s), 1690(s), 1671(s), 1180(m), 1154(m), 866(s).

Pd(CA)(CH₃CN)₂ (6)

Attempts to use ⁶ as a precursor complex were unsuccessful due to the high affinity of chloride ion for palladium(II). For example, K₂Pd(CA)(Cl)(Br) was obtained, instead of K₂Pd(CA)Br₂, by reacting ⁵ with a 100-fold excess KBr. Also, the insolubility of ⁵ in non-aqueous solvents limits its use in the kinetic studies. Therefore, the Cl⁻ ligands in ⁵ were replaced by a gravimetric method to obtain a more suitable precursor complex containing the easily-displaced CH₃CN ligand.
K$_2$Pd(CA)Cl$_2$·1/2H$_2$O (7.10 g, 15 mmole), insoluble in CH$_3$CN, was suspended in 400 ml of this solvent and 5.10 g of AgNO$_3$ (30 mmole) was added slowly while stirring. The mixture became cloudy due to the precipitation of KNO$_3$ and AgCl, and the reaction reached completion within 30 minutes. The white precipitate was collected on a pre-weighed sintered glass filter, and it was re-weighed after drying at 120 °C for 2 hours. The difference was 7.21 g. The filter was washed with water several times, dried and re-weighed. The weight difference, which is due to KNO$_3$, was 2.94 g (97% yield) and the weight of AgCl was calculated (7.21 - 2.94 = 4.27 g, 99% yield). Yellow crystals obtained upon evaporation of the solvent were washed with CH$_3$CN and ether, and vacuum dried. Trace amounts of a purple by-product were separated by washing with cold CH$_3$CN. The yield was 97% (5.76 g, 14.57 mmole). Anal. Calcd. for Pd(CA)(CH$_3$CN)$_2$: C, 30.37; H, 1.53; N, 7.08. Found: C, 30.02; H, 1.45; N, 7.07. IR (KBr pellet): 3480(s,br), 2255(m), 1695(s), 1680(s), 1635(s,br), 1390(m), 1368(m), 1270(w), 1208(m), 1161(m), 1040(w), 980(m), 865(s), 780(w), 618(m). UV/VIS (CH$_3$CN): $\lambda_{max}$ 223.0 nm ($\varepsilon$ 2.31 $\times$ 10$^4$ M$^{-1}$cm$^{-1}$), 264.0 (1.05 $\times$ 10$^4$), 305.8 (9.6 $\times$ 10$^3$). $^{13}$C NMR (CH$_3$CN): $\delta$ 102.4, 173.2 ppm (CH$_3$CN resonances excluded).

Pd(CA)(H$_2$O)$_2$·H$_2$O (7)

Even though (6) serves as a good precursor for numerous Pd(CA) complexes, a few compounds could be synthesized from (7) with better yields. K$_2$Pd(CA)Cl$_2$·1/2H$_2$O (2.37 g, 5 mmole) was dissolved in about 150 ml of water. The pH was adjusted to 2.0 with HNO$_3$, and 1.70 g of AgNO$_3$ (10 mmole) was added slowly while stirring. The reaction was completed within 1 hour. AgCl was separated by filtration in 99% yield. Yellowish-orange needle type crystals obtained by evaporating the solution to 30 ml were washed with cold water and ether, and vacuum dried. However, displacement of the CA$_2^-$ ligand and reduction of Pd(II) to Pd(0) was observed for (7) under neutral or basic conditions, and
this compound appears to be stable only in acidic media (pH 1-4). The yield was 60% (1.10 g, 3 mmole). Anal. Calcd. for Pd(CA)(H₂O)₂·H₂O: C, 19.61; H, 1.64. Found: C, 19.65; H, 1.51. IR (KBr pellet): 3540(s,br), 3300(s,br), 3200(s,br), 1690(s), 1635(s,br), 1390(m), 1320(w), 1278(w), 1190(s), 1175(s), 1165(s), 984(w), 868(s), 778(m,br). UV/VIS (H₂O, pH = 3.68 (HClO₄)): λₘₐₓ 224.0 nm (ε 1.58 X 10⁴ M⁻¹cm⁻¹), 256.0 (9.72 X 10³), 314.6 (1.05 X 10⁴).

Syntheses of Pd(CA)-Group V Donor Ligand Complexes

An immediate color change from yellow to purple was observed upon mixing (6) with 2 equivalents of phosphines or arsines in 25 ml of CH₃CN with stirring, and all the reactions gave near-quantitative yields within a day. These purple products were isolated by evaporation of CH₃CN followed by filtration. The products were washed with cold CH₃CN and ether. Most of the products were recrystallized from CH₂Cl₂, and vacuum dried.

Since some of the phosphine ligands are air-sensitive, all the reactions were carried out under anaerobic conditions. A 50 ml erlenmeyer flask was pre-weighed with a piece of parafilm (American Can Company). The phosphine was transferred quickly to the flask while flushing with nitrogen gas, and the flask was covered with the film. The number of moles was calculated from the weight difference and 1/2 equivalent of (6) was added along with anaerobic CH₃CN under an N₂ atmosphere. Once the product is formed, no air-sensitivity was observed by ³¹P NMR.

Pd(CA)(PPh₃)₂·H₂O

Triphenylphosphine (0.26 g, 1 mmole) was mixed with 0.20 g of (6) (0.5 mmole) in 25 ml of CH₃CN at room temperature. Yield: 93% (0.40 g, 0.47 mmole). Anal. Calcd. for Pd(CA)(P(C₆H₅)₃)₂·H₂O: C, 58.93; H, 3.77. Found: C, 59.21; H, 3.39. IR (KBr
pellet): 3420(m,br), 1640(m), 1580(m), 1562(w), 1530(s,br), 1485(m), 1463(w), 1443(s), 1370(s), 1360(s), 1309(m), 1240(w), 1190(w), 1165(w), 1104(m), 1002(m), 843(m), 746(m), 712(m), 690(s). UV/VIS (CH₂Cl₂): λ_{max} 229.6 nm (ε 4.91 X 10⁴ M⁻¹cm⁻¹), 278.8 (1.84 X 10⁴), 343.4 (3.87 X 10⁴), 541.8 (1.10 X 10³). ¹³C NMR (CH₂Cl₂): δ 103.3, 170.9, 174.7 ppm (phenyl carbon resonances excluded). ³¹P NMR (CH₂Cl₂): δ 34.05 ppm.

Pd(CA)(AsPh₃)₂H₂O

Triphenylarsine (0.31 g, 1 mmole) and 0.20 g of (6) (0.5 mmole) were combined in 25 ml of CH₃CN at room temperature. Yield: 95% (0.45 g, 0.48 mmole). Anal. Calcd. for Pd(CA)(As(C₆H₅)₃)₂H₂O: C, 53.40; H, 3.42. Found: C, 52.89; H, 3.10. IR (KBr pellet): 3420(m,br), 1660(m), 1642(s), 1628(s,br), 1480(w), 1440(s), 1352(s,br), 1305(m), 1234(w), 1190(w), 1162(w), 1081(m), 1027(w), 1000(m), 843(m), 735(s), 690(s). UV/VIS (CH₂Cl₂): λ_{max} 229.6 nm (ε 4.72 X 10⁴ M⁻¹cm⁻¹), 294.6 (1.67 X 10⁴), 346.8 (4.07 X 10⁴), 543.8 (1.28 X 10³).

Pd(CA)(P(CH₃)₃)₂H₂O

Trimethylphosphine (0.15 g, 1.96 mmole) and 0.39 g of (6) (0.98 mmole) were dissolved in 25 ml of CH₃CN at room temperature. Yield: 80% (0.38 g, 0.79 mmole). Anal. Calcd. for Pd(CA)(P(CH₃)₃)₂H₂O: C, 29.80; H, 4.17. Found: C, 29.92; H, 3.34. IR (KBr pellet): 3440(m,br), 2980(w,br), 2900(w,br), 2360(w), 1661(m), 1643(m), 1615(m), 1548(s,br), 1465(m), 1443(w), 1425(w), 1386(s), 1370(w), 1320(m), 1295(w), 1255(w), 990(w), 970(w), 958(s), 860(m), 844(s), 750(w).

Pd(CA)(P(i-butyl)₃)₂

Tri(i-butyl)phosphine (0.36 g, 1.8 mmole) was reacted with 0.35 g of (6) (0.89 mmole) in 25 ml of CH₃CN at room temperature. Yield: 94% (0.60 g, 0.84 mmole).
IR (KBr pellet): 3440(m,br), 2970(s,br), 2380(w), 1647(m), 1569(m), 1526(s,br),
1464(m), 1443(w), 1424(w), 1404(w), 1393(w), 1366(s), 1302(m), 1242(w), 1166(w),
1113(w), 1076(w), 1060(w), 999(w), 854(w), 840(m), 812(w), 799(w), 783(w).
UV/VIS (CH₂Cl₂): λₘₐₓ 237.8 nm (ε 2.73 X 10⁴ M⁻¹cm⁻¹), 343.4 (2.98 X 10⁴), 546.8
(1.0 X 10³). ³¹P NMR (CH₂Cl₂): δ 25.51 ppm.

Pd(CA)(P(n-butyl)₃)₂

Tri(n-butyl)phosphine (0.36 g, 1.8 mmole) and 0.35 g of (6) (0.89 mmole) were
mixed in 25 ml of CH₃CN at room temperature. Yield: 90% (0.58 g, 0.80 mmole). Anal.
Calcd. for Pd(CA)(P(n-C₄H₉)₃)₂: C, 50.19; H, 7.58. Found: C, 50.44; H, 7.73. IR
(KBr pellet): 3430(m,br), 2960(s), 2930(s), 2870(s), 2380(w), 1661(m), 1645(s),
1585(m), 1525(s,br), 1466(m), 1445(w), 1425(w), 1405(w), 1368(s), 1305(s), 1245(w),
1215(w), 1095(m), 1076(w), 1055(w), 1000(m), 970(w), 903(m), 840(s), 800(w),
777(w), 724(m). UV/VIS (CH₂Cl₂): λₘₐₓ 230.0 nm (ε 2.84 X 10⁴ M⁻¹cm⁻¹), 344.0
(2.87 X 10⁴), 548.2 (9.7 X 10²). ³¹P NMR (CH₂Cl₂): δ 30.03 ppm.

Pd(CA)(P(NMe₂)₃)₂H₂O

Tris(dimethylamino)phosphine (0.37 g, 2.26 mmole) and 0.45 g of (6) (1.13 mmole)
were reacted in 25 ml of CH₃CN at room temperature. Yield: 90% (0.67 g, 1.02 mmole).
Anal. Calcd. for Pd(CA)(P(NC₂H₆)₃)₂H₂O: C, 32.87; H, 5.82; N, 12.78. Found: C,
33.25; H, 5.67; N, 12.76. IR (KBr pellet): 3440(m,br), 3045(s,br), 2820(s,br),
2480(w,br), 2400(w), 1660(w), 1642(m), 1528(s,br), 1462(s), 1432(w), 1410(w),
1368(w), 1280(w), 1246(s), 1060(w), 1034(w), 984(m), 892(w), 832(s). ³¹P NMR
(CH₂Cl₂): δ 91.18 ppm.
Pd(CA)(P(cyclohexyl)₃)₂·H₂O

Tricyclohexylphosphine (0.31 g, 1.1 mmole) was mixed with 0.22 g of (6) (0.55 mmole) in 25 ml of CH₃CN at room temperature. Yield: 90% (0.44 g, 0.5 mmole). Anal. Calcd. for Pd(CA)(P(C₆H₁₁)₃)₂·H₂O: C, 56.54; H, 7.68. Found: C, 56.64; H, 7.61. IR (KBr pellet): 3420(m, br), 2940(s), 2865(m), 1642(m), 1530(s, br), 1463(w), 1446(m), 1375(s), 1300(m), 1280(m), 1238(w), 1201(w), 1178(w), 1135(w), 1110(w), 1078(w), 1053(w), 1003(m), 920(w), 889(w), 852(m), 841(m), 736(w). UV/VIS (CH₂Cl₂): λₘₕₐₓ 197.0 nm (ε 1.50 X 10⁴ M⁻¹cm⁻¹), 241.8 (2.39 X 10⁴), 342.6 (3.28 X 10⁴), 547.8 (1.0 X 10³). ³¹P NMR (CH₂Cl₂): δ 50.48 ppm.

Pd(CA)(P(benzyl)₃)₂

Tribenzylphosphine (0.35 g, 1.15 mmole) and 0.23 g of (6) (0.58 mmole) were combined in 25 ml of CH₃CN at room temperature. Yield: 77% (0.41 g, 0.44 mmole). Anal. Calcd. for Pd(CA)(P(CH₂C₆H₅)₃)₂: C, 62.52; H, 4.59. Found: C, 62.32; H, 4.45. IR (KBr pellet): 3450(m, br), 1644(m), 1515(s), 1499(m), 1464(w), 1455(w), 1444(w), 1406(w), 1362(s), 1312(m), 1245(w), 1233(w), 1163(w), 1146(w), 1076(w), 1036(w), 1000(w), 928(w), 896(w), 855(w), 840(m), 814(w), 775(m), 700(m). UV/VIS (CH₂Cl₂): λₘₕₐₓ 228.6 nm (ε 4.01 X 10⁴ M⁻¹cm⁻¹), 250 (shoulder, 2.00 X 10⁴), 341.2 (3.10 X 10⁴), 545.8 (1.1 X 10³). ³¹P NMR (CH₂Cl₂): δ 34.49 ppm.

Pd(CA)(P(p-chlorophenyl)₃)₂

Tris(p-chlorophenyl)phosphine (0.23 g, 0.64 mmole) and 0.13 g of (6) (0.32 mmole) were dissolved in 25 ml of CH₃CN at room temperature. Yield: 92% (0.31 g, 0.30 mmole). Anal. Calcd. for Pd(CA)(P(p-C₆H₄Cl)₃)₂: C, 48.29; H, 2.32. Found: C, 48.30; H, 2.21. IR (KBr pellet): 3520(m, br), 2470(w), 1639(m), 1578(m), 1562(m), 1524(s, br), 1480(m), 1460(w), 1390(m), 1355(s), 1303(m), 1235(w), 1189(w), 1090(s), 1016(s), 1000(w), 880(w), 844(m), 817(m), 750(s), 704(w). UV/VIS (CH₂Cl₂): λₘₕₐₓ
234.6 nm ($\varepsilon$ $7.43 \times 10^4$ M$^{-1}$cm$^{-1}$), 294 (shoulder, $1.8 \times 10^4$), 343.2 ($4.22 \times 10^4$), 540.0 ($1.2 \times 10^3$). $^{31}$P NMR (CH$_2$Cl$_2$): $\delta$ 32.03 ppm.

Pd(CA)(P(p-dimethylaminophenyl)$_3$)$_2$

Tris(p-dimethylaminophenyl)phosphine (0.24 g, 0.62 mmole) was reacted with 0.12 g of (6) (0.31 mmole) in 25 ml of CH$_3$CN at room temperature. Yield: 90% (0.31 g, 0.28 mmole). Anal. Calcd. for Pd(CA)(P(p-C$_6$H$_4$NC$_2$H$_6$)$_3$)$_2$: C, 59.16; H, 5.52; N, 7.67. Found: C, 58.83; H, 5.47; N, 7.65. IR (KBr pellet): 3440(m, br), 2370(m), 1662(m), 1646(m), 1626(m), 1609(s), 1567(m), 1558(m), 1528(s), 1516(s), 1480(m), 1466(m), 1446(m), 1427(w), 1413(w), 1404(w), 1370(s), 1299(w,br), 1234(w), 1211(m), 1006(s), 1003(w), 950(w), 841(m), 813(w), 760(w). UV/VIS (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ 228.2 nm ($\varepsilon$ $5.08 \times 10^4$ M$^{-1}$cm$^{-1}$), 287.0 ($1.04 \times 10^5$), 345.6 ($3.16 \times 10^4$), 375.6 ($2.95 \times 10^4$), 428 (shoulder, $2.3 \times 10^4$). $^{31}$P NMR (CH$_2$Cl$_2$): $\delta$ 31.91 ppm.

Pd(CA)(P(p-fluorophenyl)$_3$)$_2$H$_2$O

Tris(p-fluorophenyl)phosphine (0.32 g, 1.0 mmole) and 0.20 g of (6) (0.5 mmole) were added in 25 ml of CH$_3$CN at room temperature. Yield: 93% (0.45 g, 0.47 mmole). Anal. Calcd. for Pd(CA)(P(p-C$_6$H$_4$F)$_3$)$_2$H$_2$O: C, 52.34; H, 2.72. Found: C, 52.97; H, 2.38. IR (KBr pellet): 3460(m, br), 3105(m, br), 3085(m, br), 3150(m, br), 1640(s), 1590(s), 1527(s, br), 1500(s), 1400(m), 1360(s), 1304(s), 1240(s), 1164(s), 1098(s), 1013(m), 1000(m), 946(w), 875(w), 827(s), 708(m). UV/VIS (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ 230.4 nm ($\varepsilon$ $5.04 \times 10^4$ M$^{-1}$cm$^{-1}$), 293.6 ($1.64 \times 10^4$), 342.2 ($4.00 \times 10^4$), 541.8 ($1.2 \times 10^3$). $^{31}$P NMR (CH$_2$Cl$_2$): $\delta$ 31.45 ppm.

Pd(CA)(P(p-methoxyphenyl)$_3$)$_2$

Tris(p-methoxyphenyl)phosphine (0.26 g, 0.74 mmole) and 0.15 g of (6) (0.37 mmole) were reacted in 25 ml of CH$_3$CN at room temperature. Yield: 94% (0.35 g, 0.35
Anal. Calcd. for Pd(CA)(P(p-C6H4OCH3)3)2: C, 56.63; H, 4.16. Found: C, 57.26; H, 4.27. IR (KBr pellet): 3450(m,br), 2940(w,br), 2845(w), 2380(w), 1638(m), 1595(s), 1573(w), 1564(m), 1526(s), 1501(s), 1461(m), 1441(m), 1410(w), 1365(s), 1290(s), 1260(s), 1183(s), 1101(s), 1029(s), 1000(w), 840(m), 828(m), 801(m), 713(w). UV/VIS (CH2Cl2): λmax 242.8 nm (ε 7.43 X 104 M^-1cm^-1), 352.6 (4.54 X 10^4), 543.2 (9.5 X 10^2). 31P NMR (CH2Cl2): δ 31.88 ppm.

Pd(CA)(P(p-tolyl)3)2

Tris(p-tolyl)phosphine (0.29 g, 0.94 mmole) was mixed with 0.19 g of (6) (0.47 mmole) in 25 ml of CH3CN at room temperature. Yield: 90% (0.39 g, 0.42 mmole). Anal. Calcd. for Pd(CA)(P(p-C6H4CH3)3)2: C, 62.52; H, 4.59. Found: C, 62.28; H, 4.46. IR (KBr pellet): 3430(m,br), 2370(w), 1633(m), 1601(m), 1565(m), 1529(s,br), 1478(w), 1462(m), 1442(w), 1424(w), 1401(w), 1354(s), 1302(m), 1233(w), 1193(m), 1100(s), 1041(w), 1020(w), 1000(w), 842(m), 804(m), 703(w). UV/VIS (CH2Cl2): λmax 229.8 nm (ε 6.06 X 10^4), 345.6 (4.26 X 10^4), 540.8 (1.1 X 10^3). 31P NMR (CH2Cl2): δ 33.17 ppm.

Pd(CA)(P(p-trifluoromethylphenyl)3)2

Tris(p-trifluoromethylphenyl)phosphine (0.47 g, 1.0 mmole) and 0.20 g of (6) (0.5 mmole) were combined in 25 ml of CH3CN at room temperature. Yield: 90% (0.56 g, 0.45 mmole). Anal. Calcd. for Pd(CA)(P(p-C6H4CF3)3)2: C, 46.28; H, 1.94. Found: C, 46.55; H, 1.92. IR (KBr pellet): 3460(m,br), 1640(m), 1532(s,br), 1401(m), 1370(s), 1327(s), 1238(w), 1175(s), 1130(s), 1066(s), 1018(m), 1003(w), 960(w), 876(w), 847(w), 834(m), 708(s). UV/VIS (CH2Cl2): λmax 229.6 nm (ε 4.40 X 10^4 M^-1cm^-1), 280.4 (2.11 X 10^4), 340.8 (3.38 X 10^4), 544.2 (1.2 X 10^3). 31P NMR (CH2Cl2): δ 32.33 ppm.
Pd(\text{CA})(\text{P(m-chlorophenyl)}_3)_2

Tris(m-chlorophenyl)phosphine (0.37 g, 1.0 mmole) and 0.20 g of (6) (0.5 mmole) were dissolved in 25 ml of CH$_3$CN at room temperature. Yield: 90% (0.47 g, 0.45 mmole). Anal. Calcd. for Pd(\text{CA})(\text{P(m-C}_6\text{H}_4\text{Cl)}_3)_2$: C, 48.29; H, 2.32. Found: C, 47.83; H, 2.21. IR (KBr pellet): 3450(m,br), 2390(w), 1665(m), 1647(m), 1568(m), 1536(s,br), 1476(m), 1466(m), 1445(w), 1426(w), 1405(m), 1366(s), 1313(m), 1182(w), 1132(s), 1100(m), 1003(m), 880(w), 847(m), 786(m), 683(s). UV/VIS (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ 229.4 nm ($\varepsilon$ 5.63 X 10$^4$ M$^{-1}$cm$^{-1}$), 287.2 (1.68 X 10$^4$), 343.0 (3.43 X 10$^4$), 543.2 (1.2 X 10$^3$). $^{31}$P NMR (CH$_2$Cl$_2$): $\delta$ 33.38 ppm.

Pd(\text{CA})(\text{P(m-methoxyphenyl)}_3)_2\cdot\text{H}_2\text{O}

Tris(m-methoxyphenyl)phosphine (0.24 g, 0.69 mmole) was reacted with 0.14 g of (6) (0.35 mmole) in 25 ml of CH$_3$CN at room temperature. Yield: 94% (0.34 g, 0.33 mmole). Anal. Calcd. for Pd(\text{CA})(\text{P(m-C}_6\text{H}_4\text{OCH}_3)_3})_2\cdot\text{H}_2\text{O}$: C, 55.65; H, 4.28. Found: C, 55.67; H, 4.25. IR (KBr pellet): 3440(m,br), 2940(w,br), 2380(w), 1660(m), 1643(m), 1593(s), 1580(m), 1575(m), 1562(w), 1526(s,br), 1480(s), 1460(m), 1422(m), 1357(s), 1290(s), 1246(s), 1184(m), 1107(m), 1040(s), 996(w), 841(m), 782(m). UV/VIS (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ 229.8 nm ($\varepsilon$ 6.84 X 10$^4$ M$^{-1}$cm$^{-1}$), 279.6 (2.37 X 10$^4$), 346.4 (3.61 X 10$^4$), 541.4 (8.7 X 10$^2$).

