THE SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF BIS(ACETYLACETONATO) PALLADIUM (II) PHOSPHINE COMPLEXES

by

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CHAPTER I

INTRODUCTION

The role of palladium(II) in organometallic synthesis has been a topic of increasing interest in recent years. Although original work primarily dealt with the coordination of palladium to organic molecules, more recent work has focused upon the development of new catalytic applications of palladium(II) complexes in industrial synthesis. These applications include such important organic transformations as the oxidation of ethylene to acetaldehyde (Wacker process) and the acetoxylation of olefins and dienes. The renewed interest in palladium(II) organometallic chemistry is reflected in the appearance of several comprehensive volumes devoted[1,2,3] entirely to the chemistry of palladium and the publication of over 30 reviews in the last 15 years.

Undoubtedly, the success of new catalytic applications of palladium(II) organometallics is dependent upon a thorough understanding of pathways followed in simpler systems in which palladium-carbon bonds are formed or cleaved with an accompanying change in hybridization at the carbon-donating linkage. In turn, the structural changes and/or kinetic requirements of these palladium(II) intermediates often cause significant changes in the chemoselectivity, regioselectivity, and stereospecificity of the reaction and frequently may be demonstrated through minor modifications of the reaction conditions, especially the choice of ligands. Towards this end, the long-term goal of this investigation is to understand the mechanisms by which palladium(II)-σ-alkyl carbon bonds are made and broken without the further complication of a secondary redox process or irreversible structural modification of the ligating carbon atom.

General Chemistry of Palladium

Palladium(Pd), a silver-grey ductile metal, was first discovered by Wollaston in 1803.[4] Palladium is a relatively rare transition metal that is found in the earth's crust to the extent of approximately 8.6×10^{-13} parts, along with other platinum group metals. Of the six isotopes that occur naturally, only ^{105}Pd exhibits a magnetic moment (I = 5/2). However, no NMR studies in chemically interesting systems involving ^{105}Pd have yet been reported. The NMR frequency, as well as the sensitivity, is low and studies probably will be difficult to carry out.[5]

Palladium is one of the 4d transition metals and has the electronic configuration $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, with a full 4d shell which is relatively easy to access. Palladium exhibits chemistry similar to that of its 5d analog, platinum(Pt), with the most notable difference being that palladium is much more reactive (labile) than platinum. Palladium complexes in the (0), (I), (II) and (IV) oxidation states are all known. Many of the complexes in the (0) and (I) oxidation states form metal-metal bonded clusters, and cluster complexes in which the metal is formally in an intermediate oxidation state are well known.[6]

Virtually all of the palladium complexes used as catalysts in organic synthesis are low-spin d^8, diamagnetic Pd(II) complexes. A wide variety of palladium(II) complexes have been isolated and Pd(II) normally has a preference for soft donor ligands such as ethylene, phosphines, etc. The vast majority of Pd(II) complexes are four-coordinate square planar or exhibit a tetragonally distorted octahedral geometry. There is additional evidence that solvent molecules may occupy the apical sites of the distorted octahedral configuration.[7] Visible electronic and photoelectron spectra have been interpreted to rank the energy ordering of the d-orbitals as $d_x2\text{-}y2 > d_{xy} > d_{xz}, d_{yz} > d_z2$ in both $PtCl_4^{2-}$ and $PdCl_4^{2-}$.[8]

Substitution Reactions in Pd(II) Complexes

Like their Pt(II) analogues, Pd(II) complexes typically undergo substitution reactions by an associative mechanism via a five-coordinate transition state or intermediate. The entering ligand is thought to be initially bound in the axial position along the z-axis and subsequently transformed into an equatorial ligand through a trigonal-bypyramidal intermediate.[9,10,11] Factors in the range of 10^3 to 5 x 10^5 have been reported for the relative reactivities of Pd(II) complexes as compared to their Pt(II) analogues.[12,13] Five-coordinate species are also suspected intermediates in the cis-trans isomerization of the square-planar complexes $[PdL_2X_2]$.[14] The trend toward five-coordinate intermediates in Pd(II) square-planar complexes is largely dependent upon the size of the ligands, being facilitated by smaller groups, and probably also on electronic factors though these have remained largely unquantified. However, there is substantial evidence to show that softer donor ligands more readily form five-coordinate intermediates than do harder donor ligands.[15]

Chemistry of Pd(II) - Acetylacetonate Complexes

2,4-Pentanedione and other β-dicarbonyl compounds are very versatile ligands, exhibiting various bonding modes to metal ions. 2,4-Pentanedione (acacH), the most representative β-dicarbonyl compound, normally coordinates to a metal ion through the two oxygen atoms to form a six-membered chelate ring.[16] The chelate $Pd(acac)_2$ is reduced by triphenylphosphine under anaerobic conditions to give $Pd(PPh_3)_4$ or, in the presence of oxygen, $PdO_2(PPh_3)_2$. However, in the presence of a stoichiometric amount of triphenyl-phosphine, the bidentate O,O-bonded acetylacetonate ligand of $Pd(acac)_2$ undergoes O-to-C

linkage isomerization to yield the product $Pd(acac)_2PPh_3$ containing a monodentate $acac^-$ linkage isomer bonded through the γ-carbon atom (Equation 1)

$$Pd(O,O\text{-}acac)_2 + PPh_3 \longrightarrow Pd(O,O\text{-}acac)(\gamma\text{-}C\text{-}acac)(PPh_3). \qquad (1)$$

The addition of a two-fold excess of triphenylphosphine did not give the palladium(II) complex bearing two γ-carbon-bonded acetylacetonate ligands, but only resulted in the compound containing a single monodentate $acac^-$ linkage. While it is not yet apparent why the palladium(II) complex containing two γ-carbon-bonded acetylacetonate ligands cannot be obtained, the presence of one O-bonded acetylacetonate chelate ring may be necessary to stabilize the carbon-bonded mode of the second acetylacetonate linkage.[17,18]

Several other interesting linkage isomerization reactions of Pd(II)-acetylacetonate complexes are worthy of mention. $Pd(C_6H_5CN)_2Cl_2$ reacts with a stoichiometric amount of acacH in acetone at 0° C to afford an oxygen-bonded, dichloro-bridged acetylacetonate product (Figure 1, III) which isomerizes at room temperature to a η^3-allylic form IV in the presence of excess acacH.[19] 2,2'-Bypyridine causes subsequent bridge cleavage in the η^3-allylic form IV with an associated acetylacetonate linkage isomerization from the η^3-allylic to the η^1-terminal-carbon-bonded form V.[20,21] Although the bridge fragmentation occurrence in this reaction is readily understood in terms of stable 16-electron palladium(II) complexes[22], it is still not yet clear why structure V is preferred over an alternative η^3-allyl product in which chloride ion would be displaced in order to allow for the incoming bidentate ligand.

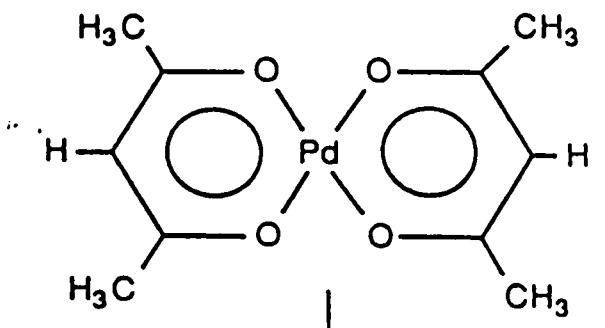
Objectives

The goals of our research are the following:

(1) The primary goal of our research is to acquire elemental analyses and a complete spectroscopic characterization [UV-vis, IR, NMR (^{1}H, ^{13}C, ^{31}P)] of the series of $Pd(acac)_2PR_3$ complexes (R = arylphosphines, amines) in order to fully elucidate all bonding modes within these complexes.

(2) In reactions involving $Pd(acac)_2$, we wish to determine what electronic inductive influence, if any, the arylphosphine and amine substituents have on the electron density at the coordinated carbanion carbon of the carbon-bonded acetylacetonate linkage.

(3) Finally, we wish to investigate the electronic and/or steric factors which may influence the rearrangement of coordinated $acac^-$ from the bidentate, O,O-bonded form to the monodentate, C-bonded form.



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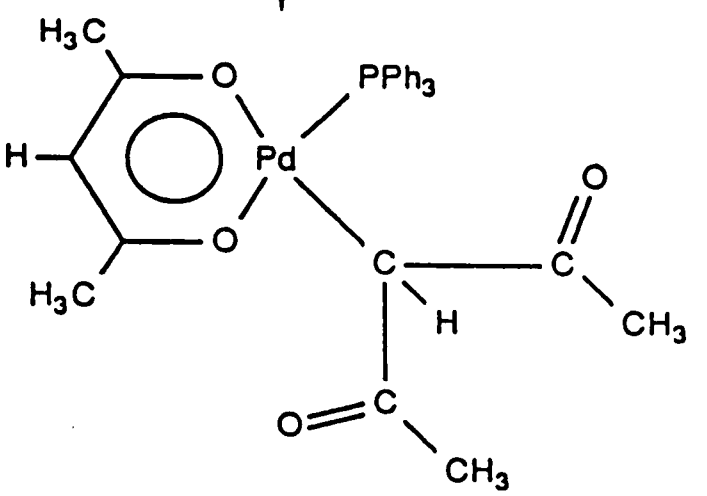

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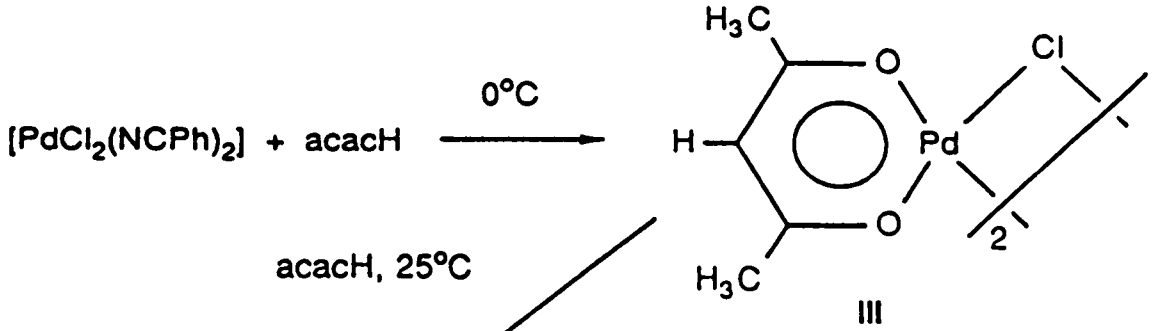

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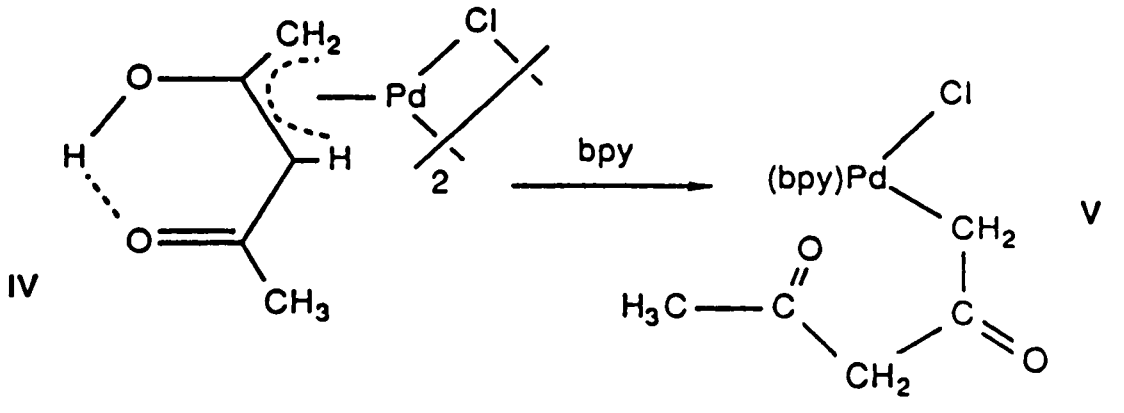


IV

V

Figure 1

Reactions of Pd(II)-Acetylacetonate Complexes

CHAPTER II

EXPERIMENTAL PROCEDURE

Materials

Reagent grade chemicals were used without further purification. The palladium(II) acetylacetonate precursor, tricyclohexylphosphine, and all of the triarylphosphines (p-H, p-CH_3O, o-CH_3O, p-F, p-Cl, p-CH_3, p-NMe_2, C_6H_5O-, p-CF_3) and amines were obtained from Strem Chemicals. Anhydrous diethyl ether ('Baker Analyzed' reagent) and dichloromethane (Aldrich HPLC grade) solvents were used without further purification. Cyclohexane was obtained as a bulk solvent from the stockroom. All of the elemental analyses reported were obtained from Desert Analytics (Tucson, Arizona).