Pd(\text{CA})(\text{P(m-toly})l_3)_2

Tris(m-toly)phosphine (0.28 g, 0.92 mmole) and 0.18 g of (6) (0.46 mmole) were added in 25 ml of CH$_3$CN at room temperature. Yield: 93% (0.39 g, 0.43 mmole). Anal. Calcd. for Pd(\text{CA})(\text{P(m-C}_6\text{H}_4\text{CH}_3)_3})_2$: C, 62.52; H, 4.59. Found: C, 62.59; H, 4.61. IR (KBr pellet): 3440(m,br), 2920(w,br), 2380(w), 1643(s), 1597(m), 1564(m), 1519(s,br), 1481(m), 1463(m), 1454(w), 1443(w), 1424(w), 1411(w), 1364(s), 1308(s), 1243(w), 1220(w), 1181(w), 1111(s), 1042(w), 1001(s), 914(w), 872(w), 842(s), 811(w), 783(s).
690(s). UV/VIS (CH2Cl2): λ_max 229.6 nm (ε 4.96 X 10^4 M^-1cm^-1), 283.6 (1.68 X 10^4), 344.4 (3.88 X 10^4), 542.8 (9.7 X 10^2). 31P NMR (CH2Cl2): δ 34.79 ppm.

Pd(CA)(P(o-methoxyphenyl)3)2

Tris(o-methoxyphenyl)phosphine (0.37 g, 0.9 mmole) and 0.18 g of 6 (0.45 mmole) were reacted in 25 ml of CH3CN at room temperature. Yield: 90% (0.41 g, 0.41 mmole). Anal. Calcd. for Pd(CA)(P(o-C6H4OCH3)3)2: C, 56.63 ; H, 4.16. Found: C, 56.22; H, 4.15. IR (KBr pellet): 3460(m,br), 2960(w,br), 2860(w), 2400(w), 1661(w), 1643(m), 1633(w), 1593(m), 1582(m), 1565(w), 1528(s,br), 1479(s), 1463(m), 1435(m), 1375(s), 1305(w), 1284(s), 1252(s), 1170(m), 1140(w), 1080(w), 1047(w), 1022(s), 841(m), 802(m), 756(s), 690(w). UV/VIS (CH2Cl2): λ_max 229.2 nm (ε 3.70 X 10^4 M^-1cm^-1), 278.6 (1.74 X 10^4), 350.2 (3.17 X 10^4), 535 (shoulder, 1.3 X 10^3 ). 31P NMR (CH2Cl2): δ 15.68 ppm.

Pd(CA)(P(o-tolyl)3)(CH3CN)2

Tris(o-tolyl)phosphine forms only a 1:1 complex with the Pd(CA) moiety, even in the presence of excess phosphine. Tris(o-tolyl)phosphine (0.30 g, 0.5 mmole) was mixed with 1 equivalent of 6 (0.20 g, 0.5 mmole) in 25 ml of CH3CN at room temperature. Yield: 93% (0.33 g, 0.47 mmole). Anal. Calcd. for Pd(CA)(P(o-C6H4CH3)3)(CH3CN)2: C, 53.20; H, 3.89; N, 4.00. Found: C, 53.43; H, 4.01; N, 4.31. IR (KBr pellet): 3440(m,br), 2380(m), 1665(m), 1648(s), 1600(w), 1588(w), 1570(m), 1531(s,br).

1482(m), 1468(m), 1458(w), 1447(w), 1430(w), 1360(s), 1310(m), 1282(m), 1255(w).

1240(w), 1206(w), 1170(w), 1142(w), 1080(w), 1037(w), 1003(w), 846(m), 810(w).

775(m), 765(m), 719(w), 678(w). UV/VIS (CH2Cl2): λ_max 230.4 nm (ε 3.29 X 10^4 M^-1cm^-1), 282.4 (1.04 X 10^4), 347.6 (2.45 X 10^4), 540 (shoulder, 1.5 X 10^3 ). 31P NMR (CH2Cl2): δ 23.09 ppm.
Attempts to Make Pd(CA)-phosphite and Antimony Complexes

Syntheses of Pd(CA) adducts with triphenylphosphite, tri(n-butyl)phosphite and triphenylantimony were not successful under the reaction conditions used for the synthesis of phosphine complexes. Upon mixing (6) with 2 equivalents of phosphites while stirring, the reaction mixtures changed color immediately from yellow to purple, followed by decomposition of the initial product to give a shiny thin film of palladium metal along the glass wall. The reductions reached completion within an hour.

Pd(CA)(bpy)

Bipyridine (0.08 g, 0.5 mmole) and 0.20 g of (6) (0.5 mmole) were combined in 25 ml of acetone at room temperature while stirring. An immediate color change from yellow to gray-brown was observed, followed by precipitation of the product. The solid was washed with cold acetone and ether, and vacuum dried. Yield: 77% (0.18 g, 0.38 mmole). Anal. Calcd. for Pd(CA)(C₁₀H₈N₂): C, 40.93; H, 1.72; N, 5.97. Found: C, 40.71; H, 1.67; N, 6.00. IR (KBr pellet): 3420(m,br), 2380(w), 1700(s), 1688(s), 1665(s), 1639(s), 1601(m), 1560(m), 1510(s,br), 1475(m), 1445(s), 1364(s), 1317(m), 1304(m), 1250(m), 1171(m), 1150(m), 1110(m), 1072(w), 1060(w), 1032(w), 1020(w), 1000(w), 897(w), 850(s), 800(w), 772(s), 720(m).

Pd(CA)(en)₂

Ethylenediamine (0.06 g, 1 mmole) and 0.20 g of (6) (0.5 mmole) were reacted in 25 ml of acetone at room temperature with stirring. The reaction mixture changed color from yellow to red, and the red product precipitated. The product was washed with cold acetone and ether, and vacuum dried. Yield: 99% (0.23 g, 0.49 mmole). Anal. Calcd. for Pd(CA)(C₂H₈N₂)₂: C, 27.70; H, 3.69; N, 12.91. Found: C, 29.94; H, 3.94; N, 11.53. IR (KBr pellet): 3420(m,br), 3200(s,br), 3100(s,br), 2370(w), 1600(s), 1515(s,br), 1370(s), 1318(m), 1270(m), 1196(w), 1136(m), 1114(m), 1064(m), 1006(w), 985(w), 895(w).
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898(w), 8342(s). UV/VIS (H₂O, pH = 3.68 (HClO₄), [Cl⁻] = 1 X 10⁻² M): λ_max 193.6 nm (ε 2.87 X 10⁴ M⁻¹cm⁻¹), 206 (shoulder, 2.5 X 10⁴ ), 323.4 (2.24 X 10⁴), 331 (shoulder, 2.2 X 10⁴ ), 529.8 (1.1 X 10²).

Attempt to Prepare Na₂Pd(CA)(N₃)₂

NaN₃ (0.07 g, 1 mmole) and 0.20 g of 6) (0.5 mmole) were combined in 25 ml of acetone at room temperature while stirring. A gradual color change from yellow to bright red was observed, followed by precipitation of the brownish-red product. The solid was collected on a sintered glass filter. However, the complex exploded upon mechanical friction when I tried to collect it! No further attempt was made to isolate the product.

Syntheses of Pd(CA)(P-P) Complexes

Syntheses of Pd(CA)(diphosphine) complexes were carried out under the same reaction conditions applied to the synthesis of monophosphine complexes. It was noted that the solubility of diphosphine complexes was reduced considerably as compared to that of Pd(CA)(PPh₃)₂ and related complexes with monophosphine ligands.

Pd(CA)(1,2-bis(diphenylphosphino)acetylene)-1/2H₂O

1,2-bis(diphenylphosphino)acetylene (0.20 g, 0.5 mmole) was mixed with 0.20 g of (6) (0.5 mmole) in 25 ml of CH₃CN at room temperature. The product is very slightly soluble in CH₃CN, but not soluble in CH₂Cl₂. Yield: 97% (0.35 g, 0.49 mmole). Anal. Calcd. for Pd(CA)(C₂₆H₂₀P₂)-1/2H₂O: C, 53.62 ; H, 2.95. Found: C, 53.50; H, 2.68. IR (KBr pellet): 3440(m,br), 2410(w), 1660(m), 1643(m), 1530(s,br), 1480(m), 1462(m), 1442(s), 1404(w), 1358(s), 1308(w), 1193(w), 1165(w), 1104(m), 1003(m), 844(m), 746(m), 689(m).
Pd(CA)(1,2-bis(diphenylphosphino)benzene)-1/2H₂O

1,2-bis(diphenylphosphino)benzene (0.22 g, 0.5 mmole) and 0.20 g of (6) (0.5 mmole) were stirred in 25 ml of CH₃CN at room temperature. The product is very slightly soluble in CH₃CN and CH₂Cl₂. Yield: 92% (0.35 g, 0.46 mmole). Anal. Calcd. for Pd(CA)(C₃₀H₂₄P₂)-1/2H₂O: C, 56.24; H, 3.28. Found: C, 56.35; H, 3.06. IR (KBr pellet): 3440(m,br), 2390(w), 1710(m), 1680(s), 1663(s), 1645(s), 1568(m), 1550(m), 1516(s,br), 1485(m), 1465(m), 1444(s), 1410(w), 1365(s), 1312(m), 1250(w), 1195(w), 1155(w), 1126(w), 1104(m), 1003(m), 863(w), 843(m), 746(m), 727(w), 696(m).

Pd(CA)(1,2-bis(diphenylphosphino)ethane)

1,2-bis(diphenylphosphino)ethane (0.18 g, 0.46 mmole) was reacted with 0.18 g of (6) (0.46 mmole) in 25 ml of CH₃CN at room temperature. The product is slightly soluble in CH₃CN and CH₂Cl₂. Yield: 90% (0.29 g, 0.41 mmole). Anal. Calcd. for Pd(CA)(C₂₆H₂₄P₂): C, 54.00; H, 3.40. Found: C, 53.85; H, 3.32. IR (KBr pellet): 3450(m,br), 2390(w), 1708(w), 1676(s), 1660(s), 1640(m), 1580(w), 1560(m), 1542(m), 1509(s,br), 1475(m), 1460(w), 1439(s), 1407(w), 1365(s), 1303(m), 1240(w), 1164(w), 1100(s), 998(m), 880(w), 853(w), 835(m), 744(m), 703(m), 686(s).

Pd(CA)(cis-1,2-bis(diphenylphosphino)ethylene)

The cis-1,2-bis(diphenylphosphino)ethylene supplied by Strem Chemicals is approximately 80% pure, containing trans-1,2-bis(diphenylphosphino)ethylene as the principal impurity. Purification was accomplished by exploiting the different solubilities of the cis- and trans-isomers. Under a nitrogen atmosphere, 50:50 CH₃CN/acetone was added slowly to 2.5 g of the crude compound with stirring until about half of the solid was dissolved. The supernatant was evaporated to isolate the cis-isomer. This process was repeated three times, giving a final yield of cis-isomer of 0.77 g. The purity of recrystallized cis-isomer was confirmed by the observation of single ³¹P NMR peak.
Cis-1,2-bis(diphenylphosphino)ethylene (0.20 g, 0.50 mmole) and 0.20 g of (6) (0.50 mmole) were dissolved in 25 ml of CH$_3$CN at room temperature. The product is slightly soluble in CH$_3$CN and CH$_2$Cl$_2$. Yield: 90% (0.32 g, 0.45 mmole). Anal. Calcd. for Pd(CA)(C$_{26}$H$_{22}$P$_2$): C, 54.15; H, 3.12. Found: C, 54.00; H, 2.98. IR (KBr pellet): 3450(m,br), 2390(w), 1710(w), 1680(s), 1662(m), 1645(m), 1570(w), 1515(s,br), 1465(w), 1445(m), 1415(w), 1370(s), 1300(w), 1250(w), 1170(m), 1107(m), 1005(m), 864(w), 840(w), 748(m), 728(w), 705(m), 693(m).

Pd(CA)(trans-1,2-bis(diphenylphosphino)ethylene)

Trans-1,2-bis(diphenylphosphino)ethylene (0.20 g, 0.50 mmole) and 0.20 g of (6) (0.50 mmole) were added in 25 ml of CH$_3$CN at room temperature. The product is not soluble in CH$_3$CN nor in CH$_2$Cl$_2$. Yield: 96% (0.34 g, 0.48 mmole). Anal. Calcd. for Pd(CA)(C$_{26}$H$_{22}$P$_2$): C, 54.15; H, 3.12. Found: C, 53.85; H, 2.99. IR (KBr pellet): 3450(m,br), 2390(w), 1661(m), 1644(m), 1632(m), 1527(s,br), 1465(m), 1442(m), 1368(s), 1316(m), 1237(w), 1185(w), 1105(m), 1001(m), 845(m), 790(w), 770(w), 745(m,), 690(m).

Syntheses of Pd(CA)-Halide and Pseudohalide Complexes

K$_2$Pd(CA)F$_2$·H$_2$O

0.20 g (0.5 mmole) of (6) was added to 20 ml of MeOH saturated with KF. The palladium reactant dissolved while a reddish-yellow precipitate formed over a 30-minute interval. The reddish-yellow product was filtered and washed with cold MeOH and ether, and vacuum dried. Yield: 65% (0.15 g, 0.32 mmole). Anal. Calcd. for K$_2$Pd(CA)F$_2$·H$_2$O: C, 16.10; H, 0.45. Found: C, 16.02; H, 0.79. IR (KBr pellet): 3420(s,br), 2370(w), 1659(s), 1636(s), 1170(m), 1080(w), 862(m), 834(w), 790(m).
UV/VIS (H₂O, pH = 3.68 (HClO₄), [F⁻] = 1 X 10⁻² M): λ_max 213.6 nm (ε 1.50 X 10⁴ M⁻¹cm⁻¹), 256 (shoulder, 7.6 X 10³ ), 310 (shoulder, 6.4 X 10³ ).

K₂Pd(CA)Br₂·H₂O

0.20 g (0.5 mmole) of (6) was dissolved in 20 ml of water, and 20 equivalents of KBr (1.19 g, 10 mmole) was added with stirring. The orange-yellow product formed rapidly, reaching completion within 15 minutes. The product was collected on a sintered glass filter, washed with cold water and ether, and vacuum dried. Yield: 70% (0.20 g, 0.35 mmole). Anal. Calcd. for K₂Pd(CA)Br₂·H₂O: C, 12.66; H, 0.35. Found: C, 12.78; H, 0.29. IR (KBr pellet): 3500(s,br), 2380(w), 1687(s), 1656(s), 1625(s), 1215(w), 1176(w), 857(s). UV/VIS (H₂O, pH = 3.68 (HClO₄), [Br⁻] = 1 X 10⁻² M): λ_max 201.2 nm (ε 1.24 X 10⁴ M⁻¹cm⁻¹), 242.2 (1.50 X 10⁴), 285.8 (2.39 X 10⁴), 310 (shoulder, 1.9 X 10⁴ ).

K₂[Pd₂(CA)₂ Br₂]·4H₂O

Attempts to recrystallize K₂Pd(CA)Br₂·H₂O from water containing equimolar KBr produced greenish-yellow plate type crystals. This crystal, which analyzes correctly for the dimer K₂[Pd₂(CA)₂ Br₂]·4H₂O, was separated and washed with cold water and ether, and vacuum dried. Anal. Calcd. for K₂[Pd₂(CA)₂ Br₂]·4H₂O: C, 15.39; H, 0.86. Found: C, 15.37; H, 0.36. IR (KBr pellet): 3610(s,br), 3480(s,br), 1710(s), 1685(s), 1664(s,br), 1250(w), 1214(w), 1176(m), 1152(m), 861(s).

Attempts to Prepare K₂Pd(CA)I₂·H₂O

Upon reacting (6) with 2 equivalents of KI in MeOH, immediate displacement of CA₂⁻ followed by the precipitation of a black powder was observed. This black product has no IR peak.
The reaction requirements for the synthesis of this complex are such that the concentration of the Pd reactant must be kept higher than that of the CN⁻ ligand, and the solvent must not dissolve the product. Otherwise, facile displacement of CA²⁻ is observed. KCN (0.13 g, 2 mmole) and 0.37 g (1 mmole) of 7 were mixed in 30 ml of MeOH with stirring. Immediate color changes from yellow to green to gray to reddish-brown were observed within a few minutes, followed by precipitation of the product. The reddish-brown solid was washed with cold MeOH and ether, and vacuum dried. Yield: 87% (0.40 g, 0.87 mmole). Anal. Calcd. for K₂Pd(CA)(CN)₂·H₂O: C, 20.82; H, 0.43; N, 6.07. Found: C, 20.69; H, 0.37; N, 6.29. IR (KBr pellet): 3400(m,br), 2380(w), 2220(m), 1660(m), 1520(s,br), 990(w), 833(m). UV/VIS (H₂O, pH = 3.68 (HClO₄)): λ max 205.2 nm (ε 2.36 X 10⁴ M⁻¹cm⁻¹), 212.6 (2.53 X 10⁴), 332.0 (2.12 X 10⁴), 340 (shoulder, 2.0 X 10⁴), 527.6 (1.6 X 10²).

Syntheses of Pd(CA)-Group VI Donor Ligand Complexes

Pd(CA) complexes with oxygen-donor ligands were prepared by using 7 in preference to 6 as a precursor because better yields could be attained. These complexes have yellow colors in general. Pd(CA)-sulfur donor complexes can be made from either 6 or 7 with good yields, and have purple colors. However, sulfur-containing ligands show a tendency to displace CA²⁻. The same strategy used to prepare K₂Pd(CA)(CN)₂·H₂O was applied for the syntheses of complexes with sulfur donor atoms. Even under these conditions, the synthesis of Pd(CA)(HSCH₂CH₂SH) was not possible due to the facile displacement of the CA²⁻ moiety.

Pd(CA)(H₂O)₂·KNO₃

AgNO₃ (0.34 g, 2 mmole) and 0.47 g (1 mmole) of 5 were stirred in 100 ml of MeOH. The solution became cloudy right away due to the precipitation of AgCl, and the
reaction was completed within 30 minutes. AgCl was separated by filtering, and the yield was 99% (0.28 g, 1.98 mmole). The supernatant was evaporated to yield yellow needle type crystals. This product was recrystallized in MeOH, washed with cold MeOH and ether, and vacuum dried. Yield: 70% (0. g, 0.53 mmole). Anal. Calcd. for Pd(CA)(H₂O)₂·KNO₃: C, 16.00; H, 0.89. Found: C, 15.64; H, 0.53. IR (KBr pellet): 3530(s,br), 3380(s,br), 1721(m), 1690(s), 1649(s,br), 1389(s), 1322(m), 1280(w), 1215(m), 1175(m), 1010(w), 982(w), 865(s), 835(w). UV/VIS (H₂O, pH = 3.68 (HClO₄), [NO₃⁻] = 1 X 10⁻² M): λ_max 237.4 nm (ε 1.08 X 10⁴ M⁻¹cm⁻¹), 253.6 (1.05 X 10⁴), 314.0 (1.08 X 10⁴).

K₂Pd(CA)(ox)·H₂O

Potassium oxalate (K₂C₂O₄; 0.18 g, 1 mmole) was mixed with excess (7) (0.40 g, 1.1 mmole, 10% excess) in 50 ml of MeOH. The solution became cloudy upon the precipitation of a yellow powder. This yellow powder slowly turned to greenish-yellow during continuous stirring (about 2 days), after which the product was separated by filtration and vacuum dried. Since (7) is soluble in MeOH, excess starting material was simply separated by washing with MeOH and ether. Yield: 95% (0.45 g, 0.95 mmole). Anal. Calcd. for K₂Pd(CA)(C₂O₄)·H₂O: C, 19.31; H, 0.40. Found: C, 19.30; H, 0.63. IR (KBr pellet): 3400(m,br), 2370(w), 1650(s,br), 1568(m), 1550(m), 1530(m), 1514(m), 1464(w), 1445(w), 1404(m), 1395(m), 1314(m), 1177(m), 1030(w). 866(m), 797(w), 775(m). UV/VIS (H₂O, pH = 3.68 (HClO₄), [ox²⁻] = 1 X 10⁻² M): λ_max 242.8 nm (ε 2.27 X 10⁴ M⁻¹cm⁻¹), 310.4 (8.35 X 10³).

K₃Pd(CA)(acac)

Acetylacetone (0.50 g, 5 mmole) and 0.37 g (1 mmole) of (7) were mixed in 30 ml of water and 1 mmole of KOH (1.40 ml of 0.713 M KOH solution) was then added slowly
while stirring. A bright yellow product precipitated within 30 minutes. The product was washed with cold water and ether, and vacuum dried. Yield: 53% (0.24 g, 0.53 mmole).

Anal. Calcd. for K_{Pd(CA)(C_5H_7O_2)}: C, 29.26; H, 1.56. Found: C, 29.30; H, 1.49. IR (KBr pellet): 3400(m,br), 1695(s), 1679(s), 1640(s,br), 1578(m), 1570(m), 1513(s), 1375(m), 1268(w), 1195(m), 1175(m), 1028(w), 867(s), 855(m), 787(m), 634(m).

UV/VIS (H_2O, pH = 3.68 (HClO_4), [acetylacetone] = 2 X 10^{-2} M): \lambda_{max} 232.0 \text{ nm (} \epsilon 1.75 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}), 310.6 (1.50 \times 10^4).

Pd(CA)(DMSO)_2

0.37 g (1 mmole) of (7) and 2 equivalents of DMSO (dimethylsulfoxide, 0.16 g, 2 mmole) were added to 30 ml of THF with stirring. The solution slowly changed from yellow to brownish-green, followed by precipitation of the product. The reaction was complete within 1 day. The product was washed with cold THF and ether, and vacuum dried. Yield: 96% (0.45 g, 0.96 mmole). Anal. Calcd. for Pd(CA)(CH_3SOCH_3)_2: C, 25.58; H, 2.58. Found: C, 25.69; H, 2.44. IR (KBr pellet): 3400(m,br), 3000(w), 2920(w), 2370(w), 1660(m), 1645(m), 1633(m), 1625(m), 1525(s,br), 1465(w), 1406(w), 1316(w), 1103(m), 1095(m), 1032(m), 993(w), 837(m), 728(w), 685(w).

K_2[Pd_2(CA)_2(SCN)_2]

Every attempt to make K_2Pd(CA)(SCN)_2 failed because of the facile displacement of CA^2- by thiocyanate ion. 0.40 g (1 mmole) of (6) and 1 equivalent of KSCN (0.10 g, 1 mmole) were reacted in 50 ml of EtOH with stirring. The solution slowly changed from yellow to brown followed by formation of greenish-yellow gel. The reaction was complete within 1 day. The product was separated by filtration and changed color from greenish-yellow to brown upon drying. The product was washed with cold THF and ether, and vacuum dried. Yield: 93% (0.38 g, 0.93 mmole). Anal. Calcd. for K_2[Pd_2(CA)_2(SCN)_2]: C, 20.48; H, 0.00; N, 3.41. Found: C, 20.50; H, 0.06; N, 3.15. IR (KBr pellet):
Attempts to Prepare Pd(CA)-Olefin Complexes

Several attempts to make Pd(CA)-olefin and diolefin complexes from (5), (6) or (7) were carried out with chloranilic acid, 2,5-dihydroxy-p-benzoquinone, tetrahydroxy-1,4-benzoquinone, 5-hydroxy-1,4-naphthoquinone, 5,8-dihydroxy-1,4-naphthoquinone, duroquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 1,2-dihydroxy-3,4,5,6-tetraoxo-1-cyclohexene (disodium salt), tetracyanoethylene, cyclooctadiene (COD) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). These ligands typically cause displacement of the CA⁻² ligand or facile reduction of Pd(II) to Pd(0), except for chloranilic acid, COD and TCNQ.