Syntheses

Syntheses of $Pd(acac)_2(PR_3)$ Complexes

The synthetic method used for the $Pd(acac)_2(PR_3)$ complexes was loosely adapted from that of Baba et al.[23] Most of the solutions became a transparent, golden-brown color immediately upon mixing the palladium(II) acetylacetonate precursor with a slight excess of the phosphine or amine in 20 mL of diethyl ether with stirring at room temperature. These reactions typically gave modest yields within a 6- to 8-hour period of time. After the reaction was allowed to proceed to completion, petroleum ether (5 mL) was added to facilitate precipitation of the product. The ether was allowed to evaporate under the hood, and the product was then suction filtered and washed with cold cyclohexane.

Since some of the phosphine ligands are air-sensitive, care was taken in transferring these phosphines. A 25-mL Erlenmeyer flask was preweighed and covered with a piece of

parafilm (American Can Company). The phosphine was transferred quickly to the flask while purging with nitrogen gas, and the flask was sealed tightly with the film. Once the product was formed, no air sensitivity was observed.

$Pd(acac)_2PPh_3$

Triphenylphosphine (0.47 g, 1.8 mmole) was mixed with 0.54 g of palladium(II) acetylacetonate (1.8 mmole) in 20 mL of diethyl ether at room temperature. Yield: 56% (0.57 g, 1 mmole). Anal. Calcd. for $Pd(acac)_2PPh_3$: C, 59.32; H, 5.16. Found: C, 59.05; H, 5.09.

$Pd(acac)_2P(p\text{-methoxyphenyl})_3$

Tris(p-methoxyphenyl)phosphine (0.32 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Yield: 55% (0.32 g, 0.49 mmole). Anal. Calcd. for $Pd(acac)_2(p\text{-}CH_3OC_6H_4)_3P$: C, 56.67; H, 5.37. Found: C, 56.61; H, 5.37.

$Pd(acac)_2P(o\text{-methoxyphenyl})_3$

Tris(o-methoxyphenyl)phosphine (0.32 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Yield: 54% (0.32 g, 0.49 mmole). Anal. Calcd. for $Pd(acac)_2(o\text{-}CH_3OC_6H_4)_3P$: C, 56.67; H, 5.37. Found: C, 55.84; H, 5.33.

$Pd(acac)_2P(p\text{-fluorophenyl})_3$

Tris(p-fluorophenyl)phosphine (0.29 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Yield: 66% (0.37 g, 0.59 mmole). Anal. Calcd. for $Pd(acac)_2(p\text{-}FC_6H_4)_3P$: C, 54.17; H, 4.22. Found: C, 52.74; H, 4.18.

$Pd(acac)_2P(p\text{-chlorophenyl})_3$

Tris(p-chlorophenyl)phosphine (0.33 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Yield: 42% (0.25 g, 0.38 mmole). Anal. Calcd. for $Pd(acac)_2(p\text{-}ClC_6H_4)_3P$: C, 50.18; H, 3.91. Found: C, 50.74; H, 3.63.

$Pd(acac)_2P(p\text{-tolyl})_3$

Tri-p-tolylphosphine (0.28 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Yield: 41% (0.22 g, 0.37 mmole). Anal. Calcd. for $Pd(acac)_2(p\text{-}CH_3C_6H_4)_3P$: C, 61.14; H, 5.79. Found: C, 59.72; H, 6.21.

$Pd(acac)_2P(cyclohexyl)_3$

Tricyclohexylphosphine (0.26 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Yield: 22% (0.11 g, 0.20 mmole). Anal. Calcd. for $Pd(acac)_2(C_6H_{11})_3P$: C, 57.48; H, 8.10. Found: C, 57.07; H, 8.13.

$Pd(acac)_2P(4\text{-dimethylaminophenyl})_3$

Tris(4-dimethylaminophenyl)phosphine (0.36 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Yield: 60% (0.37 g, 0.54 mmole). Anal. Calcd. for $Pd(acac)_2[4\text{-}(CH_3)_2NC_6H_4]_3P$: C, 58.66; H, 6.37; N, 6.04. Found: C, 58.98; H, 6.42; N, 6.22.

Attempt to Prepare $Pd(acac)_2P(p\text{-trifluoromethylphenyl})_3$

Tris(p-trifluoromethylphenyl)phosphine (0.42 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Elemental analysis shows that the product was highly impure due to contamination by unreacted palladium(II) acetylacetonate. Yield: 0.18 g. Anal. Calcd. for $Pd(acac)_2(p\text{-}CF_3C_6H_4)_3P$: C, 48.30; H, 3.40. Found: C, 39.37; H, 4.71. Calcd. for $Pd(acac)_2$: C, 39.43; H, 4.63.

Attempt to Synthesize $Pd(acac)_2NPh_3$

Triphenylamine (0.22 g, 0.91 mmole) was mixed with 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature. Elemental analysis shows that the product was almost exclusively unreacted palladium(II) acetylacetonate. Yield: 0.09 g. Anal. Calcd. for $Pd(acac)_2NPh_3$: C, 61.15; H, 5.32; N, 2.55. Found: C, 39.25; H, 4.60; N, 0.15. Calcd. for $Pd(acac)_2$: C, 39.43; H, 4.63.

Attempt to Prepare $Pd(acac)_2$(triphenylphosphite)

Triphenylphosphite (0.28 g, 0.24 mL, 0.91 mmole) was added to 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of diethyl ether at room temperature.

Elemental analysis revealed that the product was almost exclusively unreacted palladium(II) acetylacetonate. Yield: 0.15 g. Anal. Calcd. for $Pd(acac)_2(C_6H_5O)_3P$: C, 54.69; H, 4.75. Found: C, 39.34; H, 4.62. Calcd. for $Pd(acac)_2$: C, 39.43; H, 4.63.

Attempt to Synthesize $Pd(acac)_2P(n\text{-butyl})_3$

Tri-n-butylphosphine (0.18 g, 0.23 mL, 0.91 mmole) was added to 0.27 g of palladium(II) acetylacetonate (0.89 mmole) in 20 mL of benzene at room temperature. A tarry, brown product was isolated and no further attempt was made to characterize the product.

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 standards: $^1H(TMS)$, $^{31}P(PPh_3)$, $^{13}C(CDCl_3)$ with positive values denoting low field chemical shifts. All ^{13}C NMR spectra were broad band decoupled using a composite pulse decoupling (CPD) acquisition program. Infrared (IR) and UV-visible spectra (slow scan speed) were obtained on Perkin-Elmer 1600 Series FT-IR and Shimadzu UV-260 spectrophotometers, respectively.

CHAPTER III

RESULTS

Syntheses of $Pd(acac)_2PR_3$ Complexes

An extensive family of carbon-bonded acetylacetonate complexes was successfully prepared from the $Pd(acac)_2$ precursor in the presence of only a slight excess of phosphine. Even a two-fold excess of the phosphine did not afford palladium(II) complexes containing two carbon-bonded acetylacetonate ligands, but resulted in compounds containing only the 1:1 adduct. Compounds of the form Pd(O-acac)(C-acac)(PR_3) (R = arylphosphine) were isolated throughout the series with the exception of L = P(o-methoxyphenyl)3. Tris(p-trifluoromethylphenyl)phosphine, triphenylphosphite, and triphenylamine did not induce linkage isomerization of $Pd(acac)_2$.

Analytical data summarized in Table 1 verify the purity of all compounds except the tris(p-trifluoromethylphenyl)phosphine, triphenylphosphite, and triphenylamine reaction products, which essentially analyze for the $Pd(acac)_2$ precursor. The presence of $Pd(acac)_2$ impurity in the case of L = $P(o\text{-}CH_3OPh)_3$, $P(p\text{-}CH_3Ph)_3$, and $P(p\text{-}FPh)_3$ may be a result of the inability of reactions involving these phosphine ligands to proceed irreversibly to completion or the consequence of a dynamic equilibrium which exists between the $Pd(acac)_2$ precursor and the reaction products.

Spectroscopic Measurements

Infrared, NMR, and UV-visible spectroscopies were utilized to determine the influence of the phosphine substituents on the rearrangement of the acetylacetonate linkage from the bidentate O,O-bonded to the monodentate, C-bonded form. These spectral data suggest

that all of the complexes, with the exception of the o-methoxy derivative, bear one oxygen-bonded and one carbon-bonded acac linkage.

UV-visible Spectroscopy

Electronic spectroscopy provides a powerful technique by which the nature of metal-ligand bonding may be elucidated. The electronic structures of $Pd(acac)_2$ and $Pt(acac)_2$ have been studied using pseudopotential valence-only ab initio calculations and combined He I and He II photoelectron spectroscopy. A remarkable covalency between almost all of the upper filled MO's of the ligand cluster and the metal d orbitals of suitable symmetry (see Figure 2)[24] emerges from the analysis of the theoretical results on $Pd(acac)_2$. Those interactions which arise from ligand orbitals of π symmetry primarily involve filled metal $4d_{xz}$ and $4d_{yz}$ orbitals and, although of importance, do not result in significant Pd-O π overlap since contributions due to filled bonding and antibonding levels tend to cancel one another. However, the interactions with orbitals of σ symmetry involve empty $4d_{xy}$ and 5s metal orbitals and result in important ligand-to-metal charge transfer. There is no evidence of any significant metal-to-ligand back-donation, and thus the $acac^-$ anion may be regarded as primarily a σ-donor ligand. The atomic charge of the central Pd atom is theoretically indicative of an oxidation state near +1 mainly because of significant ligand-to-metal σ donation to the s and d_{xy} metal orbitals.[25]

Table 2 summarizes the major features of the electronic spectra in the series of $Pd(acac)_2$(phosphine) complexes. The UV-visible spectrum of the $Pd(acac)_2$ precursor in dichloromethane shows a strong transition ($\varepsilon > 10^4\ M^{-1}cm^{-1}$) near 230 nm, as well as an ultraviolet band ($\varepsilon \cong 10^3\ M^{-1}cm^{-1}$) of weaker intensity near 325 nm. While it is difficult to

make specific assignments of these bands without further precedent, it is evident that these two rather intense bands are associated with the $acac^-$ anion and are likely a result of the favorable Pd-O σ overlap that exists within these metal chelates. In addition to transitions involving significant ligand-to-metal charge transfer (LMCT), many of the phosphine complexes exhibit strong bands between 280 and 350 nm characteristic of the free PR_3 ligands.[26]

Infrared Spectroscopy

KBr pellet infrared (IR) spectra have proved to be quite useful in identifying $acac^-$ bonding modes in phosphine acetylacetonate complexes. It has been shown that the infrared spectrum of the O-bonded acetylacetonato ligand reflects a conjugated chelate structure in equilibrium with a small amount of the diketo form.[27,28] There is no carbonyl conjugated ketone band near 1670 cm^{-1}; a broad, very intense band does exist between 1640 and 1530 cm^{-1}. The presence of a small amount of the diketo form of the acetylacetonato ligand is substantiated by the appearance of a weak absorption peak at 1720 cm^{-1}. The predominant bands in the far infrared region of the O-bonded chelate are M-O stretching modes.[29] Nakamoto and coworkers[30] recorded the spectra of over 32 complexes in the 1700 to 300 cm^{-1} region. Of particular interest was the M-O stretching band found in the 420 to 480 cm^{-1} region, which was observed to shift to higher wave number and increase in intensity as the stability of the metal chelate increased.

The characteristic stretching frequencies of the carbon-bonded acetylacetonate complexes are presented in Table 3 (see also Figure 3). The ν(C=O) and ν(C=C) stretches of the O-bonded chelating acetylacetonate ligand appear in the 1500-1600 cm^{-1} region, while the absorption bands in the 1600-1700 cm^{-1} region, which are not found for

$Pd(acac)_2$, may be attributed to the ν(C=O) stretches of the carbon-bonded acetylacetonate ligand. The rather intense band which is observed in the 500-550 cm^{-1} region may be assigned to the ν(Pd-C) stretch.[31]

NMR Spectroscopy

The proton NMR spectra clearly confirm the coexistence of one oxygen-chelating and one carbon-bonded linkage in the series of acetylacetonate complexes listed in Table 4 (see also Figure 4). The NMR spectra of platinum(II) complexes containing the carbon-bonded acetylacetonate linkage have been extensively studied[32] and are presently referenced in assigning the NMR spectra. In the spectrum of the parent compound $Pd(acac)_2PPh_3$, three methyl-proton peaks are observed as singlets at 1.53, 2.05, and 2.18 δ with an integrated area ratio of 1:1:2. The lowest-field signal at 2.18 δ has been assigned to the two methyl groups of the carbon-bonded acetylacetonate ligand which, in the case of $Pd(acac)_2PPh_3$, are equivalent due to free rotation of the carbon-bonded linkage about the Pd-C single bond.[33] However, the two methyl groups of the oxygen-bonded acetylacetone are not equivalent on account of the asymmetry of these complexes and thus exhibit two distinct signals of equal intensities at 1.53 and 2.05 δ, the higher field signal at 1.53 δ being assigned to the methyl group cis to the phosphine ligand.[34] Lewis and coworkers[35] have established that for the platinum(II) complexes the methine proton of carbon-bonded acetylacetone resonates at higher field compared to that of the O-bonded chelating acetylacetone. This trend should also hold true for the palladium(II) complexes and, in the case of $Pd(acac)_2PPh_3$, the methine proton signal appears as a doublet due to coupling with phosphorus (J_{P-H} = 5.69 Hz).