An immediate color change from yellow to purple was observed for the reactions of (5), (6) or (7) with ligands which bear hydroxy group(s), such as 2,5-dihydroxy-p-benzoquinone, tetrahydroxy-1,4-benzoquinone, 5-hydroxy-1,4-naphthoquinone, 5,8-dihydroxy-1,4-naphthoquinone and 1,2-dihydroxy-3,4,5,6-tetraoxo-1-cyclohexene (disodium salt). However, this first step is followed by a facile ligand oxidation to give palladium metal. Tetracyanoethylene displaces the CA⁻² moiety and forms a white product which lacks the typical infra-red peaks of CA⁻², such as the C=O and C-Cl stretching bands. On the other hand, duroquinone does not react with the Pd(CA) unit.

K₂Pd(CA)₂·2H₂O

0.37 g (1 mmole) of (7) and 1 equivalent of K₂CA (0.31 g, 1 mmole) were combined in 30 ml of water with stirring. An immediate color change from yellow to bluish-purple was observed within a few minutes. Purplish-brown needle type crystals were obtained by
evaporating the water; these were washed with cold water, MeOH and ether, and vacuum
dried. Yield: 46% (0.29 g, 0.46 mmole). Anal. Calcd. for K₂Pd(CA)₂·2H₂O: C, 22.71;
H, 0.63. Found: C, 22.51; H, 0.28. IR (KBr pellet): 3400(m,br), 2450(w), 1710(m),
1690(m), 1658(s), 1640(s), 1625(s), 1525(s,br), 1460(m), 1372(m), 1260(s), 1215(m),
1168(m), 994(w), 865(m), 837(m), 800(w), 780(w), 746(w). UV/VIS (H₂O, pH = 3.68
(HClO₄)): λₘₚₙₜ 217.2 nm (ε 3.05 X 10⁴ M⁻¹cm⁻¹), 258 (shoulder, 1.3 X 10⁴ ), 320.8
(2.49 X 10⁴), 537.2 (3.5 X 10²).

Pd(CA)(TCNQ)·H₂O

0.20 g (0.5 mmole) of (6) and 1 equivalent of TCNQ (7,7,8,8-
tetracyanoquinodimethane, 0.10 g, 0.5 mmole) were allowed to react in 30 ml of THF with
stirring. The reaction is quite slow, requiring stirring for about a week. A greenish-brown
powder was obtained by filtering, washed with THF and ether, and vacuum dried. Yield:
56% (0.15 g, 0.28 mmole). Anal. Calcd. for Pd(CA)(TCNQ)·H₂O: C, 40.37; H, 1.13; N.
10.46. Found: C, 40.82; H, 2.28; N, 10.24. IR (KBr pellet): 3400(s,br), 2210(m,br),
2140(m,br), 1657(s), 1638(s), 1270(m), 1183(m), 1050(w), 1035(w), 990(w). 863(m).

Pd(CA)(COD)·THF and Pd(CA)(COD)·H₂O

Different complexes, yellow Pd(CA)(COD)·THF and dark purple Pd(CA)(COD)·H₂O,
were obtained by reacting (6) with COD (cyclooctadiene) in THF and CH₂Cl₂,
respectively. 0.60 g (1.5 mmole) of (6) and 0.18 g of COD (1.7 mmole, 10% excess)
were stirred in 50 ml of THF. The precursor complex, which is not soluble in THF,
slowly converted to the greenish-yellow product. The reaction mixture was stirred for 2
days, after which the product was isolated by filtration, washed with THF and ether, and
vacuum dried. Yield: 56% (0.60 g, 0.28 mmole). Anal. Calcd. for Pd(CA)(C₈H₁₂)·THF:
C, 43.80; H, 4.08. Found: C, 43.18; H, 3.99. IR (KBr pellet): 3460(m,br), 2950(w).
COD (0.11 g, 1.0 mmole) was mixed with 0.40 g (1.0 mmole) of (6) in CH$_2$Cl$_2$. The reaction mixture was stirred for about a week. A dark purple powder was obtained by filtration, washed with CH$_2$Cl$_2$ and ether, and vacuum dried. Yield: 98% (0.43 g, 0.98 mmole). Anal. Calcd. for Pd(CA)(C$_8$H$_{12}$)H$_2$O: C, 38.25; H, 3.21. Found: C, 38.29; H, 2.61. IR (KBr pellet): 3440(m,br), 2370(w), 1644(m), 1546(s,br), 1368(s,br), 1005(w), 990(w), 848(m), 766(w).

**Kinetic Measurements**

Kinetic measurements of CA$^{2-}$ isomerization reactions induced by the action of various phosphines on Pd(CA)(CH$_3$CN)$_2$ were performed on a Durrum Model D-110 stopped flow spectrophotometer. The tris(m-chlorophenyl)phosphine system, which reacts slowly on the stopped-flow time scale, was studied on a Perkin-Elmer Lambda-5 UV-visible spectrophotometer.

**Stopped Flow Measurements**

Most of the kinetic measurements on CA$^{2-}$ isomerization, which typically require less than 1/2 hour per run, were carried out on a stopped flow spectrophotometer under anaerobic conditions. Anaerobic CH$_3$CN stock solutions of phosphines, prepared as described for the synthesis of phosphine complexes, were diluted to obtain specific concentrations and a fresh anaerobic CH$_3$CN solution of $2 \times 10^{-4}$ M Pd(CA)(CH$_3$CN)$_2$ was prepared shortly before use in kinetic studies. These solutions were in constant contact with N$_2$ gas and introduced through Teflon needles. The N$_2$ was saturated with solvent by passing through aqueous chromous scrubbing towers followed by 2 CH$_3$CN towers. No appreciable evaporation of solutions was observed.
This instrument contains a Kel-F flow subsystem leading to a 2 cm path length observation chamber, a tungsten visible light source, and a grating monochrometer. Kepco Model ABC 1500(M) and Power/Mate power supplies were used for the photomultiplier tube and tungsten lamp, respectively. Samples to be mixed, contained in glass drive syringes submerged in water circulated from a Forma Scientific temperature control unit (temp. control ± 0.2 °C), were allowed to stand at least 30 minutes to reach temperature equilibrium before the kinetic runs were initiated.

Absorbance-time traces were transmitted to an Apple II Plus computer through ADALAB/AI 13 interface A/D converter/clock cards controlled by program Quickersample, all supplied by Interactive Microware, Inc. At least 256 absorbance-time points covering more than 10 reaction half-lives were collected in each kinetic determination and stored on a floppy disk. Graphical display of the data on the Apple II Plus computer and subsequent quantitative interpretation were accomplished through the Vidichart program from Interactive Microware, Inc., modified by the Holwerda Group. More than 50 absorbance-time points covering at least 85% of the absorbance change were used in each rate constant determination.

Pseudo-first-order conditions were applied for isomerization studies, with a fixed concentration of (6) (2 × 10⁻⁴ M) and greater than an 8-fold excess of the phosphine incoming group. The increase in purple color linked to the isomerization of the CA⁻⁻ moiety was followed at 530 nm. Observed pseudo-first-order rate constants (k_{obsd}) were derived from the least-square slopes of ln(A₀ - Aₜ) versus time plots, and all reported rate constants are the average of at least four runs.

Some bottles of CH₃CN solvent supplied by Fisher were found to have traces of contaminant(s). Contaminated CH₃CN exhibits significant absorbance at 220 nm and causes the isomerization of the CA⁻⁻ moiety with a t₁/₂ of 10 minutes, which is slow.
compared to that caused by most phosphines. Attempts to purify CH$_3$CN by distillation were not successful and it was necessary to use CH$_3$CN which showed no peak at 220 nm.

**Slow Kinetic Measurements**

The isomerization reaction of CA$^{2-}$ induced by tris(m-chlorophenyl)phosphine was aerobically studied under the same conditions as the other phosphines. $^{31}$P NMR spectra showed that no oxidation of tris(m-chlorophenyl)phosphine dissolved in anaerobic CH$_3$CN occurred within the reaction time scale (1 hour). The absorbance-time data were analyzed on a Macintosh computer using the Graph 5.4 program developed by my research advisor, Dr. Robert A. Holwerda.

**Other Instruments**

Nuclear magnetic resonance (NMR) measurements were recorded on IBM AF-300 and 200 Fourier transform NMR spectrometers, and all data are reported relative to the following external standards: $^1$H(TMS), $^{31}$P(85% H$_3$PO$_4$), $^{13}$C(TMS) with positive values indicating downfield chemical shifts. All $^{13}$C NMR spectra were broad band decoupled. Infrared (IR) and UV-visible spectra were acquired at the slowest scan speed available on Beckman Acculab 8 and Shimadzu UV-260 spectrophotometers, respectively.

Mass spectral data were obtained on a Hewlett-Packard 5995-B gas chromatograph/mass spectrometer at an ionizing current of 70 eV. All of the Pd complexes tried did not show parent peaks, and decomposed to give grayish-black tar-like material.
CHAPTER III
RESULTS

Syntheses of Pd(CA) Complexes

An extensive family of chloranilatopalladium(II) complexes was successfully prepared with excellent yields from the precursors Pd(CA)(CH\textsubscript{3}CN)\textsubscript{2} (6) and Pd(CA)(H\textsubscript{2}O)\textsubscript{2} (7). Although (6) proved to be the best starting material in most cases, owing to the ease of CH\textsubscript{3}CN displacement, (7) was a superior choice in several reactions involving hydrophilic incoming groups that are not appreciably soluble in non-aqueous solvents. Compounds of the form Pd(CA)L\textsubscript{2} (L = monodentate or 1/2 of a bidentate chelating unit) were isolated throughout except for L = P(o-tolyl)\textsubscript{3}, where the steric influence of the o-CH\textsubscript{3} substituents evidently hinders the replacement of coordinated CH\textsubscript{3}CN by a second L group at a cis position in the first coordination sphere of palladium.

On the other hand, extremely soft ligands, such as I\textsuperscript{-}, CN\textsuperscript{-}, S\textsuperscript{2-}, and olefins, initially form thermally-unstable adducts with Pd(CA) which decompose through displacement of the CA\textsuperscript{2-} ligand and/or reduction of Pd(II) to Pd(0). For this reason, K\textsubscript{2}Pd(CA)(CN)\textsubscript{2}-H\textsubscript{2}O could only be prepared in a solvent (CH\textsubscript{3}OH) where the precursor complex (7) is soluble but the incoming ligand (as KCN) and product are comparably insoluble. Also notable is the failure of the Pd(CA) moiety to form stable adducts with strongly \pi-accepting olefins such as TCNE and DDQ. Chloranilate negative charges evidently cannot be polarized towards the Pd(II) center sufficiently to promote the coordination of \pi-acid ligands.

Analytical data summarized in Table 1 confirm the purity of all compounds except the ethylenediamine adduct, which is not sufficiently soluble to permit recrystallization. Several of the phosphine complexes were isolated with a water molecule of crystallization.
even though the syntheses were carried out in dry acetonitrile. The presence of water in Pd(\(\text{CA}\))(\(\text{P(NMe}_2\text{)}_3\))\(_2\)-H\(_2\)O, Pd(\(\text{CA}\))(\(\text{PPh}_3\))\(_2\)-H\(_2\)O, and Pd(\(\text{CA}\))(\(\text{P(p-fluorophenyl)}_3\))\(_2\)-H\(_2\)O was demonstrated by mass spectral data which show the H\(_2\)O peak (m/e = 18). This water is presumably derived from the air during workup and recrystallization of the phosphine complexes, and probably is attracted through hydrogen-bonding interactions with \(\text{CA}^2\)-carbonyl groups. The mass spectrum of K\(_2\)Pd(\(\text{CA}\))Cl\(_2\)-1/2H\(_2\)O also shows the peak at m/e = 18.

Spectroscopic Measurements

Infrared, UV-visible and NMR spectroscopies were utilized to determine the influence of ligands on the bonding mode of the chloranilate dianion. These spectral data suggest that all of the compounds contain \(\text{CA}^2\)- in either the bis(carbanion) (C-\(\text{CA}\)) or p-quinone resonance form, vide infra. Chloranilate evidently is reluctant to function as a catecholate bidentate ligand. In carbon-bonded chloranilate complexes, the possibility of unequal Pd-C bond lengths must be considered along with ligand-dependent variations in the degree of bending of the six-membered ring, as shown for K\(_2\)Pd(\(\text{CA}\))Cl\(_2\)-4H\(_2\)O in Figure 1. As a p-quinone, chloranilate may function as a \(\pi\)-complexed bis(diene) donor (\(\pi\)-\(\text{CA}\)), an asymmetric bidentate ligand bonded through both C=O and C-O" oxygen atoms, or a monodentate ligand bonded through either a phenolate oxygen atom or a single C=C unit.

NMR Spectroscopy

The presence of only two resonances in the \(^{13}\text{C}\) NMR spectrum of K\(_2\)Pd(C-\(\text{CA}\))Cl\(_2\)-1/2H\(_2\)O, at 99.5 (carbanion carbons) and 169.4 ppm (carbonyl carbons), is as expected from the published X-ray structure. In order for only two types of carbon to appear in the \(^{13}\text{C}\) NMR spectrum, the interconversion of the nonequivalent Pd-C bonds (with bond lengths of 2.02 and 2.07 Å in K\(_2\)Pd(C-\(\text{CA}\))Cl\(_2\)-4H\(_2\)O)\(^{26}\) must be rapid on the NMR time scale in solution. Similarly, the two \(^{13}\text{C}\) peaks of (6) at 102.4 and 173.2 ppm,
shifted slightly downfield from the analogous peaks of the dichloro complex, indicate the presence of carbon-bonded CA\(^2\)- in the bis(acetonitrile) complex and rule out the presence of either p- or o-quinone resonance forms of the chloranilate dianion, which should give rise to at least three carbon signals. As anticipated, the displacement of CH\(_3\)CN from (6) by triphenylphosphine, a more effective σ donor ligand, induces the rearrangement of (C-CA) to (π-CA). Chloranilate \(^{13}\)C NMR resonances at 103.3 (C-Cl), 170.9 (C-O\(^-\)) and 174.7 ppm (C=O) indicate three distinct types of CA\(^2\)- carbon in the triphenylphosphine compound, excluding the possibility of monodentate CA\(^2\)- but consistent with the bis(diene) formulation.

Furthermore, magnetic equivalence of the two phosphine ligands in bis(phosphine)complexes was established by the appearance of singlets in \(^{31}\)P NMR spectra. A comparison of phosphorous-31 chemical shifts of free ligands and palladium phosphine complexes is presented in Table 2, along with electronic and steric parameters characteristic of the phosphine ligands. The electronic effect (ν, cm\(^{-1}\)) is defined as the A\(_1\) carbonyl stretching frequency of a [Ni(CO)\(_3\)L\(_1\)] compound, where L = tertiary phosphine, in CH\(_2\)Cl\(_2\). This parameter could be used to correlate changes in phosphine molecular properties such as basicity which result from electronic inductive effects. That ν is indeed a measure of electronic effects, not affected by steric factors, is suggested by the near identity in values for P(p-tolyl)\(_3\) (2066.7 cm\(^{-1}\)) and P(o-tolyl)\(_3\) (2066.6 cm\(^{-1}\)). Triarylphosphine donor atoms undergo a downfield shift on the order of 40 ppm upon coordination to the Pd(CA) center. Thus, the bis(triphenylphosphine) complex exhibits a downfield shift of 38.82 ppm. Considerably larger downfield shifts of 63 (normal-) and 65 (iso-) ppm were noted in the \(^{31}\)P NMR spectra of the tributylphosphine compounds.

In order to establish the geometrical orientation of the two phosphine ligands, \(^{2}\)J\(_{pp}\) coupling constants were evaluated for mixed complexes of the form Pd(CA)(PPh\(_3\))(P{Ph-X}\(_3\)), where X = p-F, p-CH\(_3\) and m-CH\(_3\). Dichloromethane
solutions of these complexes were generated \textit{in situ} by mixing equimolar quantities of (6), PPh$_3$ and P{Ph-X)$_3$. Singlets corresponding to Pd(CA)(PPh$_3$)$_2$-H$_2$O and Pd(CA)(P{Ph-X)$_3$)$_2$ were resolved in addition to the doublet of doublets arising from the mixed phosphine complex (Figure 3). $^2$JP coupling constants characteristic of X = p-F (25 Hz; $\delta$ = 34.51, 34.29, 34.11, 31.44, 31.32, 31.11 ppm), p-CH$_3$ (22 Hz; $\delta$ = 34.56, 34.37, 34.04, 33.29, 33.03, 32.85 ppm) and m-CH$_3$ (21 Hz; $\delta$ = 35.86, 35.69, 34.99, 34.11, 33.40, 33.22 ppm) consistently fall within the range (20-40 Hz) expected for cis coupling and well below the much larger values (300-500 Hz) typical of trans bis(phosphine)Pd(II) complexes.$^{29, 30, 31}$ Taken together, the $^{13}$C and $^{31}$P NMR results rule out the possibility that water occupies a square-planar coordination position in Pd(CA)(PR$_3$)$_2$, leaving CA$_2^+$ bonded as a monodentate ligand. Unfortunately, $^{13}$C-$^{31}$P spin-spin coupling was not observed in the carbon-13 spectrum of the triphenylphosphine complex, ruling out the use of potentially revealing multiplet splittings to distinguish among the structural alternatives.

\textbf{Infrared Spectroscopy}

KBr pellet infrared (IR) spectra are quite useful in identifying the bonding preference of coordinated chloranilate. Representative IR spectra of each linkage isomer, Pd(CA)(CH$_3$CN)$_2$ for (C-CA) and Pd(CA)(PPh$_3$)$_2$-H$_2$O, are illustrated in Figure 4, along with those of H$_2$CA and K$_2$CA-H$_2$O in Figure 5. The accessibility of two equivalent p-quinone resonance forms in K$_2$CA-H$_2$O causes the collapse of C=C, C=O and C-O$^-$ stretches to one broad peak, corresponding to C-O and C-C bond orders of 1.5. Infrared peaks of the triphenylphosphine complex at 1640, 1530, 1360 and 830 (C-Cl) cm$^{-1}$ are characteristic of complexes containing 2,5-dioxo-3,6-dichloro-1,4-benzoquinone$^{32, 33}$ and similar to those of simple chloranilate salts such as K$_2$CA-H$_2$O. Unfortunately, an extensive mixing of carbon and oxygen (phenolic and ketonic) p atomic orbitals of the CA$_2^-$
moiety hinders assignment of peaks at 1640, 1530 and 1360 cm\(^{-1}\) to localized C=O, C-O\(^{-}\) and C=C stretches, respectively. However, it would be reasonable to assume that 1640 and 1530 cm\(^{-1}\) absorptions are mainly two different CO stretches (\(v_1\) and \(v_2\)) while the 1360 cm\(^{-1}\) band (\(v_3\)) is basically a CC stretch in nature.

In contrast, the IR spectrum of Pd(C-CA)(CH\(_3CN\))\(_2\) exhibits three carbonyl absorptions above 1600 cm\(^{-1}\) (1685, 1670 and 1630), but no hybrid stretching modes between 1550 and 1350 cm\(^{-1}\). The C-Cl stretching frequency is shifted to higher energy (855 cm\(^{-1}\)) relative to that of Pd(CA)(PPh\(_3\))\(_2\)-H\(_2\)O (841 cm\(^{-1}\)), as would be anticipated for a change in the hybridization of carbon from sp\(^2\) towards sp\(^3\). Finally, the yellow Pd(C-CA)(CH\(_3CN\))\(_2\) complex shows medium-intensity bands at 1200 and 1155 cm\(^{-1}\) which are not observed in the spectra of chloranilic acid or its salts with other transition metals.\(^{28, 29}\) These bands, tentatively assigned as C-C stretches within a five-membered metallocyclic ring, are seen only in Pd(CA) complexes which also have predominant carbonyl absorptions above 1600 cm\(^{-1}\) and C-Cl stretches at energies higher than 850 cm\(^{-1}\). A comparison of diagnostic IR characteristics suggests that all Pd(CA) complexes contain either the p-quinone or the (C-CA) resonance form of chloranilate, as shown in Tables 3 and 4, respectively. Infrared results are also helpful in understanding the bonding modes of acac\(^{-}\), DMSO, NO\(_3\)^{-}, SCN\(^{-}\) and TCNQ in their chloranilatopalladium(II) complexes.

K[Pd(CA)(acac)]

The acetylacetonate anion is known to form both bidentate, O-bonded and monodentate, C-bonded linkage isomers with Pd(II) as shown below.\(^{34}\)

The oxygen-bonded form exhibits CO and CC stretches in the range 1500-1575 cm\(^{-1}\), whereas carbonyl groups of carbon-bonded acac\(^{-}\) absorb at higher frequency (1650 cm\(^{-1}\)).\(^{35}\) The facts that the C-Cl stretching frequency of K[Pd(CA)(acac)] is shifted to 855 cm\(^{-1}\) and medium intensity peaks assigned as C-C stretches are present (1195 and
1175 cm\(^{-1}\)) suggest that KPd(CA)(acac) is a (\(\text{C-CA}\)) isomer. Thus, the observed strong bands of KPd(CA)(acac) at 1578, 1570 (shoulder) and 1513 cm\(^{-1}\) must arise from CC and CO stretches of the acac\(^{-}\) moiety, providing strong evidence for the presence of an O-bonded acetylacetonate ligand.

Unfortunately, a comparison with the IR spectrum of Pd(acac)\(_2\) (1569 cm\(^{-1}\), assigned to \(v(\text{CO})\), and 1524 cm\(^{-1}\) (\(v(\text{CC})\))\(^{36, 37}\)) reveals too little change to determine the relative \(\sigma\)-donor strengths of (\(\text{C-CA}^2\)) and (\(\text{O-acac}^{-}\)) towards the Pd(II) metal center.

\([\text{Pd(CA)(DMSO)}_2]\)

The electronic structure of sulfoxides may be represented by a resonance hybrid of the structures (I) and (II):

\[
\begin{align*}
\text{(I)} & \quad \begin{array}{c}
\circ \quad \text{O} \\
\text{S}^+ \\
\text{R} \\
\text{R}
\end{array} \\
\text{(II)} & \quad \begin{array}{c}
\circ \quad \text{O} \\
\text{S}^- \\
\text{R} \\
\text{R}
\end{array}
\end{align*}
\]

If coordination occurs through oxygen, the contribution of structure (I) will increase and the S=O stretching frequency will decrease. In contrast, coordination through the sulfur atom would shift S=O stretches to higher energy according to (II).\(^{38}\) Interestingly,
SO stretching frequencies (1103, 1095 and 1032 cm\(^{-1}\)) of [Pd(CA)(DMSO)\(_2\)] are about the same as those of free DMSO (1100-1055 cm\(^{-1}\)) and much lower than in S-bonded PdCl\(_2\)(DMSO)\(_2\) (1157-1116 cm\(^{-1}\)). One may discard the possibility of an O-bonded isomer, however, since SO stretches are expected to occur well below 1000 cm\(^{-1}\) in this circumstance.\(^{39}\)

\[\text{[Pd(CA)(H\(_2\)O)\(_2\)]-KNO}_3\]

Instead of showing separate N=O and N-O stretches due to nitrato-metal complexation, [Pd(CA)(H\(_2\)O)\(_2\)]-KNO\(_3\) has only one intense NO stretch at 1389 cm\(^{-1}\), which is exactly the same as in KNO\(_3\). Thus, cocrystallization of [Pd(CA)(H\(_2\)O)\(_2\)] with KNO\(_3\) is proposed.

\[\text{K}_2[\text{Pd(CA)(SCN)}]_2\]

The empirical formula of the thiocyanate complex suggests a bridged, dimeric configuration that would permit each Pd(II) center to interact with four ligands in the most favorable square planar stereochemical arrangement. A thiocyanate CN stretching frequency higher than 2100 cm\(^{-1}\) typically reflects bonding through sulfur (2111 and 2120 cm\(^{-1}\) for (Et\(_4\)N)\(_2\)Pd(SCN)\(_4\) and (Et\(_4\)N)\(_2\)Pt(SCN)\(_4\), respectively), while N-bonded SCN\(^-\) has v(CN) less than 2100 cm\(^{-1}\).\(^{40}\) Thus, the K\(_2[\text{Pd(CA)(SCN)}]_2\) band at 2160 cm\(^{-1}\) is consistent with a sulfur-bonded isomer. The exceptionally high CN stretching frequency of K\(_2[\text{Pd(CA)(SCN)}]_2\) as compared with other S-bonded complexes indicates bridging SCN\(^-\) groups. For example, [(P(n-Pr)\(_3\))\(_2\)Pt\(_2\)(SCN)\(_4\)] exhibits both bridging (2182-2150 cm\(^{-1}\)) and terminal (2120-2100 cm\(^{-1}\)) CN stretching bands.\(^{41}\) These IR results therefore suggest a bridging structure having equivalent CN bonds, as shown below.
The Pd(CA)(TCNQ)H₂O complex has two IR peaks in the CN stretching region with approximately equal intensity (2230 and 2160 cm⁻¹), while K₂Pd(CA)(CN)₂H₂O exhibits only one CN peak at 2220 cm⁻¹. Considering that free TCNQ also exhibits only one CN stretching absorption at 2210 cm⁻¹, it appears likely that TCNQ is bound to Pd as a bidentate ligand through adjacent nitrogen atoms rather than C=C bonds.