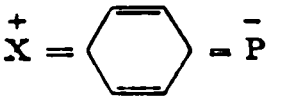
The presence of only one phosphine ligand in the bis(acetylacetonate)(phosphine) complexes was confirmed by the appearance of singlets in ^{31}P NMR spectra. A comparison of phosphorus-31 chemical shifts of free and coordinated phosphines is shown in Table 5, in addition to steric and electronic parameters associated with the phosphine ligands. Triarylphosphine donor ligands typically exhibit a downfield shift of approximately 40 ppm upon coordination to the $Pd(acac)_2$ moiety. For instance, the bis(acetylacetonato)triphenylphosphine phosphorus atom undergoes a downfield shift of 38.01 ppm upon coordination. A substantially larger downfield shift of 59.15 ppm was observed in the ^{31}P NMR spectrum of the tris(o-methoxyphenyl)phosphine complex.

In evaluating ^{31}P coordination chemical shifts in phosphine complexes, it is useful to consider some of the factors which may contribute to the phosphorus chemical shifts of the free ligands. Ramsey and coworkers[36] have formulated a general theory for interpreting chemical shifts of magnetic nuclei, in which the screening constant for a given nucleus may be expressed[37] in terms of three principal contributions (Equation 2):

$$\sigma = \sigma(\text{diamagnetic}) + \sigma(\text{paramagnetic}) + \sigma(\text{other atoms}). \qquad (2)$$

The diamagnetic term represents the shielding effect exerted on a particular nucleus by the neighboring electron cloud and most often is a dominant factor for hydrogen atoms in various chemical environments. However, this term becomes less important for other nuclei (e.g., ^{19}F, ^{31}P, ^{59}Co), where the expanded range of observed chemical shifts is primarily due to the predominance of the second term in the equation, σ(paramagnetic). This second term, which always results in a low field (positive) shift, originates from the perturbation of the electronic environment of the nucleus induced by the magnetic field, and is only critical when low energy excited states are mixed with the ground state through

configuration interaction. Finally, the third term incorporates the contributions to the chemical shift of surrounding groups or atoms within the molecule and is dependent upon $\Delta\chi \cdot R^{-3}$, where $\Delta\chi$ is defined as the anisotropy in the magnetic susceptibility tensor of the neighboring atom and R is the distance from the nucleus of interest. In general, phosphorus chemical shifts are dependent upon (a) the imbalance of the σ-bonds caused by differences in electronegativities of substituent groups and the influence of the lone pair of electrons, (b) the degree of participation of the d-orbitals and (c) departures from geometrical symmetry.[38] B.I. Ionin and coworkers[39] concluded that the ^{31}P chemical shift of phosphorus compounds in the tricoordinate state is primarily determined by the hybridization state of the lone pair of electrons. Contrastingly, the phosphorus coordination chemical shift, (δ complex - δ ligand), is primarily dependent upon (a) the paramagnetic term, (b) the influence of σ-bond formation, (c) potential dπ-dπ bonding between phosphorus and the metal, an increase in the d-electron density on phosphorus resulting in an appreciable high field ^{31}P NMR shift, (d) inductive effects of phosphorus substituents, (e) sustained ring currents in aromatic phenyl phosphine complexes, (f) the rehybridization of bonds, (g) electronegativity of the atoms connected to phosphorus and (h) steric effects (including chelation).[40] In the $(p\text{-}XC_6H_4)_3P$ compounds the initial positive charge induced on phosphorus upon complexation is only one of several important factors that must be considered when interpreting phosphorus coordination chemical shifts. In fact, there is a substantial shielding of phosphorus is due to the mesomeric effect (**1**):



(1)

This initial positive charge would therefore be reduced and the π(p-d) conjugation Ar-P will be less important. Consequently, one must consider two opposing factors when interpreting ^{31}P NMR chemical shifts of complexed Ar_3P complexes: (1) the polarization of positive charge toward phosphorus as a result of the donation of its lone pair to palladium. The size of this charge is affected by the other substituents on phosphorus, and (2) the resulting π(p-d) charge delocalization which increases the electron density on phosphorus.[41]

Finally, Tables 6 and 7 present a summary of the ^{13}C NMR chemical shift data for the $Pd(acac)_2PR_3$ complexes (see also Figure 5). Primary C-H resonances are designated as those signals which are generally within 25 to 30 percent of the intensity of the most predominant methyl or methylene resonance. The primary C-H resonances are found in the range of 20-50 ppm, being assigned to the methyl carbons of the carbon- and oxygen-bonded acetylacetonate linkages and the para-methyl substituents of the aromatic phosphine ligands. The rather intense signals at approximately 25.40 ppm are attributed to the two methyl groups of the oxygen-bonded acac ligand, which are nonequivalent due to the asymmetry which exists within these complexes. For $Pd(acac)_2PPh_3$, the peak at 99.55 ppm may be assigned to the methine carbon of the carbon-bonded acetylacetonate ligand, whereas the methine carbon of the oxygen-bonded acac linkage resonates at lower field (101.55 ppm for $Pd(acac)_2PPh_3$). Furthermore, while it is difficult to make specific shift assignments, the aromatic carbons of the phosphine ligand generally are found in the range of 110-170 ppm. It has also been demonstrated that alkyl-substituted aliphatic ketones, whether acyclic or cyclic, exhibit carbonyl chemical shifts in the range of 200 to 220 ppm. A substantial deshielding occurs with the addition of other alkyl substituents in the α-position to the carbonyl. Simple α,β-unsaturated ketone carbonyl resonances are generally found at higher field in the range of 185 to 210 ppm.[42] Thus, the diketonic

carbonyl groups of the oxygen-bonded acetylacetonate ligand resonate in the range of 185 to 187 ppm, whereas the exposed carbonyl groups of the carbon-bonded linkage appear as a distinct singlet at lower field (206.43 ppm for $Pd(acac)_2PPh_3$).

Table 1
Analytical Data

Complex	Theoretical Percentage	Found Percentage
$Pd(acac)_2PPh_3$	C: 59.32, H: 5.16	C: 59.05, H: 5.09
$Pd(acac)_2P(p\text{-}CH_3OPh)_3$	C: 56.67, H: 5.37	C: 56.61, H: 5.37
$Pd(acac)_2P(o\text{-}CH_3OPh)_3$	C: 56.67, H: 5.37	C: 55.84, H: 5.33[a]
$Pd(acac)_2P(p\text{-}CH_3Ph)_3$	C: 61.14, H: 5.79	C: 59.72, H: 6.21[b]
$Pd(acac)_2P(p\text{-}Me_2NPh)_3$	C: 58.66, H: 6.37, N: 6.04	C: 58.98, H: 6.42, N: 6.22
$Pd(acac)_2P(cyclohexyl)_3$	C: 57.48, H: 8.10	C: 57.07, H: 8.13
$Pd(acac)_2P(p\text{-}FPh)_3$	C: 54.17, H: 4.22	C: 52.74, H: 4.18[c]
$Pd(acac)_2P(p\text{-}ClPh)_3$	C: 50.18, H: 3.91	C: 50.74, H: 3.63

[a]Percentage consistent with 5% $Pd(acac)_2$ impurity (see p. 12).