This hypothesis also accounts for the successful synthesis of a TCNQ complex with Pd(CA) when similar strongly π-accepting olefins such as TCNE and DDQ failed to give isolable adducts.

**UV-visible Spectroscopy**

Electronic spectroscopy offers a third powerful technique by which the geometrical structures of chloranilate linkage isomers may be elucidated. Thus, a symmetry-forbidden π-π* (overlapping n-π*) quinonoid electronic transition between 500 and 550 nm is responsible for the deep purple colors of complexes containing chloranilate bonded as a p-quinone.⁴², ⁴³, ⁴⁴ A fully-allowed π-π* band is also seen in the near-UV between 300 and 350 nm.⁴², ⁴³, ⁴⁴ In contrast, quinonoid π-π* transitions are quenched in the
yellow, (C-CA) compounds, for which ligand-to-metal charge transfer (LMCT) transitions from ligated carbon or the variable L substituent should dominate the electronic absorption spectrum.

Table 5 presents a summary of major features in the electronic spectra of the chloranilatopalladium(II) compounds reported in this dissertation. Unfortunately, several of these chloranilate complexes are not sufficiently soluble to obtain solution-phase spectroscopic measurements. It should be noted that free ligand must be present to suppress the dissociation of L from Pd(C-CA)L₂ in aqueous solutions, except in the case of K₂[Pd(CA)(SCN)]₂. Spectra obtained in the absence of excess L are exactly the same as that of Pd(CA)(H₂O)₂H₂O, as shown in Figure 6, suggesting 100 % conversion to Pd(CA)(H₂O)₂ on the time scale of 0 to 3 minutes.

Dichloromethane solutions of the phosphine and arsine compounds typically exhibit strong (ε > 10⁴ M⁻¹cm⁻¹) transitions near 230, 280 and 340 nm; a weaker visible band (ε ≅ 10³ M⁻¹cm⁻¹) is found near 540 nm. The lowest energy UV and visible transitions are readily assigned to quinonoid π-π* bands,²⁴ shifted by the interaction of ligand π orbitals with Pd(II) 4d orbitals. However, phosphorus (or arsenic) p orbital(σ)-to-Pd(II) 4dₓ²₋ᵧ²(σ) LMCT transitions are also expected to occur near 340 nm; for trans-Pd(PPh₃)₂Cl₂, λ_max = 346 nm (ε 10⁴ M⁻¹cm⁻¹).⁴⁵ Phosphine and arsine complex bands between 250 and 300 nm fall near the analogous transitions of free PR₃ (or AsR₃) ligands containing aromatic R groups, and therefore must be ligand-centered in nature. Consistent with this hypothesis is the absence of strong 250-300 nm absorption features in phosphine complexes with R = i-butyl, n-butyl and cyclohexyl. The extremely intense peak found near 230 nm (225-245 nm) in all phosphine complexes could possibly be a metal-to-ligand charge transfer (MLCT) transition of the type Pd(II) dπ-phosphorus 3dπ or π* of the CA₂-moiety. The energies and intensities of Pd(π-CA)(PR₃)₂ charge transfer bands vary only slightly with R group changes, as may be seen by comparing the spectral data for R =
C₆H₅, p-(CH₃)C₆H₄ and p-(OCH₃)C₆H₄. Although spectral features within the family of phosphine complexes are quite similar, the significant impact of PR₃ ligands on Pd-CA²⁻ bonding is apparent from the comparison of the Pd(CA)(PPh₃)₂·H₂O spectrum with that of purple K₂Pd(CA)(CN)₂·H₂O. Thus, the near-UV and visible chloranilate π-π* bands of the cyanide complex are blue-shifted by 11 and 14 nm, respectively; the corresponding energy shifts are 9.7 × 10² and 4.9 × 10² cm⁻¹.

The yellow compounds classified as (C-CA) isomers on the basis of their IR characteristics also have UV-visible electronic spectra that differ markedly from those of the purple compounds which contain the (π-CA) linkage isomer. The precursor complexes (5), (6) and (7) are typical of the (C-CA) class, exhibiting three strong transitions with comparable intensities near 220, 260 and 310 nm and no visible absorption maxima. The positions and intensities of Pd((C-CA)L₂ electronic transitions are remarkably insensitive to the nature of the L group, suggesting that all three major bands primarily involve the CA²⁻ chromophore. Bands in the 215-250 nm region are π-π* transitions of the localized carbonyl groups in the bent, non-quinonoid resonance form of the chloranilate dianion. The two remaining prominent UV features are most likely separate carbon(σ)-to-Pd(II) (σ) LMCT bands involving the electron pairs localized on the chloranilate carbon atoms which bear chlorine substituents.

**Kinetic Studies of Isomerization**

**Overview**

Kinetic studies of chloranilate linkage isomerization were carried out on Pd(C-CA)(CH₃CN)₂ with various triphenylphosphine incoming groups in order to understand the electronic and steric effects of substituents on the rate parameters without complications which may arise from the use of mixed arylalkyl phosphines:
Typical 530 nm absorbance-time data are shown in Figure 7, and the corresponding plot of $\ln(A_{\infty} - A_t)$ versus time is shown in Figure 8. Logarithmic plots were generally found to be linear for at least 90% of the total absorbance change, and pseudo-first-order rate constants were derived from the least-squares slopes of these plots. Observed pseudo-first-order rate constants ($k_{\text{obsd}}$) show saturation behavior upon increasing the phosphine concentration, as shown in Figure 9. In no case was there evidence for Pd(II) reduction or displacement of the CA$_2^-$ moiety, even with 200-fold excesses of the phosphine ligands.

Unfortunately, the low solubility of several potentially interesting phosphine substrates, such as P(cyclohexyl)$_3$, P(benzyl)$_3$ and 1,2-bis(diphenylphosphino)benzene, prevented kinetic studies of their reactions with (6) in acetonitrile solution.

**Mechanistic Model**

As a working hypothesis, a mechanism is proposed on the basis that: 1) observed pseudo-first-order rate constants approach a saturation limit with increasing PR$_3$ concentration, suggesting rate-limiting linkage isomerization following a rapid pre-equilibrium and 2) the much slower isomerization rates observed for several kinetic experiments ($t_{1/2} \geq 1$ hour) with PR$_3$ as the limiting reagent compared to $t_{1/2} \leq 5$ minutes. (limiting reagent = [Pd(C-CA)(CH$_3$CN)$_2$]) indicate that [Pd(C-CA)(PR$_3$)$_2$] rather than [Pd(C-CA)(CH$_3$CN)(PR$_3$)] must be the predominant precursor to [Pd($\pi$-CA)(PR$_3$)$_2$] in the presence of excess PR$_3$.

Assuming that $K_{f1} \gg K_{f2}$ (due to the formation of cis-[Pd(C-CA)(PR$_3$)$_2$]) and that the PR$_3$ association equilibria are established rapidly on the time scale of the $k_1$ rate-determining step, $k_{\text{obsd}}$ for isomerization can be expressed through Eq. (3-1) (see Appendix for the derivation).
\[ \text{Pd}(\text{C-CA})(\text{CH}_3\text{CN})_2 + \text{PR}_3 \overset{K_{f_1}}{\rightleftharpoons} \text{Pd}(\text{C-CA})(\text{PR}_3)(\text{CH}_3\text{CN}) + \text{CH}_3\text{CN} \]

\[ \text{Pd}(\text{C-CA})(\text{PR}_3)(\text{CH}_3\text{CN}) + \text{PR}_3 \overset{K_{f_2}}{\rightleftharpoons} \text{Pd}(\text{C-CA})(\text{PR}_3)_2 + \text{CH}_3\text{CN} \]

\[ \text{Pd}(\text{C-CA})(\text{PR}_3)_2 \overset{k_{1,\text{slow}}}{\longrightarrow} \text{Pd}(\pi\text{-CA})(\text{PR}_3)_2 \]

\[ \frac{d}{dt} [\text{Pd}(\pi\text{-CA})(\text{PR}_3)_2] = k_{\text{obsd}} [\text{Pd}(\text{C-CA})]_{\text{total}} \]  \hspace{1cm} (3-1)

where \( k_{\text{obsd}} = \frac{k_1 K_{f_2} [\text{PR}_3]}{1 + K_{f_2} [\text{PR}_3]} \) and

\[ [\text{Pd}(\text{C-CA})]_{\text{total}} = [\text{Pd}(\text{C-CA})(\text{CH}_3\text{CN})_2] + [\text{Pd}(\text{C-CA})(\text{PR}_3)_2] \]

According to Eq. (3-1), the graph of the ln(A∞ - A_t) versus time should be a straight line, where the slope is \( k_{\text{obsd}} \). One can rearrange Eq. (3-1) to obtain a linear relationship between \( (k_{\text{obsd}})^{-1} \) and \( [\text{PR}_3]^{-1} \) as shown in Eq. (3-2).

\[ \frac{1}{k_{\text{obsd}}} = \frac{1 + K_{f_2} [\text{PR}_3]}{k_1 K_{f_2} [\text{PR}_3]} = \frac{1}{k_1 K_{f_2}} \left[ \frac{1}{[\text{PR}_3]} + \frac{1}{k_1} \right] \]  \hspace{1cm} (3-2)

A plot of \( (k_{\text{obsd}})^{-1} \) versus \( [\text{PR}_3]^{-1} \) should give a straight line with \( 1/k_1 K_{f_2} \) as slope and \( 1/k_1 \) as intercept. In this way, the \( k_1 \) value can be calculated from \( 1/(\text{intercept}) \) and \( K_{f_2} \) from \( (\text{intercept})/(\text{slope}) \).

**Temperature Dependence Study**

The concentration dependence of \( k_{\text{obsd}} \) for linkage isomerization induced by triphenylphosphine was obtained according to Eq. (3-1) from 25.0 °C to 45.4 °C at approximately 5 °C intervals. The \( k_{\text{obsd}} \) data at each temperature show saturation behavior...
Plots of $k_{\text{obsd}}$ versus $[\text{PPh}_3]$ are shown in Figure 10. The linear plots of $(k_{\text{obsd}})^{-1}$ versus $[\text{PPh}_3]^{-1}$, in accordance with Eq. (3-2), are shown in Figure 11. The rate parameters $k_1$ and $K_{f_2}$ obtained from the inverse plots are collected in Table 7.

The Effects of Substituents

The effects of substituents on the rate of chloranilate linkage isomerization were studied for the reactions of (6) with various tris(mono-substituted)phenyl phosphines. Again, the $k_{\text{obsd}}$ data show saturation behavior for each phosphine ligand. The $k_{\text{obsd}}$ data and rate parameters are collected in Tables 8 and 9, respectively and plots of $k_{\text{obsd}}$ versus phosphine concentration are shown in Figure 12. Double inverse plots of $(k_{\text{obsd}})^{-1}$ versus $[\text{phosphines}]^{-1}$ are displayed in Figure 13.

Isomerization Kinetics with Bidentate Phosphine Ligands

Since most phosphine complexes synthesized have 2 phosphorus donor atoms, kinetic isomerization studies with several bidentate phosphine ligands, including 1,2-bis(diphenylphosphino)acetylene, cis-1,2-bis(diphenylphosphino)ethylene and trans-1,2-bis(diphenylphosphino)ethylene, were carried out as a comparison with the reactivity of monodentate phosphines. Absorbance-time data obtained for isomerization reactions induced by 1,2-bis(diphenylphosphino)acetylene and cis-1,2-bis(diphenylphosphino)ethylene showed clean pseudo-first-order relationships. On the other hand, first order analytical plots were non-linear in the case of trans-1,2-bis(diphenylphosphino)ethylene and no further attempt was made to analyze these data.

The concentration dependences of $k_{\text{obsd}}$ for the isomerization reactions induced by 1,2-bis(diphenylphosphino)acetylene and cis-1,2-bis(diphenylphosphino)ethylene are collected in Table 10 and pictured in Figure 14. The dependence of $k_{\text{obsd}}$ on [cis-1,2-bis(diphenylphosphino)ethylene] was similar to that observed with monophosphines, yielding a linear double inverse plot (Figure 15). The rate parameters for cis-1,2-
bis(diphenylphosphino)ethylene, based on Eq. (3-2), are \( k_1 = (3.65 \pm 0.01) \times 10^{-2} \text{ s}^{-1} \) and \( K_f = (1.9 \pm 0.2) \times 10^3 \text{ M}^{-1} \).

In contrast, \( k_{\text{obsd}} \) for the 1,2-bis(diphenylphosphino)acetylene incoming group decreases upon increasing the ligand concentration. A mechanism involving rapid pre-equilibrium formation of a dead-end complex, \([\text{Pd}(\pi\text{-CA})(\text{P-P})]\) where P-P acts as a monodentate ligand, is proposed to explain the unusual relation between \( k_{\text{obsd}} \) and [1,2-bis(diphenylphosphino)acetylene], as shown in Figure 16. The rate of isomerization expected from this hypothesis is as follows (see Appendix);

\[
\frac{d}{dt} [\text{Pd}(\pi\text{-CA})]_{\text{total}} = [\text{Pd}(\pi\text{-CA})]_{\text{total}} \left(\frac{k_1}{1 + \frac{K_d[\text{P-P}]}{K_{fc}}}\right)
\]

where

\[
k_{\text{obsd}} = \frac{k_1}{1 + \frac{K_d[\text{P-P}]}{K_{fc}}}
\]

P-P = 1,2-bis(diphenylphosphino)acetylene

\( k_1 = \) Isomerization rate of 1:1 adduct, \([\text{Pd}(\pi\text{-CA})(\text{P-P})]\)

\( K_d = \) Formation constant of a dead-end complex, \([\text{Pd}(\pi\text{-CA})(\text{P-P})_2]\)

\( K_{fc} = \) Formation constant of \([\text{Pd}(\pi\text{-CA})(\text{P-P})]\)

According to Eq. (3-3), a plot of \( (k_{\text{obsd}})^{-1} \) \textit{versus} [P-P] should be a straight line with \( 1/k_1 \) as intercept and \( K_d/k_1K_{fc} \) as slope. The \( k_1 \) value can be calculated from \( 1/(\text{intercept}) \), \((5.09 \pm 0.47) \times 10^{-2} \text{ s}^{-1} \), and \( K_d/K_{fc} \) from \((\text{slope})/(\text{intercept}) \), \((2.4 \pm 0.4) \times 10^3 \text{ M}^{-1} \). A non-linear least-squares analysis gave the same values for \( k_1 \) and \( K_d/K_{fc} \). The linear plot of \( (k_{\text{obsd}})^{-1} \) \textit{versus} [1,2-bis(diphenylphosphino)acetylene] is shown in Figure 17.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Theoretical Percentage</th>
<th>Found Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(P(phenyl)(_3))(_2)(\cdot)H(_2)O</td>
<td>C; 58.93, H; 3.77</td>
<td>C; 59.21, H; 3.39</td>
</tr>
<tr>
<td>Pd(CA)(As(phenyl)(_3))(_2)(\cdot)H(_2)O</td>
<td>C; 53.40, H; 3.42</td>
<td>C; 52.89, H; 3.10</td>
</tr>
<tr>
<td>Pd(CA)(P(CH(_3))(_3))(_2)(\cdot)H(_2)O</td>
<td>C; 29.80, H; 4.17</td>
<td>C; 29.92, H; 3.34</td>
</tr>
<tr>
<td>Pd(CA)(P(i-butyl)(_3))(_2)</td>
<td>C; 50.19, H; 7.58</td>
<td>C; 49.97, H; 7.67</td>
</tr>
<tr>
<td>Pd(CA)(P(n-butyl)(_3))(_2)</td>
<td>C; 50.19, H; 7.58</td>
<td>C; 50.44, H; 7.73</td>
</tr>
<tr>
<td>Pd(CA)(P(NMc(_2))(_3))(_2)(\cdot)H(_2)O</td>
<td>C; 32.87, H; 5.82, N; 12.78</td>
<td>C; 33.25, H; 5.67, N; 12.76</td>
</tr>
<tr>
<td>Pd(CA)(P(cyclohexyl)(_3))(_2)(\cdot)H(_2)O</td>
<td>C; 56.54, H; 7.68</td>
<td>C; 56.64, H; 7.61</td>
</tr>
<tr>
<td>Pd(CA)(P(benzyl)(_3))(_2)</td>
<td>C; 62.52, H; 4.59</td>
<td>C; 62.32, H; 4.45</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C(_6)H(_4)Cl)(_3))(_2)</td>
<td>C; 48.29, H; 2.32</td>
<td>C; 48.30, H; 2.21</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C(_6)H(_4)NMe(_2))(_3))(_2)</td>
<td>C; 59.16, H; 5.52, N; 7.67</td>
<td>C; 58.83, H; 5.47, N; 7.65</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C(_6)H(_4)F)(_3))(_2)(\cdot)H(_2)O</td>
<td>C; 52.34, H; 2.72</td>
<td>C; 52.97, H; 2.38</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C(_6)H(_4)OCH(_3))(_3))(_2)</td>
<td>C; 56.63, H; 4.16</td>
<td>C; 57.26, H; 4.27</td>
</tr>
<tr>
<td>Pd(CA)(P(tolyl)(_3))(_2)</td>
<td>C; 62.52, H; 4.59</td>
<td>C; 62.28, H; 4.46</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C(_6)H(_4)CF(_3))(_3))(_2)</td>
<td>C; 46.28, H; 1.94</td>
<td>C; 46.55, H; 1.92</td>
</tr>
<tr>
<td>Pd(CA)(P(m-C(_6)H(_4)Cl)(_3))(_2)</td>
<td>C; 48.29, H; 2.32</td>
<td>C; 47.83, H; 2.21</td>
</tr>
<tr>
<td>Pd(CA)(P(m-C(_6)H(_4)OCH(_3))(_3))(_2)(\cdot)H(_2)O</td>
<td>C; 55.65, H; 4.28</td>
<td>C; 55.67, H; 4.25</td>
</tr>
<tr>
<td>Pd(CA)(P(m-tolyl)(_3))(_2)</td>
<td>C; 62.52, H; 4.59</td>
<td>C; 62.59, H; 4.61</td>
</tr>
<tr>
<td>Pd(CA)(P(o-C(_6)H(_4)OCH(_3))(_3))(_2)</td>
<td>C; 56.63, H; 4.16</td>
<td>C; 56.22, H; 4.15</td>
</tr>
<tr>
<td>Pd(CA)(P(o-tolyl)(_3))(CH(_3)CN)-CH(_3)CN</td>
<td>C; 53.20, H; 3.89, N; 4.00</td>
<td>C; 53.43, H; 4.01, N; 4.31</td>
</tr>
<tr>
<td>Pd(CA)(dppa)-1/2H(_2)O(^a)</td>
<td>C; 53.62, H; 2.95</td>
<td>C; 53.50, H; 2.68</td>
</tr>
<tr>
<td>Pd(CA)(dppb)-1/2H(_2)O(^b)</td>
<td>C; 56.24, H; 3.28</td>
<td>C; 56.35, H; 3.06</td>
</tr>
<tr>
<td>Pd(CA)(dppe)-1/2H(_2)O(^c)</td>
<td>C; 54.00, H; 3.40</td>
<td>C; 53.85, H; 3.32</td>
</tr>
<tr>
<td>Pd(CA)(cis-dpe)-1/2H(_2)O(^d)</td>
<td>C; 54.15, H; 3.12</td>
<td>C; 54.00, H; 2.98</td>
</tr>
<tr>
<td>Pd(CA)(trans-dpe)-1/2H(_2)O(^e)</td>
<td>C; 54.15, H; 3.12</td>
<td>C; 53.85, H; 2.99</td>
</tr>
<tr>
<td>Pd(CA)(bpy)</td>
<td>C; 40.93, H; 1.72, N; 5.97</td>
<td>C; 40.71, H; 1.67, N; 6.00</td>
</tr>
<tr>
<td>Pd(CA)(en)(_2)</td>
<td>C; 27.70, H; 3.69, N; 12.91</td>
<td>C; 29.94, H; 3.94, N; 11.53</td>
</tr>
<tr>
<td>Pd(CA)(DMSO)(_2)</td>
<td>C; 25.58, H; 2.58</td>
<td>C; 25.69, H; 2.44</td>
</tr>
<tr>
<td>K(_2)Pd(CA)(CN)(_2)-H(_2)O</td>
<td>C; 20.82, H; 0.43, N; 6.07</td>
<td>C; 20.69, H; 0.37, N; 6.29</td>
</tr>
</tbody>
</table>
Table 1. Continued.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Theoretical Percentage</th>
<th>Found Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(CH3CN)2</td>
<td>C; 30.37, H; 1.53, N; 7.08</td>
<td>C; 30.02, H; 1.45, N; 7.07</td>
</tr>
<tr>
<td>Pd(CA)(H2O)2·H2O</td>
<td>C; 19.61, H; 1.64</td>
<td>C; 19.65, H; 1.51</td>
</tr>
<tr>
<td>Pd(CA)(TCNQ)·H2O</td>
<td>C; 40.37, H; 1.13, N; 10.46</td>
<td>C; 40.82, H; 2.28, N; 10.24</td>
</tr>
<tr>
<td>K2Pd(CA)(F)2·H2O</td>
<td>C; 16.10, H; 0.45</td>
<td>C; 16.02, H; 0.79</td>
</tr>
<tr>
<td>K2Pd(CA)(Cl)2·1/2H2O</td>
<td>C; 15.29, H; 0.21, Cl; 30.08, K; 16.59</td>
<td>C; 15.12, H; 0.43, Cl; 29.94, K; 16.71</td>
</tr>
<tr>
<td>K2Pd(CA)(Br)2·H2O</td>
<td>C; 15.39, H; 0.86</td>
<td>C; 15.37, H; 0.36</td>
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<tr>
<td>K2Pd(CA)(Br)2·4H2O</td>
<td>C; 16.00, H; 0.89</td>
<td>C; 15.64, H; 0.53</td>
</tr>
<tr>
<td>Pd(CA)(H2O)2·KNO3</td>
<td>C; 19.31, H; 0.40</td>
<td>C; 19.30, H; 0.63</td>
</tr>
<tr>
<td>K2Pd(CA)(ox)·H2O</td>
<td>C; 12.66, H; 0.35</td>
<td>C; 12.78, H; 0.29</td>
</tr>
<tr>
<td>KPd(CA)(acac)</td>
<td>C; 15.86, H; 0.86</td>
<td>C; 15.37, H; 0.36</td>
</tr>
<tr>
<td>K2Pd(CA)(SCN)2</td>
<td>C; 15.39, H; 0.86</td>
<td>C; 15.37, H; 0.36</td>
</tr>
<tr>
<td>K2Pd(CA)2·2H2O</td>
<td>C; 20.48, H; 0.00, N; 3.41</td>
<td>C; 20.50, H; 0.06, N; 3.15</td>
</tr>
<tr>
<td>Pd(CA)(COD)·THF</td>
<td>C; 22.71, H; 0.63</td>
<td>C; 22.51, H; 0.28</td>
</tr>
<tr>
<td>Pd(CA)(COD)·H2O</td>
<td>C; 43.80, H; 3.99</td>
<td>C; 43.18, H; 3.99</td>
</tr>
<tr>
<td></td>
<td>C; 38.25, H; 3.21</td>
<td>C; 38.29, H; 2.61</td>
</tr>
</tbody>
</table>

\( ^{a} \) dppa = bis(diphenylphosphino)acetylene.

\( ^{b} \) dppb = 1,2-bis(diphenylphosphino)benzene.

\( ^{c} \) dppe = 1,2-bis(diphenylphosphino)ethane.

\( ^{d} \) cis-dpee = 1,2-cis-bis(diphenylphosphino)ethylene.

\( ^{e} \) trans-dpee = 1,2-trans-bis(diphenylphosphino)ethylene.
Table 2

$^{31}$P NMR Chemical Shift and other Data for Phosphine Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{31}$P(C)$^a$ (ppm)</th>
<th>$^{31}$P(L)$^b$ (ppm)</th>
<th>$\Delta^{31}$P$^c$ (ppm)</th>
<th>$\nu^d$ (cm$^{-1}$)</th>
<th>$\sigma^e$</th>
<th>Angle$^f$ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(P(phenyl)$_3$)$_2$·H$_2$O</td>
<td>34.05</td>
<td>-4.77</td>
<td>38.82</td>
<td>2068.9</td>
<td>0</td>
<td>145</td>
</tr>
<tr>
<td>Pd(CA)(P(CH$_3$)$_3$)$_2$·H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td>2064.1</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>Pd(CA)(P(i-butyl)$_3$)$_2$</td>
<td>25.51</td>
<td>-40</td>
<td>65</td>
<td>2059.7</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>Pd(CA)(P(n-butyl)$_3$)$_2$</td>
<td>30.03</td>
<td>-33</td>
<td>63</td>
<td>2060.3</td>
<td>132</td>
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</tr>
<tr>
<td>Pd(CA)(P(NMe$_2$)$_3$)$_2$·H$_2$O</td>
<td>91.18</td>
<td>122</td>
<td>-31</td>
<td>2061.9</td>
<td>157</td>
<td></td>
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<tr>
<td>Pd(CA)(P(cyclohexyl)$_3$)$_2$·H$_2$O</td>
<td>50.48</td>
<td>11.4</td>
<td>39.08</td>
<td>2056.4</td>
<td>170</td>
<td></td>
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<tr>
<td>Pd(CA)(P(benzyl)$_3$)$_2$</td>
<td>34.49</td>
<td>-10.09</td>
<td>44.58</td>
<td>2066.4</td>
<td>165</td>
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</tr>
<tr>
<td>Pd(CA)(P(p-PhCl)$_3$)$_2$</td>
<td>32.03</td>
<td>-7.75</td>
<td>39.78</td>
<td>2072.8</td>
<td>0.24</td>
<td>145</td>
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<tr>
<td>Pd(CA)(P(p-PhNMe$_2$)$_3$)$_2$</td>
<td>31.91</td>
<td>-10.91</td>
<td>42.82</td>
<td>2071.3</td>
<td>0.15</td>
<td>145</td>
</tr>
<tr>
<td>Pd(CA)(P(p-PhF)$_3$)$_2$·H$_2$O</td>
<td>31.45</td>
<td>-8.32</td>
<td>39.77</td>
<td>2071.1</td>
<td>0.15</td>
<td>145</td>
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<tr>
<td>Pd(CA)(P(p-PhOC$_3$)$_3$)$_2$</td>
<td>31.88</td>
<td>-9.56</td>
<td>41.44</td>
<td>2066.1</td>
<td>-0.12</td>
<td>145</td>
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<tr>
<td>Pd(CA)(P(p-tolyl)$_3$)$_2$</td>
<td>33.17</td>
<td>-7.37</td>
<td>40.54</td>
<td>2066.7</td>
<td>-0.14</td>
<td>145</td>
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<tr>
<td>Pd(CA)(P(p-PhCF$_3$)$_3$)$_2$</td>
<td>32.33</td>
<td>-5.20</td>
<td>37.53</td>
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<td>145</td>
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<tr>
<td>Pd(CA)(P(m-PhCl)$_3$)$_2$</td>
<td>33.38</td>
<td>-3.75</td>
<td>37.13</td>
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<td>0.37</td>
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<tr>
<td>Pd(CA)(P(m-PhOCH$_3$)$_3$)$_2$·H$_2$O</td>
<td>34.79</td>
<td>-4.54</td>
<td>39.33</td>
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<td>-0.06</td>
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<tr>
<td>Pd(CA)(P(m-tolyl)$_3$)$_2$</td>
<td>34.79</td>
<td>-4.54</td>
<td>39.33</td>
<td>2067.2</td>
<td>-0.06</td>
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<tr>
<td>Pd(CA)(P(o-PhOCH$_3$)$_3$)$_2$</td>
<td>15.68</td>
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<td>53.67</td>
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<td>Pd(CA)(P(o-tolyl)$_3$)(CH$_3$CN)$_2$</td>
<td>23.09</td>
<td>-29.44</td>
<td>52.53</td>
<td>2066.6</td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ $^{31}$P(C) = $^{31}$P chemical shift for the Pd(CA)(PR$_3$)$_2$ complex.

$^b$ $^{31}$P(L) = $^{31}$P chemical shift for the (PR$_3$) ligand.

$^c$ $\Delta^{31}$P = Difference between $^{31}$P(C) and $^{31}$P(L).

$^d$ $\nu$ = Electronic effect of the phosphine.

$^e$ $\sigma$ = Hammett $\sigma$ value.

$^f$ Angle = cone angle of phosphines.
Figure 3

Typical $^{31}$P NMR Spectra of Mixed Phosphine Complexes

$\text{Pd(CA)(PPh}_3)(\text{P(m-tolyl)}_3)$ (A),
$\text{Pd(CA)(P(m-tolyl)}_2$ (B),
$\text{Pd(CA)(PPh}_3)_2$ (C)
Figure 4

IR Spectra of Pd(η²-CA)(CH₃CN)₂ (A) and Pd(η²-CA)(PPh₃)₂ (B)
Figure 5

IR Spectra of H$_2$CA (A) and K$_2$CA·H$_2$O (B)
Table 3

Principal IR Peaks of Pd(CA)(PPh$_3$)$_2$ and Analogous Compounds

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_1$(CO)</th>
<th>$\nu_2$(CO)</th>
<th>$\nu_3$(CC)</th>
<th>C-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(P(phenyl)$_3$)$_2$·H$_2$O</td>
<td>1640</td>
<td>1529</td>
<td>1364</td>
<td>841</td>
</tr>
<tr>
<td>Pd(CA)(As(phenyl)$_3$)$_2$·H$_2$O</td>
<td>1660</td>
<td>1529</td>
<td>1356</td>
<td>843</td>
</tr>
<tr>
<td>K$_2$Pd(CA)$_2$·2H$_2$O</td>
<td>b</td>
<td>1528</td>
<td>1374</td>
<td>839</td>
</tr>
<tr>
<td>Pd(CA)(COD)-H$_2$O</td>
<td>1644</td>
<td>1544</td>
<td>1370</td>
<td>848</td>
</tr>
<tr>
<td>Pd(CA)(bpy)</td>
<td>1665, 1639</td>
<td>1512</td>
<td>1366</td>
<td>853</td>
</tr>
<tr>
<td>Pd(CA)(en)$_2$</td>
<td>1600</td>
<td>1519</td>
<td>1369</td>
<td>831</td>
</tr>
<tr>
<td>Pd(CA)(DMSO)$_2$</td>
<td>1645</td>
<td>1524</td>
<td></td>
<td>837</td>
</tr>
<tr>
<td>K$_2$Pd(CA)(CN)$_2$·H$_2$O</td>
<td>1660</td>
<td>1531</td>
<td></td>
<td>835</td>
</tr>
<tr>
<td>Pd(CA)(P(CH$_3$)$_3$)$_2$·H$_2$O</td>
<td>1643</td>
<td>1546</td>
<td>1384</td>
<td>843</td>
</tr>
<tr>
<td>Pd(CA)(P(i-butyl)$_3$)$_2$</td>
<td>1647</td>
<td>1525</td>
<td>1367</td>
<td>839</td>
</tr>
<tr>
<td>Pd(CA)(P(n-butyl)$_3$)$_2$</td>
<td>1645</td>
<td>1526</td>
<td>1362</td>
<td>841</td>
</tr>
<tr>
<td>Pd(CA)(P(NMe$_2$)$_3$)$_2$·H$_2$O</td>
<td>1642</td>
<td>1530</td>
<td>1369</td>
<td>834</td>
</tr>
<tr>
<td>Pd(CA)(P(cyclohexyl)$_3$)$_2$·H$_2$O</td>
<td>1642</td>
<td>1531</td>
<td>1374</td>
<td>841</td>
</tr>
<tr>
<td>Pd(CA)(P(benzyl)$_3$)$_2$</td>
<td>1644</td>
<td>1505</td>
<td>1362</td>
<td>841</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C$_6$H$_4$Cl)$_3$)$_2$</td>
<td>1639</td>
<td>1524</td>
<td>1355</td>
<td>844</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C$_6$H$_4$NMe$_2$)$_3$)$_2$</td>
<td>1646</td>
<td>1516</td>
<td>1369</td>
<td>840</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C$_6$H$_4$F)$_3$)$_2$·H$_2$O</td>
<td>1640</td>
<td>1528</td>
<td>1362</td>
<td>830</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C$_6$H$_4$OCH$_3$)$_3$)$_2$</td>
<td>1638</td>
<td>1527</td>
<td>1367</td>
<td>832</td>
</tr>
<tr>
<td>Pd(CA)(P(p-tolyl)$_3$)$_2$</td>
<td>1633</td>
<td>1530</td>
<td>1354</td>
<td>842</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C$_6$H$_4$CF$_3$)$_3$)$_2$</td>
<td>1640</td>
<td>1532</td>
<td>1369</td>
<td>834</td>
</tr>
<tr>
<td>Pd(CA)(P(m-C$_6$H$_4$Cl)$_3$)$_2$</td>
<td>1647</td>
<td>1533</td>
<td>1355</td>
<td>846</td>
</tr>
<tr>
<td>Pd(CA)(P(m-C$_6$H$_4$OCH$_3$)$_3$)$_2$·H$_2$O</td>
<td>1643</td>
<td>1527</td>
<td>1358</td>
<td>841</td>
</tr>
<tr>
<td>Pd(CA)(P(m-tolyl)$_3$)$_2$</td>
<td>1643</td>
<td>1528</td>
<td>1363</td>
<td>842</td>
</tr>
<tr>
<td>Pd(CA)(P(o-C$_6$H$_4$OCH$_3$)$_3$)$_2$</td>
<td>1643</td>
<td>1527</td>
<td>1375</td>
<td>842</td>
</tr>
<tr>
<td>Pd(CA)(P(o-tolyl)$_3$)(CH$_3$CN)$_2$</td>
<td>1648</td>
<td>1529</td>
<td>1358</td>
<td>844</td>
</tr>
</tbody>
</table>
Table 3. Continued.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_1$(CO)$^a$ (cm$^{-1}$)</th>
<th>$\nu_2$(CO)$^a$ (cm$^{-1}$)</th>
<th>$\nu_3$(CC)$^a$ (cm$^{-1}$)</th>
<th>C-Cl (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(dppa)-1/2H$_2$O$^c$</td>
<td>1660, 1643</td>
<td>1529</td>
<td>1358</td>
<td>845</td>
</tr>
<tr>
<td>Pd(CA)(dppb)-1/2H$_2$O$^d$</td>
<td>1663, 1645</td>
<td>1516</td>
<td>1363</td>
<td>841</td>
</tr>
<tr>
<td>Pd(CA)(dppe)-1/2H$_2$O$^e$</td>
<td>1676, 1640</td>
<td>1512</td>
<td>1363</td>
<td>839</td>
</tr>
<tr>
<td>Pd(CA)(cis-dpee)-1/2H$_2$O$^f$</td>
<td>1680, 1645</td>
<td>1511</td>
<td>1366</td>
<td>837</td>
</tr>
<tr>
<td>Pd(CA)(trans-dpee)-1/2H$_2$O$^g$</td>
<td>1661, 1644</td>
<td>1526</td>
<td>1362</td>
<td>844</td>
</tr>
</tbody>
</table>

$^a$ Hybrid of C=O, C-O$^-$ and C=C stretches.

$^b$ Cannot be measured accurately due to the presence of interferences.

$^c$ dppa = bis(diphenylphosphino)acetylene.

$^d$ dppb = 1,2-bis(diphenylphosphino)benzene.

$^e$ dppe = 1,2-bis(diphenylphosphino)ethane.

$^f$ cis-dpee = 1,2-cis-bis(diphenylphosphino)ethylene.

$^g$ trans-dpee = 1,2-trans-bis(diphenylphosphino)ethylene.
## Table 4

IR Data for Complexes Containing the (C-CA) Resonance Form

<table>
<thead>
<tr>
<th>Complex</th>
<th>C=O (cm⁻¹)</th>
<th>C-Cl (cm⁻¹)</th>
<th>C-C (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(COD)·THF</td>
<td>1680</td>
<td>861</td>
<td>1120</td>
</tr>
<tr>
<td>Pd(CA)(TCNQ)·H₂O</td>
<td>1657, 1638</td>
<td>864</td>
<td>1183</td>
</tr>
<tr>
<td>Pd(CA)(CH₃CN)₂</td>
<td>1695, 1680, 1635</td>
<td>866</td>
<td>1208, 1161</td>
</tr>
<tr>
<td>Pd(CA)(H₂O)₂·H₂O</td>
<td>1690, 1635</td>
<td>867</td>
<td>1213, 1190, 1175, 1165</td>
</tr>
<tr>
<td>K₂Pd(CA)(F)₂·H₂O</td>
<td>1659, 1636</td>
<td>861</td>
<td>1170, 1080</td>
</tr>
<tr>
<td>K₂Pd(CA)(Cl)₂·1/2H₂O</td>
<td>1694, 1661, 1628</td>
<td>865</td>
<td>1214, 1180, 1161</td>
</tr>
<tr>
<td>K₂Pd(CA)(Br)₂·H₂O</td>
<td>1687, 1656</td>
<td>867</td>
<td>1215, 1176</td>
</tr>
<tr>
<td>K₂[Pd₂(CA)₂(Br)₂]·4H₂O</td>
<td>1710, 1685, 1664</td>
<td>863</td>
<td>1176, 1152</td>
</tr>
<tr>
<td>K₂Pd(CA)(ox)·H₂O</td>
<td>1650</td>
<td>866</td>
<td>1177</td>
</tr>
<tr>
<td>Pd(CA)(H₂O)₂·KNO₃</td>
<td>1690, 1649</td>
<td>864</td>
<td>1215, 1175</td>
</tr>
<tr>
<td>K₂(Pd(CA)(SCN))₂</td>
<td>1690, 1652</td>
<td>867</td>
<td>1190, 1163</td>
</tr>
<tr>
<td>KPd(CA)(acac)</td>
<td>1695, 1679, 1640</td>
<td>868</td>
<td>1195, 1175</td>
</tr>
<tr>
<td>K₂Pd(CA)₂·2H₂O</td>
<td>1658, 1640, 1625</td>
<td>868</td>
<td>1215, 1168</td>
</tr>
<tr>
<td>Green Intermediate</td>
<td>1720, 1690</td>
<td>866</td>
<td>1180, 1154</td>
</tr>
</tbody>
</table>
Table 5
Ultraviolet-Visible Spectra of Chloranilato-Palladium(II) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>U.V. Data^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(P(phenyl)₃)₂·H₂O</td>
<td>CH₂Cl₂</td>
<td>229.6 (4.91 \times 10^4), 278.8 (1.84 \times 10^4), 343.4 (3.87 \times 10^4), 541.8 (1.1 \times 10^3)</td>
</tr>
<tr>
<td>Pd(CA)(As(phenyl)₃)₂·H₂O</td>
<td>CH₂Cl₂</td>
<td>229.6 (4.72 \times 10^4), 294.6 (1.67 \times 10^4), 346.8 (4.07 \times 10^4), 543.8 (1.28 \times 10^3)</td>
</tr>
<tr>
<td>Pd(CA)(P(CH₃)₃)₂·H₂O</td>
<td>CH₂Cl₂</td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(P(i-butyl)₃)₂</td>
<td>CH₂Cl₂</td>
<td>237.8 (2.73 \times 10^4), 343.4 (2.98 \times 10^4), 546.8 (1.0 \times 10^3)</td>
</tr>
<tr>
<td>Pd(CA)(P(n-butyl)₃)₂</td>
<td>CH₂Cl₂</td>
<td>230.0 (2.84 \times 10^4), 344.0 (2.87 \times 10^4), 548.2 (9.7 \times 10^2)</td>
</tr>
<tr>
<td>Pd(CA)(P(NMe₂)₃)₂·H₂O</td>
<td>CH₂Cl₂</td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(P(cyclohexyl)₃)₂·H₂O</td>
<td>CH₂Cl₂</td>
<td>197.0 (1.50 \times 10^4), 241.8 (2.39 \times 10^4), 342.6 (3.28 \times 10^4), 547.8 (1.0 \times 10^3)</td>
</tr>
<tr>
<td>Pd(CA)(P(benzyl)₃)₂</td>
<td>CH₂Cl₂</td>
<td>228.6 (4.01 \times 10^4), 250 (2.0 \times 10^4)^*, 341.2 (3.10 \times 10^4), 545.8 (1.1 \times 10^3)</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C₆H₄Cl)₃)₂</td>
<td>CH₂Cl₂</td>
<td>234.6 (7.43 \times 10^4), 294 (1.8 \times 10^4)^*, 343.2 (4.22 \times 10^4), 540.0 (1.2 \times 10^3)</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C₆H₄NMe₂)₃)₂</td>
<td>CH₂Cl₂</td>
<td>228.2 (5.08 \times 10^4), 287.0 (1.04 \times 10^5), 345.6 (3.16 \times 10^4), 375.6 (2.95 \times 10^4), 428 (2.3 \times 10^4)^*</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C₆H₄F)₃)₂·H₂O</td>
<td>CH₂Cl₂</td>
<td>230.4 (5.04 \times 10^4), 293.6 (1.64 \times 10^4), 342.2 (4.00 \times 10^4), 541.8 (1.2 \times 10^3)</td>
</tr>
<tr>
<td>Pd(CA)(P(p-C₆H₄OCH₃)₃)₂</td>
<td>CH₂Cl₂</td>
<td>242.8 (7.43 \times 10^4), 352.6 (4.54 \times 10^4), 543.2 (9.5 \times 10^2)</td>
</tr>
<tr>
<td>Pd(CA)(P(p-tolyl)₃)₂</td>
<td>CH₂Cl₂</td>
<td>229.8 (6.06 \times 10^4), 345.6 (4.26 \times 10^4), 540.8 (1.1 \times 10^3)</td>
</tr>
</tbody>
</table>
Table 5. Continued.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>U.V. Data&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CA)(P(p-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;CF&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH₂Cl₂</td>
<td>229.6 (4.40 X 10⁴), 280.4 (2.11 X 10⁴), 340.8 (3.38 X 10⁴), 544.2 (1.2 X 10³)</td>
</tr>
<tr>
<td>Pd(CA)(P(m-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Cl)&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH₂Cl₂</td>
<td>229.4 (5.63 X 10⁴), 287.2 (1.68 X 10⁴), 343.0 (3.43 X 10⁴), 543.2 (1.2 X 10³)</td>
</tr>
<tr>
<td>Pd(CA)(P(m-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;0CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;-H₂O</td>
<td>CH₂Cl₂</td>
<td>229.8 (6.84 X 10⁴), 279.6 (2.37 X 10⁴), 346.4 (3.61 X 10⁴), 541.4 (8.7 X 10²)</td>
</tr>
<tr>
<td>Pd(CA)(P(m-tolyl)&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH₂Cl₂</td>
<td>229.6 (4.96 X 10⁴), 283.6 (1.68 X 10⁴), 344.4 (3.88 X 10⁴), 542.8 (9.7 X 10²)</td>
</tr>
<tr>
<td>Pd(CA)(P(o-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;0CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH₂Cl₂</td>
<td>229.2 (3.70 X 10⁴), 278.6 (1.74 X 10⁴), 350.2 (3.17 X 10³)<em>, 535 (1.3 X 10³)</em></td>
</tr>
<tr>
<td>Pd(CA)(P(o-tolyl)&lt;sub&gt;3&lt;/sub&gt;)(CH₃CN)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH₂Cl₂</td>
<td>230.4 (3.29 X 10⁴), 282.4 (1.04 X 10⁴), 347.6 (2.45 X 10⁴), 540 (1.5 X 10³)*</td>
</tr>
<tr>
<td>Pd(CA)(dppe)-1/2H₂O&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(dppb)-1/2H₂O&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(dppe)-1/2H₂O&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(cis-dpce)-1/2H₂O&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(trans-dpce)-1/2H₂O&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(bpy)</td>
<td></td>
<td>Not soluble</td>
</tr>
<tr>
<td>Pd(CA)(cn)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>watert&lt;sup&gt;g&lt;/sup&gt;</td>
<td>193.6 (2.87 X 10⁴), 206 (2.5 X 10⁴)*, 323.4 (2.24 X 10⁴), 331 (2.2 X 10⁴), 529.8 (1.1 X 10³)</td>
</tr>
<tr>
<td>Pd(CA)(DMSO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>Not soluble</td>
</tr>
</tbody>
</table>
Table 5. Continued.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>U.V. Data(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{K}_2\text{Pd(CA)(CN)}_2\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>(205.2\ (2.36 \times 10^4), 212.6\ (2.53 \times 10^4), 332.0\ (2.12 \times 10^4),)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(340\ (2.0 \times 10^4)^*, 527.6\ (1.6 \times 10^3))</td>
</tr>
<tr>
<td>(\text{Pd(CA)(CH}_3\text{CN)}_2)</td>
<td>CH(_3\text{CN})</td>
<td>(223.0\ (2.31 \times 10^4), 264.0\ (1.05 \times 10^4), 305.8\ (9.6 \times 10^3))</td>
</tr>
<tr>
<td>(\text{Pd(CA)(H}_2\text{O)}_2\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>(224.0\ (1.58 \times 10^4), 256.0\ (9.72 \times 10^3), 314.6\ (1.05 \times 10^4))</td>
</tr>
<tr>
<td>(\text{Pd(CA)(TCNQ)}\cdot\text{H}_2\text{O})</td>
<td></td>
<td>Undergoes isomerization in water</td>
</tr>
<tr>
<td>(\text{K}_2\text{Pd(CA)(F)}_2\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>(213.6\ (1.50 \times 10^4), 256\ (7.6 \times 10^3)^<em>, 310\ (6.4 \times 10^3)^</em>)</td>
</tr>
<tr>
<td>(\text{K}_2\text{Pd(CA)(Cl)}_2\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>(236.0\ (2.17 \times 10^4), 263.6\ (1.79 \times 10^4), 312.4\ (1.46 \times 10^4))</td>
</tr>
<tr>
<td>(\text{K}_2\text{Pd(CA)(Br)}_2\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>(201.2\ (1.24 \times 10^4), 242.2\ (1.50 \times 10^4),)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(285.8\ (2.39 \times 10^4), 310\ (1.9 \times 10^4)^*)</td>
</tr>
<tr>
<td>(\text{K}_2\text{[Pd(CA)(Br)}_2\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>Decomposes in solution</td>
</tr>
<tr>
<td>(\text{Pd(CA)(H}_2\text{O)}_2\cdot\text{KNO}_3)</td>
<td>water</td>
<td>(237.4\ (1.08 \times 10^4), 253.6\ (1.05 \times 10^4), 314.0\ (1.08 \times 10^4))</td>
</tr>
<tr>
<td>(\text{K}_2\text{Pd(CA)(ox)}\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>(242.8\ (2.27 \times 10^4), 310.4\ (8.35 \times 10^3))</td>
</tr>
<tr>
<td>(\text{K}_2\text{Pd(CA)(acac)})</td>
<td>water</td>
<td>(232.0\ (1.75 \times 10^4), 310.6\ (1.50 \times 10^4))</td>
</tr>
<tr>
<td>(\text{K}_2\text{[Pd(CA)(SCN)}_2)</td>
<td>water</td>
<td>(219.0\ (1.79 \times 10^4), 258\ (1.1 \times 10^4)^*, 319.0\ (1.71 \times 10^4))</td>
</tr>
<tr>
<td>(\text{K}_2\text{Pd(CA)}_2\cdot\text{H}_2\text{O})</td>
<td>water</td>
<td>(217.2\ (3.05 \times 10^4), 258\ (1.3 \times 10^4)^*), (320.8\ (2.49 \times 10^4), 537.2\ (3.5 \times 10^2))</td>
</tr>
<tr>
<td>(\text{Pd(CA)(COD)}\cdot\text{THF})</td>
<td></td>
<td>Not soluble</td>
</tr>
<tr>
<td>(\text{Pd(CA)(COD)}\cdot\text{H}_2\text{O})</td>
<td></td>
<td>Not soluble</td>
</tr>
</tbody>
</table>

\(^a\) Data = \(\lambda_{\text{max}}\) (\(\varepsilon, \text{M}^{-1}\cdot\text{cm}^{-1}\)).