[b]Percentage consistent with 7% $Pd(acac)_2$ impurity (see p. 12).

[c]Percentage consistent with 10% $Pd(acac)_2$ impurity (see p. 12).

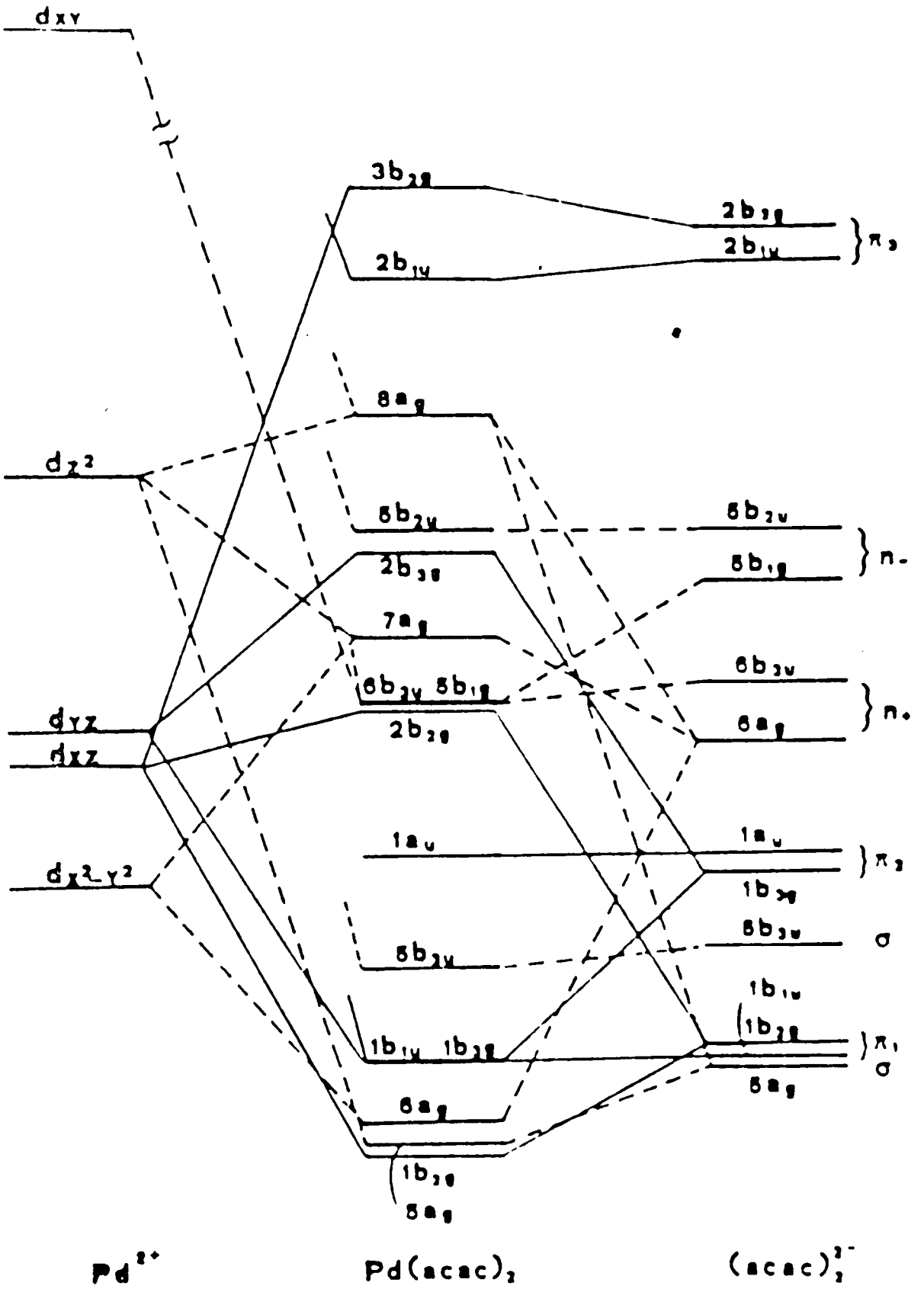


Figure 2

Molecular Orbital Diagram of $Pd(acac)_2$

σ and π interactions are shown by dashed and solid lines, respectively. Only filled levels are represented.

Source: Reference 24

Table 2

Ultraviolet-Visible Spectra of Acetylacetonato-Palladium(II) Complexes

Complex	Solvent	U.V. Data[a]
$Pd(acac)_2$	CH_2Cl_2	229.6 (2.36×10^4), 326.6 (1.07×10^4)
$Pd(acac)_2PPh_3$	CH_2Cl_2	229.6 (2.88×10^4), 345.8 (4.38×10^3)*
$Pd(acac)_2P(p\text{-}CH_3OPh)_3$	CH_2Cl_2	242.0 (3.87×10^4), 274.0 (2.49×10^4)*
		352.0 (5.28×10^3)
$Pd(acac)_2P(o\text{-}CH_3OPh)_3$	CH_2Cl_2	231.2 (2.08×10^4), 291.4 (1.49×10^4)
		325.6 (6.18×10^3)*
$Pd(acac)_2P(p\text{-}CH_3Ph)_3P$	CH_2Cl_2	228.0 (3.53×10^4)
$Pd(acac)_2P(p\text{-}Me_2NPh)_3$	CH_2Cl_2	228.0 (3.90×10^4), 285.0 (6.27×10^4)
		396.4 (9.80×10^3)
$Pd(acac)_2P(cyclohexyl)_3$	CH_2Cl_2	229.6 (2.81×10^4)
$Pd(acac)_2P(p\text{-}FPh)_3$	CH_2Cl_2	214.0 (1.18×10^4), 228.0 (3.25×10^4)
		325.4 (8.23×10^3)*
$Pd(acac)_2P(p\text{-}ClPh)_3$	CH_2Cl_2	234.2 (5.93×10^4), 326.8 (1.65×10^4)

[a]Data = λ_{max} (ε, $M^{-1}cm^{-1}$)

* * = Shoulder

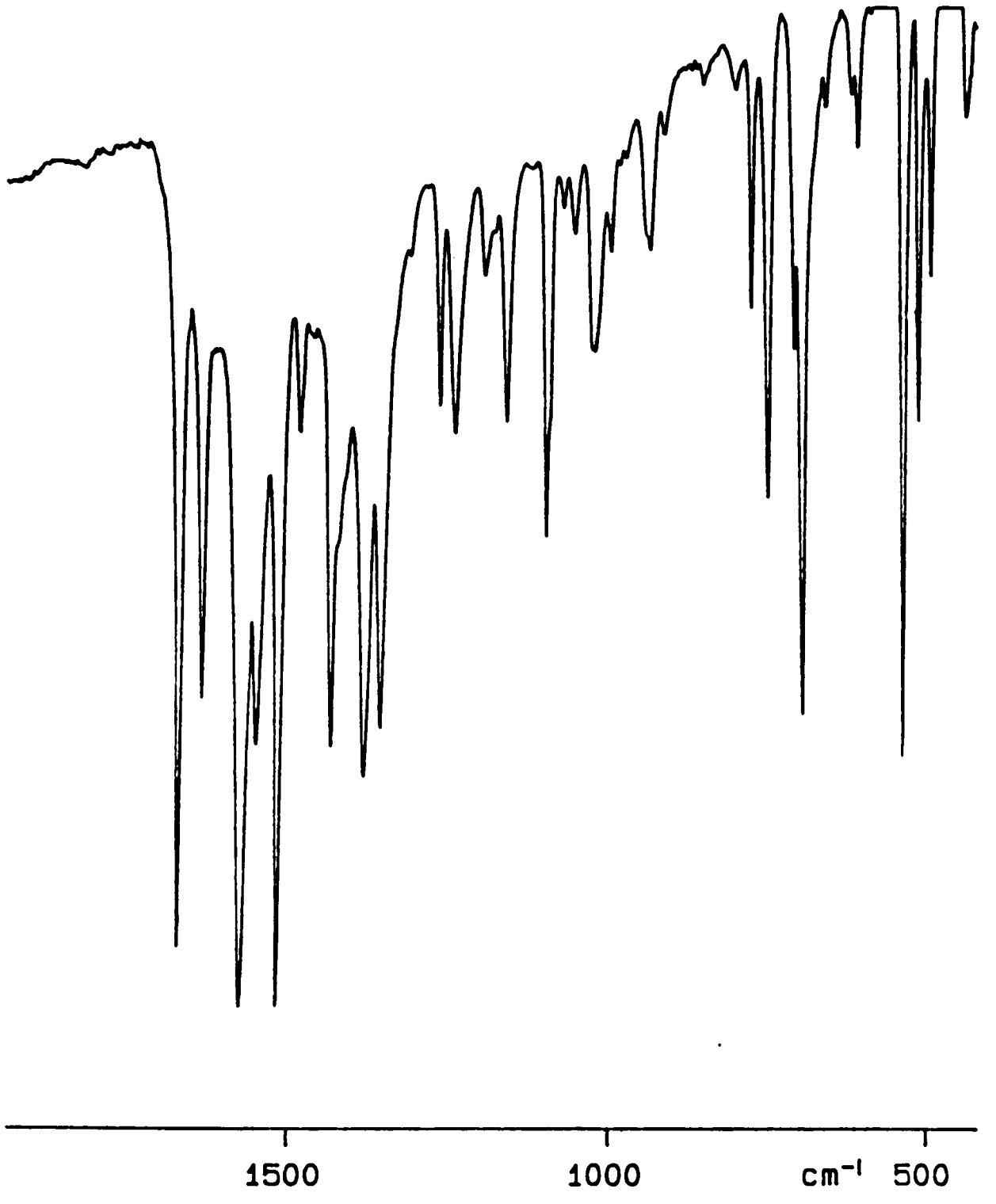


Figure 3

Infrared Spectrum of $Pd(acac)_2(PPh_3)$

Table 3

IR Data for Complexes Containing the C-bonded and O-bonded Linkage Isomers[a,b]

Complex	C-bonded acac		O-bonded acac	
	ν(CO)	ν(Pd-C)	ν(CO) +	ν(CC)
$Pd(acac)_2PPh_3$	1671 vs 1635 s	537 vs	1574 vs 1517 vs	1550 s
$Pd(acac)_2P(p\text{-}CH_3OPh)_3$	1666 s 1635 sh	544 s	1594 vs 1516 vs	1550 s
$Pd(acac)_2P(o\text{-}CH_3OPh)_3$			1571 vs 1522 s	1549 s
$Pd(acac)_2P(p\text{-}CH_3Ph)_3$	1672 vs 1643 vs	528 vs	1578 vs 1517 sh	1550 sh
$Pd(acac)_2P(p\text{-}Me_2NPh)_3$	1686 sh 1654 sh	532 m	1569 vs 1509 vs	1548 vs
$Pd(acac)_2P(cyclohexyl)_3$	1672 vs 1655 s	534 m	1583 vs 1515 vs	1550 sh
$Pd(acac)_2P(p\text{-}FPh)_3$	1676 vs 1643 s	536 vs	1577 vs 1517 vs	1542 sh
$Pd(acac)_2P(p\text{-}ClPh)_3$	1673 vs 1641 m	531 s	1576 vs 1516 vs	1548 sh

[a]Infrared Spectra in KBr Pellet (cm^{-1})