\(^b\) dppa = bis(diphenylphosphino)acetylene.

\(^c\) dppb = 1,2-bis(diphenylphosphino)benzene.

\(^d\) dppe = 1,2-bis(diphenylphosphino)ethane.
Table 5. Continued.

e cis-dpee = 1,2-cis-bis(diphenylphosphino)ethylene.

f trans-dpee = 1,2-trans-bis(diphenylphosphino)ethylene.

g pH = 3.68 (HClO₄).

h pH = 3.68 (HClO₄), 1.0 X 10⁻² M⁻¹ of ligand.

i pH = 3.68 (HClO₄), 2.0 X 10⁻² M⁻¹ of ligand.

* * = Shoulder
Ultra-violet Spectra of Pd(C-CA)(H₂O)₂ (A), K₂Pd(C-CA)Cl₂·1/2H₂O (B), K₂Pd(C-CA)Br₂·H₂O (C) and KPd(C-CA)(acac) (D) in Aqueous HClO₄ Solution ([H⁺] = 2.1 × 10⁻⁴ M)
Figure 7

Typical Absorbance versus Time Plot for the Reaction between Pd(C-CA)(CH₃CN)₂ and Tri(m-chlorophenyl)phosphine in CH₃CN Solution (25.0 °C)
Figure 8

Typical $\ln(A_{\infty} - A_t)$ versus Time Plot for the Reaction between Pd(C-CA)(CH$_3$CN)$_2$ and Tri(m-chlorophenyl) phosphine in CH$_3$CN Solution (25.0 °C)
Figure 9

Typical Saturation Behavior of $k_{\text{obsd}}$ with Increasing [PPh$_3$] for the Reaction between Pd(C-CA)(CH$_3$CN)$_2$ and PPh$_3$ in CH$_3$CN Solution (25.0 °C)
Table 6

Pseudo-First-Order Rate Constants for the Reaction of [Pd(C-CA)(CH$_3$CN)$_2$] with Triphenylphosphine in CH$_3$CN Solution$^a$

<table>
<thead>
<tr>
<th>[PPh$_3$], mM</th>
<th>25.0 °C</th>
<th>30.4 °C</th>
<th>34.7 °C</th>
<th>38.6 °C</th>
<th>45.4 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>2.32</td>
<td>2.92</td>
<td>3.16</td>
<td>4.01</td>
<td>4.47</td>
</tr>
<tr>
<td>2.0</td>
<td>2.85</td>
<td>3.61</td>
<td>3.89</td>
<td>4.82</td>
<td>5.70</td>
</tr>
<tr>
<td>3.0</td>
<td>3.70</td>
<td>4.97</td>
<td>5.50</td>
<td>6.66</td>
<td>8.22</td>
</tr>
<tr>
<td>4.0</td>
<td>4.37</td>
<td>6.08</td>
<td>6.81</td>
<td>8.49</td>
<td>10.59</td>
</tr>
<tr>
<td>6.0</td>
<td>4.97</td>
<td>7.43</td>
<td>8.49</td>
<td>11.05</td>
<td>14.13</td>
</tr>
<tr>
<td>10.0</td>
<td>5.86</td>
<td>8.51</td>
<td>10.77</td>
<td>14.50</td>
<td>19.71</td>
</tr>
<tr>
<td>24.0</td>
<td>11.07</td>
<td>15.65</td>
<td>20.80</td>
<td>31.95</td>
<td></td>
</tr>
<tr>
<td>32.0</td>
<td>11.10</td>
<td>17.10</td>
<td>23.01</td>
<td>34.81</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>7.41</td>
<td>11.63</td>
<td>18.07</td>
<td>24.66</td>
<td>36.99</td>
</tr>
</tbody>
</table>

$^a$ Initial concentration of [Pd(C-CA)(CH$_3$CN)$_2$] = 0.20 mM. Uncertainty in rate constants estimated at ± 2%.
Figure 10

Saturation Behaviors of $k_{obsd}$ for the Reaction of Pd(C-CA)(CH$_3$CN)$_2$ with PPh$_3$ in CH$_3$CN Solution at Variable Temperature
Figure 11

Linear Relationships of $(k_{\text{obsd}})^{-1}$ versus $[\text{PPh}_3]^{-1}$ at Variable Temperature
Table 7
Rate Parameters for the Reaction of \([\text{Pd(C-CA)(CH}_3\text{CN})_2]\)
with PPh\(_3\) in CH\(_3\)CN Solution\(^a\)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(k_1, \text{s}^{-1})</th>
<th>(K_{f2}, \text{M}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>((8.44 \pm 0.02) \times 10^{-2})</td>
<td>((2.47 \pm 0.08) \times 10^2)</td>
</tr>
<tr>
<td>30.4</td>
<td>((1.39 \pm 0.04) \times 10^{-1})</td>
<td>((1.74 \pm 0.06) \times 10^2)</td>
</tr>
<tr>
<td>34.7</td>
<td>((2.19 \pm 0.01) \times 10^{-1})</td>
<td>((1.07 \pm 0.02) \times 10^2)</td>
</tr>
<tr>
<td>38.6</td>
<td>((3.01 \pm 0.01) \times 10^{-1})</td>
<td>((9.6 \pm 0.1) \times 10^1)</td>
</tr>
<tr>
<td>45.4</td>
<td>((5.71 \pm 0.02) \times 10^{-1})</td>
<td>((5.4 \pm 0.1) \times 10^1)</td>
</tr>
</tbody>
</table>

\(^a\) Rate parameters are calculated from double inverse plots based on Eq. (3-2), as described in the text. Standard deviations are shown.
Table 8

Pseudo-First-Order Rate Constants for the Reaction of \([\text{Pd(C-CA)}(\text{CH}_3\text{CN})_2]\) with Various Mono-Substituted Phenylphosphines in CH\(_3\text{CN}\) Solution\(^a\)

<table>
<thead>
<tr>
<th>[PR(_3)], mM</th>
<th>p-CH(_3)</th>
<th>p-Cl</th>
<th>p-F</th>
<th>p-OCH(_3)</th>
<th>m-CH(_3)</th>
<th>m-Cl</th>
<th>m-OCH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.1195</td>
<td>0.00549</td>
<td></td>
<td></td>
<td>0.03167</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>0.1387</td>
<td>0.00664</td>
<td>0.01247</td>
<td>0.03399</td>
<td>0.0008527</td>
<td>0.01618</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.1559</td>
<td>0.0102</td>
<td>0.0183</td>
<td>0.29</td>
<td>0.03610</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.1701</td>
<td>0.012</td>
<td>0.02356</td>
<td>0.3023</td>
<td>0.03791</td>
<td>0.001318</td>
<td>0.02506</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1796</td>
<td>0.02867</td>
<td>0.3116</td>
<td>0.03896</td>
<td>0.001861</td>
<td>0.03294</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>0.1973</td>
<td>0.0168</td>
<td>0.03303</td>
<td>0.3213</td>
<td>0.03953</td>
<td>0.002294</td>
<td>0.03635</td>
</tr>
<tr>
<td>6.0</td>
<td>0.2055</td>
<td>0.03999</td>
<td>0.3312</td>
<td>0.04034</td>
<td>0.002634</td>
<td>0.04262</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.0255</td>
<td>0.04597</td>
<td>0.338</td>
<td>0.04130</td>
<td>0.002634</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.0385</td>
<td>0.05795</td>
<td>0.3514</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>0.0362</td>
<td>0.0638</td>
<td>0.356</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Initial concentration of \([\text{Pd(C-CA)}(\text{CH}_3\text{CN})_2]\) = 0.20 mM. Uncertainty in rate constants estimated at ± 2%.

\(^b\) p stands for para-substituted and m for meta-substituted phenyl.
Table 9

Rate Parameters for the Reactions of \([\text{Pd(C-CA)(CH}_3\text{CN)}_2]\) with Tris(mono-substitutedphenyl)phosphines in CH\(_3\)CN Solution\(^a\)

<table>
<thead>
<tr>
<th>Phosphines</th>
<th>(k_1, \text{s}^{-1})</th>
<th>(K_{f2}, \text{M}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>triphenylphosphine</td>
<td>((8.44 \pm 0.02) \times 10^{-2})</td>
<td>((2.47 \pm 0.08) \times 10^{2})</td>
</tr>
<tr>
<td>tri-(p-tolyl)phosphine</td>
<td>((2.44 \pm 0.01) \times 10^{-1})</td>
<td>((6.1 \pm 0.4) \times 10^{2})</td>
</tr>
<tr>
<td>tri-(p-chlorophenyl)phosphine</td>
<td>((8.26 \pm 0.06) \times 10^{-2})</td>
<td>((4.4 \pm 0.2) \times 10^{1})</td>
</tr>
<tr>
<td>tri-(p-fluorophenyl)phosphine</td>
<td>((1.37 \pm 0.01) \times 10^{-1})</td>
<td>((5.1 \pm 0.2) \times 10^{1})</td>
</tr>
<tr>
<td>tri-(p-methoxyphenyl)phosphine</td>
<td>((3.68 \pm 0.01) \times 10^{-1})</td>
<td>((1.19 \pm 0.06) \times 10^{3})</td>
</tr>
<tr>
<td>tri-(m-tolyl)phosphine</td>
<td>((4.35 \pm 0.01) \times 10^{-2})</td>
<td>((1.71 \pm 0.05) \times 10^{3})</td>
</tr>
<tr>
<td>tri-(m-chlorophenyl)phosphine</td>
<td>((4.44 \pm 0.03) \times 10^{-3})</td>
<td>((1.21 \pm 0.06) \times 10^{2})</td>
</tr>
<tr>
<td>tri-(m-methoxyphenyl)phosphine</td>
<td>((6.56 \pm 0.02) \times 10^{-2})</td>
<td>((1.63 \pm 0.05) \times 10^{2})</td>
</tr>
</tbody>
</table>

\(^a\) Rate parameters are calculated from double inverse plots based on Eq. (3-2), as described in the text. Standard deviations are shown. Temperature is 25.0 °C for each system.
Figure 12

Saturation Behaviors of $k_{\text{obsd}}$ for the Reactions of Pd(C₂CA)(CH₃CN)₂ with Tris(mono-substitutedphenyl)phosphines in CH₃CN Solution (25.0 oC)
Figure 12. Continued.
Figure 12. Continued.
Figure 12. Continued.
Figure 12. Continued.
Figure 12. Continued.
Figure 12. Continued.
Figure 13

Linear Relationships of \((k_{\text{obsd}})^{-1}\) versus \([PR_3]^{-1}\) for the Reactions of Pd(CA)(CH\(_3\)CN)\(_2\) with Tris(mono-substitutedphenyl) phosphine in CH\(_3\)CN Solution (25.0 °C)
Figure 13. Continued.
Figure 13. Continued.
Figure 13. Continued.
Figure 13. Continued.
Figure 13. Continued.
Figure 13. Continued.
Table 10

Pseudo-First-Order Rate Constants for the Reactions of [Pd(C-CA)(CH3CN)2] with Diphosphines in CH3CN Solution

<table>
<thead>
<tr>
<th>[Phosphine], mM</th>
<th>dppa$^b$</th>
<th>cis-dpee$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.02561</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.02106</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.01821</td>
<td>0.02251</td>
</tr>
<tr>
<td>1.0</td>
<td>0.01439</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>0.01151</td>
<td>0.02477</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td></td>
<td>0.02663</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td>0.02805</td>
</tr>
<tr>
<td>2.7</td>
<td>0.005746</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td></td>
<td>0.02897</td>
</tr>
<tr>
<td>3.6</td>
<td>0.005352</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td>0.03431</td>
</tr>
<tr>
<td>6.0</td>
<td></td>
<td>0.03264</td>
</tr>
<tr>
<td>10.0</td>
<td></td>
<td>0.03735</td>
</tr>
</tbody>
</table>

$^a$ Initial concentration of [Pd(C-CA)(CH3CN)2] = 0.20 mM. Uncertainty in rate constants estimated at ± 2%. Temperature is 25.0 °C for each system.

$^b$ dppa = bis(diphenylphosphino)acetylene.

$^c$ cis-dpee = cis-1,2-bis(diphenylphosphino)ethylene.
Plots of $k_{\text{obsd}}$ versus $[\text{bis(diphenylphosphino)acetylene}]$ and $[\text{cis-1,2-bis(diphenylphosphino)ethylene}]$ for Reactions with Pd($\text{C}_2\text{CA}$)(CH$_3$CN)$_2$ in CH$_3$CN Solution (25.0 °C)
Figure 15

Linear Relationship of $(k_{obs})^{-1}$ versus $[\text{cis-dpee}]^{-1}$ for the Reaction of Pd(C-CA)(CH$_3$CN)$_2$ with Cis-1,2-bis(diphenylphosphino)ethylene in CH$_3$CN Solution (25.0 $^\circ$C)
Figure 16

Proposed Mechanism for the Reaction between Pd(C-CA)(CH$_3$CN)$_2$ and Bis(diphenylphosphino)acetylene
Figure 17

Linear Relationship between \((k_{\text{obsd}})^{-1}\) (s) and [dppa] for the Reaction between Bis(diphenylphosphino)acetylene and Pd(\(\text{C-CA}\))(CH\(_3\)CN)\(_2\)
CHAPTER IV
DISCUSSION

The Chemistry of Pd(\(\pi\)-CA)\((\text{PR}_3)_2\) Complexes

General Review

The predominant synthetic precursor utilized to prepare chloranilatopalladium(II) compounds, Pd(\(\text{C-CA}\))(CH\(_3\)CN\(_2\)), is superior to K\(_2\)Pd(\(\text{C-CA}\))Cl\(_2\)-1/2H\(_2\)O in terms of both reactivity (2-3 hours versus several days) and convenience for the purpose of conducting kinetic studies of CA\(^2-\) linkage isomerization induced by the attack of triarylphosphines on the Pd(II) center in a non-aqueous solvent. Without this new precursor, an extensive class of Pd(CA) compounds could not have been prepared and mechanistic studies would have been complicated greatly, if not altogether impractical.

Several collaborative attempts to solve the x-ray crystal structure of Pd(CA)(PPh\(_3\))\(_2\)-H\(_2\)O have failed owing to the tendency of crystals to fracture and crumble under mechanical stress or upon long-standing after crystal growth. Although the attempt to solve the structure by direct methods is continuing, spectroscopic results presented in this dissertation support an unambiguous and convincing structural assignment. Thus, electronic and infrared spectra of Pd(CA)(PPh\(_3\))\(_2\)-H\(_2\)O and related compounds clearly establish the presence of the chloranilate dianion in its p-quinone resonance form. The 3-line carbon-13 NMR spectrum of coordinated chloranilate demands a symmetric ligation mode in which CA\(^2-\) functions as a bidentate ligand. The magnetic equivalence of the two phosphorus atoms in all [Pd(CA)(\text{PR}_3)_2] compounds studied considered along with the \(\text{2J}_{pp}\) coupling constants indicates that the phosphine ligands consistently adopt a cis stereochemistry. Finally, the failure of the bulky P(o-tolyl)_3 ligand to form a bis(phosphine) complex testifies further to the reluctance of phosphine ligands to force
chloranilate into a monodentate ligation mode by occupying trans coordination positions.

The structure of the phosphine complexes in best agreement with the spectral data is the
bis(diene), (π-CA) linkage isomer, [Pd(π-CA)(PR3)2], shown below.

\[
\begin{array}{c}
\text{PR}_3 \\
\text{PR}_3 \\
\end{array}
\]

The general tendency of bis(phosphine) complexes to absorb water molecules during
workup can be explained by hydrogen-bonding with phenolate -O\(^-\) groups in these (π-CA)
linkage isomers.

It was hoped that compounds with chelating diphosphines would contribute to the
understanding of palladium(II)-chloranilate bonding by stabilizing and constraining the
movement of the two-phosphorus donor atom set in the first coordination sphere of
palladium. Unfortunately, the extremely low solubilities of diphosphine-Pd(CA) adducts
coupled with the possibility of bidentate bridging between two Pd centers by several of
these ligands rules out firm structural assignments at this time. Thus, a product from the
reaction of a diphosphine with [Pd(C-CA)(CH3CN)2] which analyzes correctly for the
simple empirical formula [Pd(π-CA)(R2P(bridge)PR2)] may actually have the binuclear
structure [Pd(π-CA)(R2P(bridge)PR2)2Pd(π-CA)] or consist of a mixture of mononuclear
and binuclear species. The infrared spectra of these compounds do indicate the presence of
p-quinonoid chloranilate, however, as is obvious from their deep purple colors.
By analogy to other compounds with these diphosphine ligands, the adducts of 1,2-bis(diphenylphosphino)benzene and cis-1,2-bis(diphenylphosphino)ethylene with Pd(CA) almost certainly are bidentate, mononuclear species considering the stereochemical rigidity of the 2P donor atom set. In contrast, 1,2-bis(diphenylphosphino)acetylene and trans-1,2-bis(diphenylphosphino)ethylene can only form binuclear or polymeric complexes with Pd(II), assuming that rotation about the C=C double bond cannot be induced upon bonding of phosphorus to palladium(II). However, 1,2-bis(diphenylphosphino)acetylene appears to induce isomerization of the (CA²-) moiety through a bidentate 1:1 intermediate complex, as demonstrated by the retardation of the reaction with increasing concentration of the dppa incoming group. Several interesting structural alternatives may be considered, including (III) and (IV).

Finally, 1,2-bis(diphenylphosphino)ethane is capable of opting for either bridging or chelating bidentate modes.

Analysis of Spectral Data

The infrared, ultraviolet-visible and nuclear magnetic resonance spectra of bis(phosphine)chloranilatopalladium(II) complexes were interpreted to determine the influence of phosphine substituents on bonding to the (π-CA) moiety, especially the extent to which the σ-inductive and steric (cone angle) effects of phosphine Lewis bases are reflected in σ-donation from and back-bonding to π-complexed chloranilate. Such ground
state influences will also provide a valuable perspective in assessing the structural similarity of the activated complex in phosphine-induced (\(\text{C-CA}\)) to (\(\pi\text{-CA}\)) linkage isomerization to that of the \([\text{Pd}(\pi\text{-CA})(\text{PR}_3)_2]\) product.

Infrared Spectroscopy

At the outset of this work, it was anticipated that the considerable basicity range spanned by the trialkyl- and triarylphosphines examined would lead to significant variations in the carbon-carbon bond order of chloranilate coordinated as a diene. According to the well-documented Dewar-Chatt-Duncunson model of olefin \(\pi\) complexation,\(^{51, 52}\) the \(\text{C=CA}^2\) bond order within CA\(^2\)- could be reduced substantially by the synergistic coupling of ligand \(\pi\)-bonding electron \(\sigma\) donation to the unoccupied Pd(II) \(d_{x^2-y^2}\) orbital with back-bonding from the completely filled Pd(II) \(d_{xy, dxz, dyz}\) into the \(\pi^*\) orbitals of the quinone. Such bond order reductions have been reported for Pd(0) complexes of several neutral benzoquinones, in which highfield shifts of \(\delta(\text{H})\) NMR lines for quinone protons of 0.4 to 1.7 ppm are typical.\(^{25}\) Furthermore, since the lowest unoccupied molecular orbital (LUMO) of p-benzoquinone has \(\text{C}=\text{O}\) \(\pi^*\) character (Figure 18),\(^{23}\) \(\pi\) back-bonding can be conveniently followed through a red-shift of the \(\text{C}=\text{O}\) stretching frequency compared to that of the free quinone. Thus, for Pd(0)(p-C\(_6\)H\(_4\)O\(_2\))(PR\(_3\))\(_2\) complexes. CO bond orders are decreased in the order of decreasing electronic parameters (\(\nu\)). For example, CO stretches are: 1657 cm\(^{-1}\) (free p-C\(_6\)H\(_4\)O\(_2\)) > 1639 cm\(^{-1}\) (P(\(\text{OPh}\))\(_3\), \(\nu = 2085.3\) cm\(^{-1}\)) > 1632 cm\(^{-1}\) (P(p-C\(_6\)H\(_4\)Cl)\(_3\), \(\nu = 2072.8\) cm\(^{-1}\)) > 1632 cm\(^{-1}\) (PPh\(_3\), \(\nu = 2068.9\) cm\(^{-1}\)) > 1627 cm\(^{-1}\) (P(p-C\(_6\)H\(_4\)OCH\(_3\))\(_3\), \(\nu = 2066.1\) cm\(^{-1}\)) > 1613 cm\(^{-1}\) (P(n-Bu)\(_3\), \(\nu = 2060.3\) cm\(^{-1}\)).\(^{25}\) Considering the propensity of simple olefins and dienes for \(\sigma\)-bonding and \(\pi\) back-bonding in organometallic compounds, the carbon-carbon and carbon-oxygen bond orders generally are expected to decrease with increasing electron-releasing character of the complementary ligands.
Unfortunately, due to the localized π system, chloranilate C=C stretches (ν3) in (π-CA) complexes are different in nature from those of either H2CA or K2CA·H2O, ruling out comparisons with simple systems. However, a comparison within [Pd(π-CA)(PR3)2] compounds (Table 2) reveals a surprising insensitivity of ν3 to the electron-donating capacity of the phosphine ligands. Thus, the values characteristic of unsubstituted triphenylphosphine (1364 cm⁻¹) and its p-methoxy (1367 cm⁻¹) or p-trifluoromethyl (1369 cm⁻¹) derivatives are essentially identical in spite of the presence of strong electron-releasing and electron-withdrawing substituents in the latter two compounds, respectively. A range of only 30 cm⁻¹ in ν3(CC) (1354-1384 cm⁻¹) is spanned by the 18 diverse alkyl-, aryl- and aminophosphines compared in Table 3. Looked at in another way, the magnitude of the downfield shift of δ(31P) in complexed relative to free PR3 (Δ(31P), Table 3) provides an accurate measure of electron-donating ability (electronic polarization) of a phosphorus atom towards the Pd(II) center. A plot of ν3(CC) versus Δ(31P) (Figure 19) shows no correlation between the two physical characteristics, implying that the bonding interaction between Pd(II) dπ and chloranilate π systems is weak, at best, and little affected by variations in the (PR3)2 donor set.

Considering now π back-bonding from Pd(II) to chloranilate π* orbitals, both a decrease in ν1(CO) and ν2(CO) is expected. Consistent with the insensitivity of ν3(CC) to variations in PR3 described above, the CA2- ν1(CO) and ν2(CO) bands are nearly invariant, as shown in Table 2 (1633-1647 cm⁻¹ and 1505-1546 cm⁻¹ for ν1(CO) and ν2(CO) of the bisphosphine complexes, respectively), and fall, for the most part, close to the analogous features of K2CA, implying that back-bonding from Pd(II) to chloranilate π* orbitals is weak, if present at all. This conclusion is consistent with the failure of potent π-acid ligands such as TCNE to form stable complexes with Pd(CA).

Similarly, the C-Cl stretching frequencies of (π-CA) palladium(II) compounds with PR3 and AsR3 donors are essentially invariant (832-846 cm⁻¹), confirming that the impact
of P or As Lewis basicity on the hybridization of the carbon atoms carrying chlorine substituents is negligible.

Electronic Spectroscopy

On consideration of the infrared results as a whole, chloranilate bonded as \((\pi-\text{CA})\) may be classified as a "hard" ligand, in contrast to the majority of olefins and dienes, by virtue of its reluctance to either donate its \(\pi\)-electron pairs to palladium or accept d\(\pi\) electron density from the metal center. The electrostatic contribution to Pd(II)-CA\(^{2-}\) bonding therefore should not be underestimated, especially in view of the fact that no complexes are known between neutral 1,4-benzoquinones and divalent palladium. Electronic spectra of the \([\text{Pd}(\pi-\text{CA})(\text{PR}_3)_2]\) compounds are similar to the UV-visible spectrum of K\(_2\text{CA} \cdot \text{H}_2\text{O}\), consistent with presence of an essentially ionic, "hard" chloranilate ligand, but small perturbations in both band positions and intensities reveal a small covalent contribution to the bonding. A qualitative molecular orbital diagram of the chloranilate \(\pi\)-bonding system (Figure 18)\(^{23}\) is useful in assigning the electronic transitions of the \([\text{Pd}(\pi-\text{CA})(\text{PR}_3)_2]\) complexes summarized in Table 5. Although these complexes have only approximate C\(_{2v}\) symmetry, the UV-visible spectrum of coordinated chloranilate is most conveniently interpreted by comparison with the parent 1,4-benzoquinone molecule (D\(_{2h}\)).\(^{42, 43, 44}\)

The \(\pi\)-electronic configuration of 1,4-benzoquinones, in order of increasing LCAO-MO energy, is \((b_{1u})^2(b_{2g})^2(b_{1u})^2(b_{3g})^2\). On this basis, both symmetry-allowed \(b_{1u}-b_{2g}\) (LUMO) \((1B_{3u} \leftarrow 1A_g)\) and symmetry-forbidden \(b_{3g}-b_{2g}\) \((1B_{1g} \leftarrow 1A_g)\) \(\pi-\pi^*\) transitions are expected, along with a \(n(O)-\pi^*\) band at lower energy.\(^{42, 43, 44}\) From this analysis and the spectrum of free CA\(^{2-}\), the intense bands of \([\text{Pd}(\pi-\text{CA})(\text{PR}_3)_2]\) compounds near 340 and 540 nm may be assigned to the \(1B_{3u} \leftarrow 1A_g\) and \(1B_{1g} \leftarrow 1A_g\) transitions, respectively. The forbiddenness of the latter transition is relaxed somewhat by the lowering of symmetry to point group C\(_{2v}\) in \((\pi-\text{CA})\) complexes, for which the Laporte selection rule associated
with the inversion operation does not apply. The impact of symmetry lowering on band intensity is readily seen by comparing the 520 nm extinction coefficient of CA$^{2-}$ in water ($1.74 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$) with the values of $8.7 \times 10^2$ to $1.3 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ associated with unsymmetrically-complexed CA$^{2-}$ in the corresponding transitions of phosphine complexes.

The extinction coefficients of the near-ultraviolet transitions of $[\text{Pd(\pi-CA)(PR}_3)_2]$ compounds ($2.87 \times 10^4$ to $4.54 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) are substantially larger than that of an oxygen-bonded, monodentate CA$^{2-}$ ligand in a 1:1 complex with Cr(III) ($\varepsilon_{340} = 1.64 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), ruling out symmetry lowering as the source of the intensity increase. As was pointed out previously, P($\sigma$)-to-Pd 4$d_x^2$-$y^2$ LMCT transitions evidently overlap the quinonoid $\pi$-$\pi^*$ band, increasing the near-ultraviolet absorptivity and preventing a straightforward analysis of phosphine substituent effects on the positions of the separate transitions. In any case, $\lambda_{\text{max}}$ values fall within the narrow interval 341-353 nm.

Phosphine substituent effects on the $1\text{B}_{1g} \leftarrow 1\text{A}_g$ $\pi$-$\pi^*$ transition may be examined without interference from other spectral features, however, as shown in Figure 20. A reasonably linear correlation (correlation coefficient = 0.9) between band maximum energy and phosphine electronic factor ($v$) is found, with positive slope (17.3), implying that the gap between $b_{3g}$ and $b_{2g}$ ($\pi^*$) molecular orbitals is reduced with increasing basicity of the PR$_3$ ligands. Red-shifts of the $1\text{B}_{1g} \leftarrow 1\text{A}_g$ band induced by the best $\sigma$-donor phosphines are readily understood in terms of the mixing of chloranilate and palladium $b_{3g}$ symmetry orbitals (Figure 18), destabilizing the higher energy (ligand) molecular orbital by the introduction of partial metallic character. In this way, the lower energy $b_{3g}$ (metal) orbital would be correspondingly stabilized by acquiring covalency with the chloranilate ligand. Although the $1\text{B}_{1g} \leftarrow 1\text{A}_g$ band energies of all 18 phosphine complexes examined differ by no more than 500 cm$^{-1}$, it is clear that the "hard" ionic model of ($\pi$-CA) must be modified slightly to allow for limited covalency in bonding to palladium(II).
The assignment of the extremely intense feature near 230 (228-243) nm in the ultraviolet spectra of all phosphine and arsine complexes with Pd(CA) is not obvious, since the free ligands do not exhibit similar bands and phosphorus (or arsenic) to Pd(II) LMCT transitions occur at much lower energy. This high energy electronic transition must be fully spin- and symmetry-allowed, in view of extinction coefficients in the range $2.4 \times 10^4$ to $7.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. Since the band maximum falls at 229 ± 1 nm in 12 of the 16 ultraviolet spectra of $[\text{Pd(\pi-CA)(PR}_3]_2$ compounds reported, it is extremely unlikely that the PR$_3$ ligand functions as either an electron donor or acceptor in a charge transfer transition to or from Pd(II). This conclusion is underscored by the observation that the bands of phosphorus ($[\text{Pd(\pi-CA)(PPh}_3]_2)$ and arsenic ($[\text{Pd(\pi-CA)(AsPh}_3]_2)$ donor complexes have essentially identical $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ values. Although there is no precedent for a quinone $\pi$ ($b_{1u}$) to $4d_x^2y^2$ ($a_g$) ligand-to-metal charge transfer transition, such an assignment would account for the insensitivity of transition energy to complementary ligand electronic characteristics. The possibility of $d\pi$-to-quinone $\pi^*$ (LUMO $b_{2g}$) metal-to-ligand charge transfer should also be considered, but such a transition would be essentially $g(4d)$-$g(b_{2g}\pi^*)$ in character even in the actual $C_{2v}$ symmetry of the palladium complexes, imparting Laporte forbiddenness that is inconsistent with the actual band intensities.

Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy

Phosphine $^{31}\text{P}$ NMR resonances generally undergo a 40-65 ppm downfield shift upon coordination to Pd(II), suggesting considerable polarization of phosphorus $3p$ electron density towards the electrophilic Pd(II) center. A comparison of $\Delta\delta^{31}\text{P}$ parameters between $[\text{Pd(\pi-CA)(PPh}_3]_2\cdot\text{H}_2\text{O}$ (38.82 ppm) and trans-$[\text{PdCl}_2(\text{PPh}_3]_2$ (28.8 ppm) confirms that the (\pi-CA) ligand is a poorer donor towards Pd(II) than chloride ion, as expected from the infrared and UV-visible results. The more basic trialklyphosphines
show larger $\Delta^{(31P)}$ values than the triarylphosphines, in which conjugation between the phosphorus atom and phenyl rings partially buffers the donor atom against the depletion of electron density by bonding to palladium. The greater polarizability of trialkylphosphines is also shown by their ability to cause the largest red shifts in the visible $\pi-\pi^*$ band of $[\text{Pd}(\pi-\text{CA})(\text{PR}_3)_2]$ complexes. The atypical behavior of $\text{P(NMe}_2\text{)}_3$, which experiences a 31 ppm upfield shift upon coordination to Pd(II), may be explained by the $\pi$ back-bonding from filled Pd(II) d$\pi$ to empty phosphorus 3d$\pi$ orbitals, aided by energy lowering of P(3d) due to the electronegative substituents (NMe$_2$) on the phosphorus atom.\textsuperscript{54}

**Kinetics of Linkage Isomerization**

Linkage isomerization of (C-CA) to (\pi-CA) is induced by the substitution of a poor $\sigma$-donor (CH$_3$CN) by a stronger nucleophile (triarylphosphine) to reduce the $\sigma$-donor capability of carbon-bonded chloranilate. Spectroscopic measurements confirmed that this isomerization is triggered by the attack of all phosphines considered on $[\text{Pd(C-CA)(CH}_3\text{CN)}_2]$, even in the case of P(o-tolyl)$_3$ where only one phosphine ligand could be accommodated in the first coordination sphere of palladium. These reactions contrast strongly with phosphine influences on the rates of $\beta$-elimination and reductive elimination of alkyl groups in cis-PdL$_2R_2$ compounds (L = tertiary phosphine).\textsuperscript{55, 56, 57} Thus, reductive elimination of cis alkyl groups depends upon the prior dissociation of a phosphine ligand, such that the rate is strongly inhibited by excess phosphine in solution.

**Determination of Mechanism**

All of the kinetic data are consistent with the proposed intermediate complex mechanism in which rapidly-formed $[\text{Pd(C-CA)}(\text{PPh}_3)_2]$ undergoes rate-limiting linkage isomerization without the assistance of external phosphine. It should be noted, however, that small deviations between observed rate constants near the saturation limit and corresponding values computed from the least squares fit of the data may reflect the
association of a third phosphine ligand into an axial coordination position in some cases.

Before interpreting the rate parameters based on the intermediate complex mechanism, it is important to point out that two other kinetically indistinguishable mechanisms would give rise to the same rate law, leading to rate saturation at high phosphine concentrations. Therefore, a justification of the reasons for not favoring activated intermediate or dead end complex mechanisms will now be presented.

Activated Intermediate Mechanism

The activated intermediate mechanism features the reversible formation of a steady state intermediate from \([\text{Pd(C-CA)(CH}_3\text{CN)}_2]\) without the assistance of the phosphine entering group, followed by a second irreversible step in which this transient species is scavenged by the phosphine to form products:

\[
\text{Pd(C-CA)(CH}_3\text{CN)}_2 \xrightarrow{k_1} \frac{1}{k_{-1}} \text{[Pd(C-CA)(CH}_3\text{CN)}_2]^*} \\
\text{[Activated Intermediate]} + \text{PR}_3 \xrightarrow{k_2} \text{Pd(π-CA)(CH}_3\text{CN)(PR}_3) \\
\]

The \(k_2\) step in such a pathway presumably would involve a conformation change in carbon-bonded chloranilate or a rearrangement within the first coordination sphere of palladium that would activate the Pd-C \(\sigma\) bonds towards cleavage. Assuming that \([\text{Pd(C-CA)(CH}_3\text{CN)}_2]^*\) is a steady-state intermediate, the rate law predicted from this mechanism is:

\[
\frac{d[\text{Pd(π-CA)(PR}_3)_2]}{dt} = \frac{k_1k_2[\text{PR}_3][\text{Pd(π-CA)}]}{k_{-1} + k_2[\text{PR}_3]} . \tag{4.1}
\]
According to Eq. (4-1), the rate constant $k_2$, which is numerically identical to the parameter $k_1$ in the intermediate complex mechanism, should be rigorously independent of the nature of the phosphine incoming group. Since experimental $k_1$ values actually show a significant dependence on triphenylphosphine substituents, the activated intermediate mechanism must be ruled out.

Dead End Complex Mechanism

The dead end complex mechanism, more common in enzymatic than inorganic transformations, requires the rapid formation of a complex from $PR_3$ and the palladium reactant which is incapable of rearranging to the ($\pi$-CA) product by intramolecular linkage isomerization or through the attack of another $PR_3$ molecule on the complex. In this case, product formation would depend on the scavenging of uncomplexed $[Pd(CA)(CH_3CN)_2]$ by $PR_3$:

$$
PR_3 + Pd(CA)(CH_3CN)_2 \xrightleftharpoons{Q_d} Dead End Complex
$$

$$
PR_3 + Pd(CA)(CH_3CN)_2 \rightarrow_{k_2} (\pi$-CA) Complex
$$

Under pseudo first order conditions for $[Pd(CA)(CH_3CN)_2]$, this mechanism generates yet another rate law which predicts saturation at high phosphine concentrations, owing to the complete conversion of the palladium starting material to the putative dead end complex:

$$
\frac{d[Pd(\pi$-CA)(PR$_3$)$_2]}{dt} = \frac{k_2[PR_3][Pd(CA)]_{total}}{1 + Q_d[PR_3]}.
$$

(4-2)

This mechanism is very difficult to disprove in most kinetic studies where isolation or direct observation of intermediate species is impractical. Fortunately, the mechanism is
largely a theoretical construct and has little bearing on actual inorganic substitution mechanisms. The vast majority of intermediate complexes in both inorganic substitution and redox reactions are active participants in the pathways leading to final products, and the dead end complex mechanism has only been successfully defended once in the transition metal mechanistic literature. Practically speaking, dead end complexes would have been readily apparent as contaminants in the synthesis of \([\text{Pd}(\pi\text{-CA})(\text{PR}_3)_2]\) complexes, but no such impurities were actually observed.

**Temperature Dependence Results**

Eyring and van't Hoff plots of \(\ln(k_{1}/T)\) versus \(1/T\) and \(\ln(K_{21})\) versus \(1/T\) (Figure 21), respectively, for linkage isomerization induced by PPh\(_3\) yield the activation parameters of the isomerization step (\(\Delta H^\ddagger = 17.1 \pm 0.3\) kcal/mole; \(\Delta S^\ddagger = -6 \pm 2\) eu) and standard enthalpy/entropy changes corresponding to the uptake of a second PPh\(_3\) ligand by \([\text{Pd}(\pi\text{-CA})(\text{PPh}_3)(\text{CH}_3\text{CN})]\) (\(\Delta H^0 = -14.0 \pm 1.0\) kcal/mole; \(\Delta S^0 = -36 \pm 3\) eu). The standard enthalpy and entropy changes related to \(K_{21}\) are consistent with the bonding of a second PPh\(_3\) ligand to Pd(II) at a sterically hindered coordination position cis to the first PPh\(_3\) unit, which imposes a cone angle of 145°. Indeed, an exceptionally negative \(\Delta S^0(K_{21})\) is primarily responsible for the unusually small \(K_{21}\) values that give rise to kinetic saturation behavior. In contrast, the activation barrier for linkage isomerization is predominantly enthalpic, as would be anticipated considering the stability of 5-membered chelate rings containing one or more sp\(^3\) hybridized carbon donor(s) to palladium(II).

The overall substitutional reactivity of Pd(II) in the triphenylphosphine-induced linkage isomerization reaction, as measured by the product \(K_{21}k_1\) (2.1 \times 10\(^1\) M\(^{-1}\)s\(^{-1}\), 25.0 °C.; \(\Delta H^\ddagger = 3.1\) kcal/mole; \(\Delta S^\ddagger = -42\) eu), is typical of that observed in related ligand exchange processes. Thus, these parameters closely resemble those for cyanide.
exchange in Pd(CN)_{4}^{2-} \ (k \ (24 \ ^{\circ}C.) = 1.2 \times 10^{2} \ \text{M}^{-1}\text{s}^{-1}, \ 25 \ ^{\circ}C.; \ \Delta H^{\ddagger} = 4 \ \text{kcal/mole}; \ \Delta S^{\ddagger} = -45 \ \text{eu}).^{63}

Substituent Effects on the Rate of Linkage Isomerization

The influence of phosphine substituents on the rate parameters $k_1$ and $K_{f2}$ may be understood in terms of both inductive and steric contributions. The correlation of isomerization rate and phosphine association constants with electronic factors ($v$) and $\Delta(31P)$ measurements was made on a series of structurally-similar, para-substituted triphenylphosphine derivatives in order to minimize differences in the steric contribution to the free energy of activation. Figure 22 illustrates a linear relationship between log($k_1$) and $\Delta(31P)$ for the phosphines with p-H, p-Cl, p-F, p-CH$_3$ and p-OCH$_3$ substituents. Since $\Delta(31P)$ is a sensitive measure of phosphorus 3p electronic polarization induced by complexation to the Pd(II) center, enhancements in $k_1$ with increasing $\Delta(31P)$ imply that such polarization of electron density towards Pd(II) plays a significant role in destabilizing the bonds to the carbanion leaving group. In this way, the mechanism of PR$_3$-induced chloranilate linkage isomerization resembles the well-established $\sigma$ trans effect in Pt(II) substitution reactions,$^{1,6}$ where a potent $\sigma$-donor ligand trans to the leaving group forces electron density onto the metal center, which in turn repels the lone pair utilized by the leaving group to ligate Pt. Since chloranilate evidently does not function effectively as a $\pi$-acid in the [Pd(C-CA)(PPh$_3$)$_2$] products, the driving force of the linkage isomerization process must be derived primarily from the Coulombic destabilization of Pd-carbanion C bonds brought about by the competition between "soft" donor ligands for $\sigma$ overlaps with the Pd 4$d_{x^2-y^2}$ orbital. Looked at in another way, the log($k_1$)-$\Delta(31P)$ correlation argues for an "early" transition state, in which the activated complex more closely resembles the (C-CA) reactant than the ($\pi$-CA) product, whose bonding characteristics to Pd(II) are little affected by the extent of phosphine polarization.
Given a relatively constant steric interaction with the first PR$_3$ ligand in a cis coordination position, the pre-equilibrium binding of a second PR$_3$ molecule is expected to be governed entirely by the Lewis basicity of the phosphine. On this basis, the linearity of a log(K$_f$) versus electronic factor (v) plot for para-substituted phosphines (Figure 23) is not surprising. Likewise, the falloff in $k_1$ values for m-CH$_3$, m-OCH$_3$ and m-Cl derivatives as compared with the analogous p-substituted phosphines is easily accounted for by noting the failure of a meta substituent to be fully conjugated with the phosphorus atom through a mediating phenyl ring. For this reason, the potential inductive contributions of these meta substituents to phosphorus atom polarizability are considerably muted, resulting in attenuated linkage isomerization rates. We note, however, that the $k_1$(para)/$k_1$(meta) ratio is considerably larger for the chlorine substituent than for the methyl and methoxy groups, indicating that inductive effects cannot entirely account for the reactivity differences between para- and meta-substituted triphenylphosphines.

Comparative K$_f$ values for para- versus meta-substituted triphenylphosphines are not easily understood. Larger steric repulsions between cis P{Ph-m-X}$_3$ ligands, based on cone angle expansions, should uniformly constrain the K$_f$(meta)/K$_f$(para) ratio to a value considerably less than unity. Nevertheless, this ratio is actually greater than 1 in the case of X = CH$_3$ and Cl, but follows the prediction well with X = OCH$_3$. A simple inductive effect argument cannot solve this puzzle, since para electron-donating substituents presumably enhance the Lewis basicity of phosphorus more effectively than m-X groups, providing additional incentive for the K$_f$(meta)/K$_f$(para) ratio to become smaller. Since the cone angles of sterically-crowded P{Ph-m-X}$_3$ ligands are larger than those of their p-X counterparts, the phosphorus lone pair orbital acquires more 3p (and less 3s) character, possibly enhancing overlap with the palladium 4d$_{x^2-y^2}$ orbital and lone pair polarizability. Further experimentation with other substituents is required, however, before the actual impact of these factors on K$_f$ can be assessed with confidence.
Isomerization Reactions Induced by Diphosphine Ligands

According to the proposed intermediate complex mechanism, a good chelating phosphine such as cis-1,2-bis(diphenylphosphino)ethylene (cis-dpee) could ligate Pd(II) strongly with a large formation constant, generating a [Pd(C-CA)(cis-dpee)] intermediate quantitatively in the presence of a very small excess of the phosphine ligand. In this event, observed rate constants for linkage isomerization would be independent of cis-dpee concentration, adopting the $k_1$ value characteristic of the chelated intermediate complex. In fact, the cis-dppe linkage isomerization kinetics showed saturation behavior similar to that observed with monophosphine entering groups. The cis-dppe $k_1$ and $K_{f2}$ values of $(3.65 \pm 0.01) \times 10^{-2}$ s$^{-1}$ and $(1.86 \pm 0.22) \times 10^3$ M$^{-1}$, respectively, are little different from the $P(m$-tolyl)$_3$ rate parameters, suggesting that palladium is not chelated by the diphosphine in the presence of excess cis-dpee, but rather is ligated by two cis-dpee molecules functioning as monodentate ligands. Since the primary purpose of the cis-dpee kinetic experiment was to establish the influence of diphosphine chelation on the linkage isomerization rate, this goal could not be achieved. Similarly, attempted kinetic studies with other diphosphines were frustrated by a variety of problems, including poor solubilities of the free phosphines or palladium products in acetonitrile and the facility of dimerization side reactions.

Linkage isomerization triggered by 1,2-bis(diphenylphosphino)acetylene (dppa) offers an intriguing contrast to the other kinetic studies in that the rate of isomerization is strongly retarded with increasing phosphine concentration. Analysis of the rate data suggests that the formation of a [Pd(C-CA)(dppa)$_2$] dead end complex is responsible for the observed phosphine inhibition behavior. A possible structure of this dead end complex places dppa phosphorus atoms in two equatorial and two axial coordination positions.

The observed rate law follows easily if it is assumed that this bis(dppa) complex is incapable of linkage isomerization (for reasons that are very much unclear) and that the [Pd(C-CA)(dppa)] complex, containing a single dppa ligand chelated through equatorial
coordination positions, is an active intermediate. The kinetically-determined $K_d/K_{fc}$ ratio of $2.4 \times 10^3 \text{M}^{-1}$ is consistent with either the excessively small "bite" size of (III) or large "bite" of the dppa ligand (IV), destabilizing chelation because of the steric strain required to place the donors 90° apart in cis coordination positions. The P-Pd-(acetylene) bond angle and P-Pd-P bond angle estimated for chelated dppa from known bond lengths (1.8 Å for P-C(sp), 1.2 Å for C(sp)-C(sp)) and atomic radii (P = 1.10 Å, Pd(II) = 1.35 Å, CRC Handbook (F-121)) are close to 60° and 180°, respectively. Regarding the apparent reluctance of the [Pd(C-CA)(dppa)$_2$] dead end complex to undergo linkage isomerization, possible contributing factors include a requirement that such isomerization be accompanied by dimerization in order to stabilize the (π-CA) product and the prevention of axial attack by solvent molecules which conceivably could stabilize a polar activated complex. Unfortunately, the lack of structural data on both intermediates and the final product in the Pd(π-CA)-dppa system prevents a more detailed interpretation of this interesting kinetic behavior.
Infrared Spectroscopy

Several of the carbon-bonded chloranilate complexes reported above were not sufficiently soluble or stable in solution to permit the measurement of nuclear magnetic resonance spectra over a period of 10 minutes to several hours. Fortunately, solid state infrared spectroscopy provides an unambiguous means by which carbon-bonded chloranilate may be distinguished from \( \pi \text{-CA} \) and other linkage isomers. Three characteristic infrared features: 1) the appearance of three closely-spaced C=O stretches above 1600 cm\(^{-1} \); 2) the observation of 1-3 medium-intensity bands in the 1100-1250 cm\(^{-1} \) region which do not appear in p-quinone spectra; and 3) a shift in the C-Cl vibration to higher energy (\( > 850 \text{ cm}^{-1} \)) provide unambiguous criteria for the identification of \([\text{Pd(C-CA)} \text{L}_2]\) compounds. The absence of hybrid \( v_2(\text{CO}) \) and \( v_3(\text{CC}) \) features near 1530 and 1350 cm\(^{-1} \), respectively, is entirely consistent with the proposed complete disruption of the chloranilate delocalized π-system upon σ bonding to palladium(II) through chlorine-bearing carbanion carbon atoms. Even though x-ray crystallographic data are not available for any of the new compounds assigned to the \( \text{C-CA} \) class in this dissertation, the striking similarities between their infrared spectra and that of the parent \( \text{K}_2\text{Pd(C-CA)Cl}_2\cdot 4\text{H}_2\text{O} \) compound leaves no doubt that all contain the bent, boat chloranilate conformation, ligated to Pd(II) through carbon.

The new \( \text{C-CA} \) peaks near 1200 cm\(^{-1} \) are most reasonably assigned as weakly-allowed C-C vibrations, possibly mixed with some Pd-C stretching character, similar to those observed in the structurally-analogous norbornane molecule. Thus, 2-chlorobicyclo[2,2,1]heptane (1260, 1318 cm\(^{-1} \)), 7-chloro-2-bromobicyclo[2.2.1]heptane (1240, 1260, 1300, 1315 cm\(^{-1} \)) and 2,7-dichlorobicyclo[2,2,1]heptane (1270, 1310, 1325 cm\(^{-1} \)) (Sadttler IR Spectra) exhibit well-defined C-C stretches at slightly higher energy than the distinctive new bands of the \( \text{C-CA} \) complexes. These C-C stretches are expected to be
sensitive to the chloranilate bend angle and carbon atom hybridization, and therefore are potentially revealing with regard to the bonding interaction between Pd(II) and CA\textsuperscript{2-}. Within neutral [Pd(C-CA)L\textsubscript{2}] complexes, a red-shift in the highest energy C-C vibration is observed with increasing softness of the L group, i.e., 1213 cm\textsuperscript{-1} (H\textsubscript{2}O) > 1208 cm\textsuperscript{-1} (CH\textsubscript{3}CN) > 1183 cm\textsuperscript{-1} (TCNQ) > 1120 cm\textsuperscript{-1} (COD). The smaller range in this v(C-C) energy for carbon-bonded compounds with anionic ligands precludes the assignment of a definitive trend. A tendency towards increased p-character in the carbanion donor orbital with decreasing softness of the complementary donor group would maximize the covalency of the Pd(II)-(C-CA) \( \sigma \) bonds and increase C-C stretching frequencies.

Electronic Spectroscopy

In the course of measuring the electronic spectra of carbon-bonded chloranilate compounds in weakly acidic aqueous solution (pH = 3.8), it was discovered the complexes with L = F\textsuperscript{-}, Cl\textsuperscript{-}, Br\textsuperscript{-}, acac\textsuperscript{-} and ox\textsuperscript{2-} rapidly hydrolyze to [Pd(C-CA)(H\textsubscript{2}O)\textsubscript{2}] in the absence of excess L in solution. This reaction appears to be acid-catalyzed, since no appreciable displacement of chloride from [Pd(C-CA)Cl\textsubscript{2}]\textsuperscript{2-} was observed within 15 minutes in neutral solution. This hydrolysis reaction is contrary to expectations from hard-soft acid-base theory, since the hard water molecule is among the poorest of ligands towards the soft Pd(II) center. The thermodynamic driving force of these ligand displacement reactions may be strengthening of the Pd-chloranilate C sigma bonds engendered by the departure of the competing soft donor ligands. A kinetic trans effect therefore may be linked to carbon-bonded CA\textsuperscript{2-} which is triggered by factors other than the \( \sigma \)-donating ability of the functional unit in its ground state configuration. Further investigation of this puzzling behavior is needed to better define the bonding within the unexpectedly stable [Pd(C-CA)(H\textsubscript{2}O)\textsubscript{2}]\textsubscript{2}H\textsubscript{2}O molecule, and also to clarify the basis for its reductive decomposition in alkaline solutions.
The ultraviolet spectra of \([\text{Pd(C-CA)L}_2]\) compounds exhibit a strong band near 220 nm which is readily assigned to the \(\pi-\pi^*\) transition of the localized chloranilate carbonyl groups. Two other features, with similar extinction coefficients on the order of \(10^4 \text{ M}^{-1} \text{ cm}^{-1}\), are consistently found in the vicinity of 310 and 230-260 nm. It was established that these strong bands are not ligand-centered or L-to-Pd(II) charge transfer absorptions, leaving carbanion carbon-to-palladium(II) charge transfer as the most reasonable spectroscopic assignment for both transitions. Unfortunately, an extensive literature review failed to produce a precedent for Pd(II)-C LMCT transitions, but analogous bands originating from the \(\sigma\)-bonding electrons of halide and sulfur-donor ligands are well-known. Such an assignment is supported by the fact that the X-ray crystal structure of \(\text{K}_2\text{Pd(C-CA)Cl}_2-4\text{H}_2\text{O}\) shows inequivalent Pd-C bonds, with a substantial bond length difference of 0.05 Å. Assuming that the interconversion of these inequivalent carbon atoms is slow on the spectroscopic time scale (Born-Oppenheimer approximation), two distinguishable C-to-Pd(II) LMCT bands with different energies could be observed.

Figure 24 illustrates an intriguing linear relationship between the band maximum energy difference between the two proposed C-to-Pd(II) LMCT bands and the energy of the feature at shorter wavelength. The quality of this correlation suggests the presence of a single variable structural feature in the (C-CA) class which strongly influences the relative energies of the carbon atoms implicated in the LMCT transitions. This variable most reasonably is the difference in length between the two Pd-C bonds, which imparts an asymmetric character to the chelating dicarbanion unit. The spectroscopic results show that the higher frequency LMCT band varies in energy considerably more than other transition, which varies little from 310 nm with variations in the L group. On this basis, we propose a bonding model in which one chloranilate C-Cl carbon atom retains full sp\(^3\), carbanion character in all \([\text{Pd(C-CA)L}_2]\) complexes, while the other C-Cl carbon atom, bonded more
weakly, is capable of assuming partial allylic character (sp² hybridization), as shown below.

Although this model cannot be fully defended on the basis of results presented in this dissertation, it does provide an intriguing hypothesis to be tested in further work on (C-CA) complexes.

However, this hypothesis can be supported by the following observations:

(1). Simple molecular model studies, using known covalent radii and bond angles of Pd(II) and carbon atoms with appropriate hybridization states, suggest unfavorable overlap between carbon (p or sp³ orbital) and Pd(II) dₓ²₋₂ᵧ² orbitals in both dicarbanion and diallylic extremes, as shown in Figures 25 and 26, respectively. Thus, the CA²⁻
moiety in $K_2[\text{Pd(C-CA)Cl}_2]$-$4\text{H}_2\text{O}$ assumes unsymmetric coordination to maximize bonding interactions.

(2) The Pd(II)-C bond lengths calculated from the sum of the covalent radii of Pd(II) and carbon are: Pd-C(sp$^3$) = 2.07 Å; Pd-C(sp$^2$) = 1.97 Å; Pd-C(sp) = 1.90 Å. The Pd-C bond lengths of $K_2[\text{Pd(C-CA)Cl}_2]$ are 2.07 and 2.02 Å, suggesting considerable sp$^2$ character for the shorter Pd-C bond.

(2) Other bidentate C-donor ligands form symmetric complexes. Thus, Pd-C bond lengths are: 2.019 and 2.026 Å in $[\text{Pd(C}_4\text{(CO}_2\text{Me})_4](bpy)]$; 2.124 and 2.141 Å for $[\text{Pd(CH}_2\text{CO}_2\text{COCH}_2)(\text{PPh}_3)_2]$. Unlike CA$^2-$, these symmetric ligands can not utilize allylic resonance forms.

(3) Since a carbon p orbital is more polarizable than a sp$^3$ hybrid, substitution of Cl with weaker σ-donor ligands would facilitate allylic resonance, which could be demonstrated by a lengthening of C-O and a shortening of Pd-C bonds. Indeed, a comparison of bond lengths between $K_2[\text{Pd(C-CA)Cl}_2]$ and $K_2[\text{Pd}_2(\text{C-CA})_2(\mu-\text{Cl})_2]$ shows: 1) an increase in C=O bond length (1.29 (dimer) versus 1.27 (monomer)); 2) a further decrease in Pd-C bond lengths (2.01 and 2.05 Å for dimer versus 2.07 and 2.02 Å in monomer).

Factors Influencing Isomerization

A hypothesis was presented for the preference of the (C-CA) mode over the (π-CA) isomer for weak σ-donors or good π-acceptors. This proved to true in most cases, as shown below.

(1) Group V donor ligands: Less polarizable nitrogen donors form (C-CA) complexes, while other group V donor ligands prefer the (π-CA) mode.

a) (C-CA) complex: Pd(CA)(CH$_3$CN)$_2$ and Pd(CA)(TCNQ)·H$_2$O (TCNQ bonds through nitrogen, not ethylene.)
b) \((\pi\text{-CA})\) complex: Pd(CA)(bpy) and all of the phosphine complexes

(2) Group VI donor ligands: Oxygen donor ligands prefer the \((\text{C}\text{-CA})\) mode. On the other hand, sulfur ligands prefer \((\pi\text{-CA})\) ligation except in case of SCN\(^-\), which is less polarizable due to the formation of a bridged complex.

a) \((\text{C}\text{-CA})\) complex: Pd(CA)(H\(_2\)O)\(_2\)-H\(_2\)O, K\(_2\)Pd(CA)(ox)-H\(_2\)O, KPd(CA)(acac), and K\(_2\)[Pd\(_2\)(CA)\(_2\)(SCN)\(_2\)]

b) \((\pi\text{-CA})\) complex: Pd(CA)(DMSO)\(_2\)

(3) Group VII donor ligands: F\(^-\), Cl\(^-\), and Br\(^-\) prefer the \((\text{C}\text{-CA})\) mode.

a) \((\text{C}\text{-CA})\) complex: K\(_2\)Pd(CA)F\(_2\)-H\(_2\)O, K\(_2\)Pd(CA)Cl\(_2\)-1/2H\(_2\)O, K\(_2\)Pd(CA)Br\(_2\)-H\(_2\)O and K\(_2\)[Pd\(_2\)(CA)\(_2\)Br\(_2\)]-4H\(_2\)O

(4) Olefin donors: Only 2 complexes were successfully synthesized.

a) K\(_2\)Pd(CA)\(_2\)-2H\(_2\)O: As expected, one CA\(^-\) is in the \((\text{C}\text{-CA})\) mode (\(\sigma\)-donor), and the other is \((\pi\text{-CA})\).

b) Pd(CA)(COD): The complex synthesized in THF is \((\text{C}\text{-CA})\)-bonded (Pd(CA)(COD)-THF), while the product obtained in CH\(_2\)Cl\(_2\) is \((\pi\text{-CA})\)-bonded. Also, CN\(^-\) prefers to form a \((\pi\text{-CA})\) complex, suggesting that the \(\sigma\)-donor ability of CN\(^-\) is the dominating factor.

The exceptional \(\sigma\)-donor strength of the dicarbanion resonance form, \((\text{C}\text{-CA})\), is apparent according to the facts that TCNQ prefers to bond through nitrogen over the olefin double bonds, and it is difficult to synthesize Pd(CA) complexes with soft ligands, such as I\(^-\), CN\(^-\), S\(_2\)\(^2-\) and various olefins. However, the \(\pi\)-accepting ability of \(\pi\)-chloranilate is weaker, if present at all, than was anticipated. Thus, the primary reason for the strong \(\pi\)-donor ability of \(\pi\)-chloranilate appears to be stabilizing interaction of the \((\text{C}\text{-CA})\) Pd(II)-C bonds by competing \(\sigma\) donation from L groups in Pd(\((\text{C}\text{-CA})\))L\(_2\) compounds.

Also, it appears that isomerization of the (CA\(^2-\)) moiety can be controlled by solvent properties alone, as demonstrated by the syntheses of Pd(\((\text{C}\text{-CA})\))(COD) and
Pd(π-CA)(COD)·H2O in THF and CH2Cl2, respectively. This suggests a duality of the COD ligand: σ-donor in Pd(π-CA)(COD)·H2O versus π-acceptor in Pd(C-CA)(COD). Unfortunately, the insolubility of these complexes hindered further study.
Figure 18

Qualitative $\pi$-LCAO-MO Diagram of $p$-Benzquinone and Pd(II) Metal

Symmetry-forbidden Transition (540 nm)

Symmetry-allowed Transition (340 nm)

$\pi$-LCAO of $p$-Benzquinone
8 Electrons

Pd(II) $d\pi$ orbitals
6 Electrons
Figure 19

Relationship between $\Delta^{31P}$ NMR Chemical Shift (ppm) versus $\nu_3$(CC) (cm$^{-1}$) of Bis(para-substituted)phenylphosphine Complexes
Figure 20
Relationship between $\pi-\pi^*$ Asymmetric UV Bands (cm$^{-1}$) versus Electronic Effect (cm$^{-1}$) of Bisphosphine Complexes
Figure 21

Eyring and van't Hoff Plots of Chloranilate Isomerization Reaction
Induced by Triphenylphosphines in CH₃CN Solution
Figure 22

Relationship between $k_{\text{obsd}}$ (s$^{-1}$) versus $\Delta(\text{31P NMR Chemical Shift})$ (ppm) of Bis(para-substituted)phenylphosphine Complexes.
Figure 23

Relationship between $K_{12} (M^{-1})$ versus Electronic Effect (cm$^{-1}$) of Bis(para-substituted)phenylphosphine Complexes
Figure 24

Linear Relationship between the Band Maximum Energy Difference between the Two Proposed C-to-Pd(II) LMCT Bands and the Energy of the Feature at Shorter Wavelength
Empty Pd(II) d Orbital

2.07 Å (Pd(II)-C(sp³))

sp³ (carbon) Orbital

109.5°

Smaller than 90°

Smaller than Theoretical Value

(360° - 109.5°)/2 = 125.25°

1.50 Å X sin(109.5°/2)

(1.50Å = C(sp³)-C(sp³))

120°

1.46 Å (sp²(C)-(sp²(C))

Figure 25

Bonding Scheme of [K₂Pd(C₂CA)Cl₂] in Dicarbanion Mode
Empty Pd(II) d Orbital

1.97 Å (Pd(II)-C(sp^2))

p Orbital (Carbon)

1.46 Å X sin(120°/2)
(C(sp^2)-C(sp^2))

Close to 90°

Larger than 90°

120°

1.46 Å (C(sp^2)-C(sp^2))

Figure 26

Bonding Scheme of [K₂Pd(C₂CA)Cl₂] in Diallylic Mode
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15, 1140.
1479.
1195.
1037.


APPENDIX

RATE EXPRESSION FOR ISOMERIZATION OF
THE (CA\textsuperscript{2-}) MOIETY

(A) Isomerization Induced by PR\textsubscript{3}

The rate of isomerization of the CA\textsuperscript{2-} moiety induced by a PR\textsubscript{3} incoming group can be expressed as Eq. (1) for the hypothesis.

\[
\frac{d}{dt}[\text{Pd}(\pi\text{-CA})(\text{PR}_3)_2] = \frac{d}{dt}[\text{Pd}(\pi\text{-CA})]\text{total} = k_1[\text{Pd}(\text{C}\text{-CA})(\text{PR}_3)_2] \tag{1}
\]

Since only the (\pi\text{-CA}) moiety absorbs at 530 nm, one can observe the changes of [Pd(\pi\text{-CA})]\text{total} upon time, but not those of [Pd(\text{C}\text{-CA})(\text{PR}_3)_2] directly. The changes of [Pd(\text{C}\text{-CA})]\text{total} can be obtained by using Eq. (2).

\[
[Pd]_\text{total} = 2 \times 10^{-4} \text{ M} = [Pd(\pi\text{-CA})]_\text{total} + [Pd(\text{C}\text{-CA})]_\text{total} \tag{2}
\]

The Eq. (2) must be rearranged in terms of observable values, [Pd(\text{C}\text{-CA})]\text{total}, to calculate the rate of isomerization reaction. Assuming that the formation of Pd(\text{C}\text{-CA})(\text{PR}_3)_2 is a rapid pre-equilibrium, one obtains the following equations (Eq. (3) and (4));

\[
K_{f1} = \frac{[\text{Pd}(\text{C}\text{-CA})(\text{CH}_3\text{CN})(\text{PR}_3)]}{[\text{Pd}(\text{C}\text{-CA})(\text{CH}_3\text{CN})_2][\text{PR}_3]} \tag{3}
\]

\[
K_{f2} = \frac{[\text{Pd}(\text{C}\text{-CA})(\text{PR}_3)_2]}{[\text{Pd}(\text{C}\text{-CA})(\text{CH}_3\text{CN})(\text{PR}_3)][\text{PR}_3]} \tag{4}
\]

Using Eq. (3) and (4), one can express [Pd(\text{C}\text{-CA})]\text{total} as shown in Eq. (5):
\[ [\text{Pd(C-CA)}]_{\text{total}} = [\text{Pd(C-CA)}(\text{PR}_3)_2] + [\text{Pd(C-CA)}(\text{CH}_3\text{CN})(\text{PR}_3)] \]
\[ + [\text{Pd(C-CA)}(\text{CH}_3\text{CN})_2] \]
\[ = [\text{Pd(C-CA)}(\text{PR}_3)_2] \left(1 + \frac{1}{K_{f2}[\text{PR}_3]} + \frac{1}{K_{f1}K_{f2}[\text{PR}_3]^2} \right). \] 

(5)

Substitution of Eq.(5) to Eq.(1) leads to;

\[
\frac{d}{dt} [\text{Pd(\pi-CA)}(\text{PR}_3)_2] = \frac{k_1 [\text{Pd(C-CA)}]_{\text{total}}}{1 + \frac{1}{K_{f2}[\text{PR}_3]} + \frac{1}{K_{f1}K_{f2}[\text{PR}_3]^2}}.
\] 

(6)

Assuming \(K_{f1} \gg K_{f2}\), Eq.(6) can be simplified as the following;

\[
\frac{d}{dt} [\text{Pd(\pi-CA)}(\text{PR}_3)_2] = \frac{k_1 [\text{Pd(C-CA)}]_{\text{total}}}{1 + \frac{1}{K_{f2}[\text{PR}_3]}}
\]
\[= \frac{k_1 K_{f2}[\text{PR}_3]}{1 + K_{f2}[\text{PR}_3]} [\text{Pd(C-CA)}]_{\text{total}} \]
\[= k_{\text{obsd}} [\text{Pd(C-CA)}]_{\text{total}} \]

where \(k_{\text{obsd}} = \frac{k_1 K_{f2}[\text{PR}_3]}{1 + K_{f2}[\text{PR}_3]} \). 

(7)

(B) Isomerization Induced by DPPA

The rate of \((\text{CA}^2^-)\) isomerization for the hypothesis presented for linkage isomerism induced by 1,2-bis(diphenylphosphino)acetylene is the following:
\[
\frac{d}{dt} [\text{Pd}(&\pi-)\text{CA})(P-P)] = \frac{d}{dt} [\text{Pd}(&\pi-)\text{CA})]_{\text{total}} = k_1[\text{Pd}(&\pi-)\text{CA})(P-P)]
\]

where P-P = 1,2-bis(diphenylphosphino)acetylene.

From the proposed dead-end mechanism, one can obtain:

\[
K_{f1} = \frac{[\text{Pd}(&\pi-)\text{CA})(\text{CH}_3\text{CN})(P-P)]}{[\text{Pd}(&\pi-)\text{CA})(\text{CH}_3\text{CN})_2][P-P]}
\]

\[
K_{fc} = \frac{[\text{Pd}(&\pi-)\text{CA})(P-P)]}{[\text{Pd}(&\pi-)\text{CA})(\text{CH}_3\text{CN})(P-P)]}
\]

\[
K_d = \frac{[\text{Pd}(&\pi-)\text{CA})(P-P)_2]}{[\text{Pd}(&\pi-)\text{CA})(\text{CH}_3\text{CN})(P-P)]}
\]

By the same reasons explained for the reaction between (6) and monophosphines, Eq. (8) is rearranged to Eq. (12):

\[
\frac{d}{dt} [\text{Pd}(&\pi-)\text{CA})]_{\text{total}} = \frac{k_1K_{f1}K_{fc}[P-P][\text{Pd}(&\pi-)\text{CA})]_{\text{total}}}{1 + K_{f1}[P-P] + K_{f1}K_{fc}[P-P] + K_dK_{f1}[P-P]^2}
\]

Assuming \(K_{f1} \gg 1\), Eq. (12) can be simplified as the following:

\[
\frac{d}{dt} [\text{Pd}(&\pi-)\text{CA})]_{\text{total}} = k_{\text{obsd}} [\text{Pd}(&\pi-)\text{CA})]_{\text{total}}
\]

where \(k_{\text{obsd}} = \frac{k_1}{1 + \frac{K_d[P-P]}{K_{fc}}}
\).