[b]vs: very strong, s: strong, m: medium, sh: shoulder

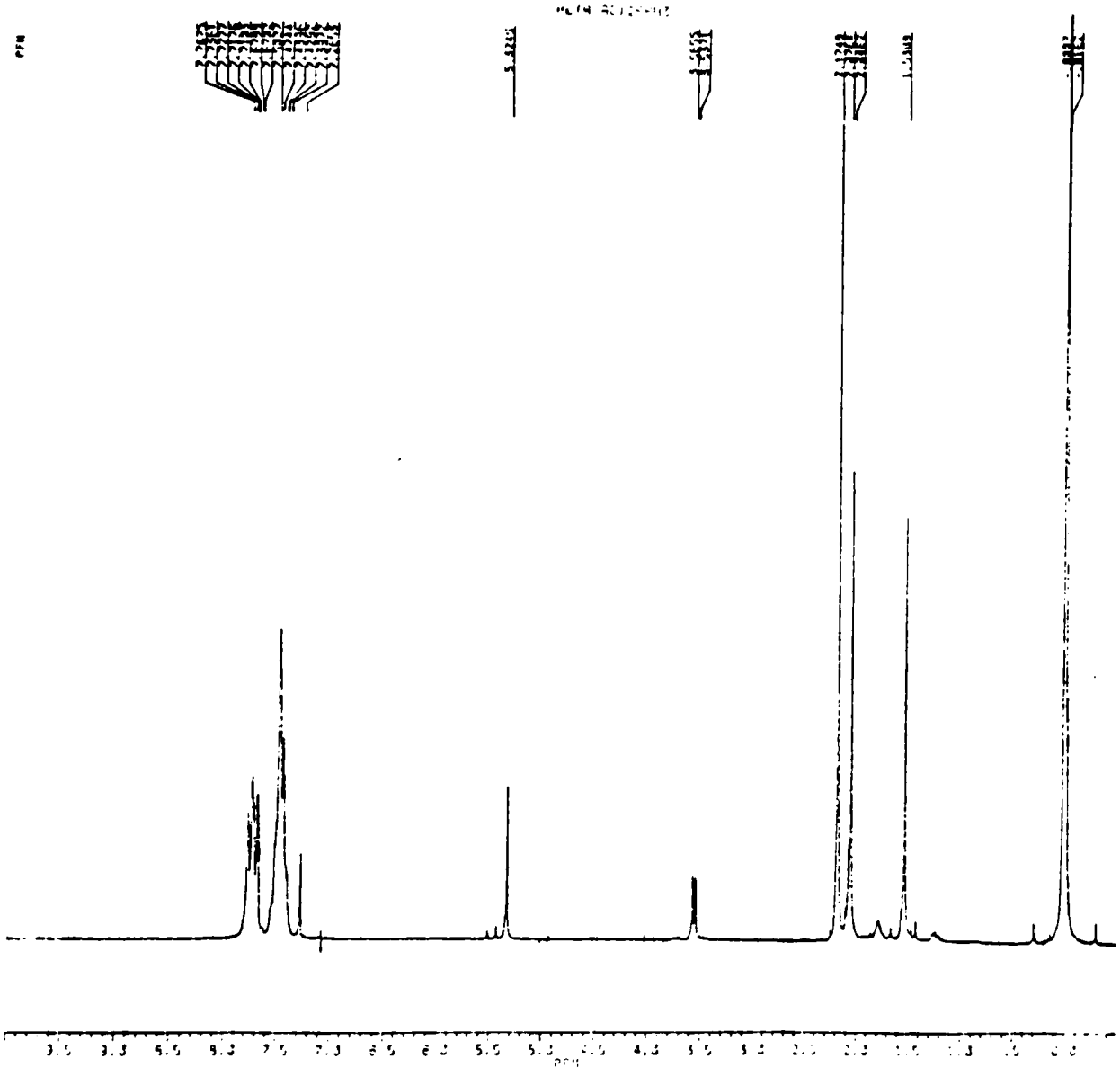
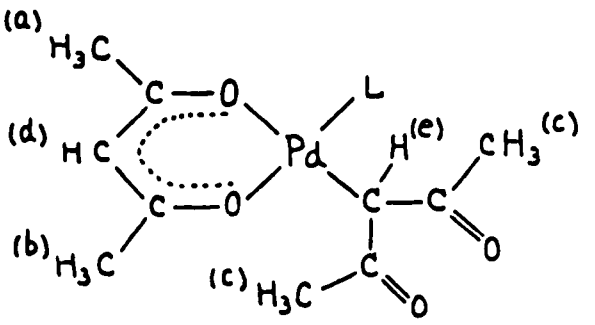


Figure 4

Proton NMR Spectrum of $Pd(acac)_2(PPh_3)$

Table 4

Proton NMR Data for Complexes Containing the O-bonded and C-bonded Linkage Isomers[a]



Complex/ Uncertain Assignments	O-bonded acac ligand CH3(a)	CH3(b)	CH(d)	C-bonded acac ligand CH3(c)	CH(e)	JP-H (Hz)	Phenyl CH3
Pd(acac)2	2.08	2.08	5.43				
Pd(acac)2PPh3	1.53	2.05	5.33	2.18	3.55[b]	5.69	
Pd(acac)2P(p-CH3OPh)3	1.58	2.05	5.32	2.19	3.54[b]	5.42	3.84
Pd(acac)2P(o-CH3OPh)3 (1.32,1.42,2.21,3.49,3.55)	1.42	2.07	5.17 5.43				3.74
Pd(acac)2P(p-CH3Ph)3 (1.43, 2.08)	1.56	2.04	5.32 5.43	2.18	3.52[b]	5.22	2.39
Pd(acac)2P(p-Me2NPh)3 (2.01)	1.56	2.08	5.4[c]	2.20	----[d]	----[d]	2.98
Pd(acac)2P(cyclohexyl)3	1.28	1.89	5.35	2.31	3.35[b]	----[d]	
Pd(acac)2P(p-FPh)3 (0.84, 0.87, 0.91)	1.23	1.39	5.30	2.44	3.54[b]	7.06	
Pd(acac)2P(p-ClPh)3 (2.12)	1.63	2.05	5.43	2.08	3.6[c]	----[d]	

[a]NMR data recorded at 200 MHz in CDCl3 (δ values relative to internal TMS). All signals except the following are singlets.

[b]Doublet due to coupling of CH(e) to phosphorus.

[c]Only two significant figures reported due to low signal intensity.

[d]Values not able to be experimentally determined.

Table 5

^{31}P NMR Chemical Shift and other Data for Phosphine Complexes[a]

Complex	$^{31}P(A)$[b] (ppm)	$^{31}P(L)$[c] (ppm)	$\Delta^{31}Pd$ (ppm)	σ_p[e] (ppm)	Angle[f] (degrees)
$Pd(acac)_2PPh_3$	38.00	-0.01	38.01	0	145
$Pd(acac)_2P(p\text{-}CH_3OPh)_3$	34.45	-4.76	39.21	-0.268	145
$Pd(acac)_2P(o\text{-}CH_3OPh)_3$	25.42	-33.73	59.15		
$Pd(acac)_2P(p\text{-}CH_3Ph)_3$	36.20	-2.51	38.71	-0.170	145
$Pd(acac)_2P(p\text{-}Me_2NPh)_3$	37.53	-5.90	43.43	-0.83	145
$Pd(acac)_2P(cyclohexyl)_3$	42.71	16.58	26.13		170
$Pd(acac)_2P(p\text{-}FPh)_3$	32.33	-3.67	36.00	0.062	145
$Pd(acac)_2P(p\text{-}ClPh)_3$	32.38	-3.13	35.51	0.227	145

a ^{31}P NMR data recorded at 300 MHz in $CDCl_3$ (ppm values relative to external PPh_3 standard).

b $^{31}P(A)$ = ^{31}P chemical shift for the $Pd(acac)_2PR_3$ complex.

c $^{31}P(L)$ = ^{31}P chemical shift for the (PR_3) ligand.

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

e σ_p = Hammett constant of p-X phenyl substituent.[43]

f Angle = cone angle of phosphine.[43]

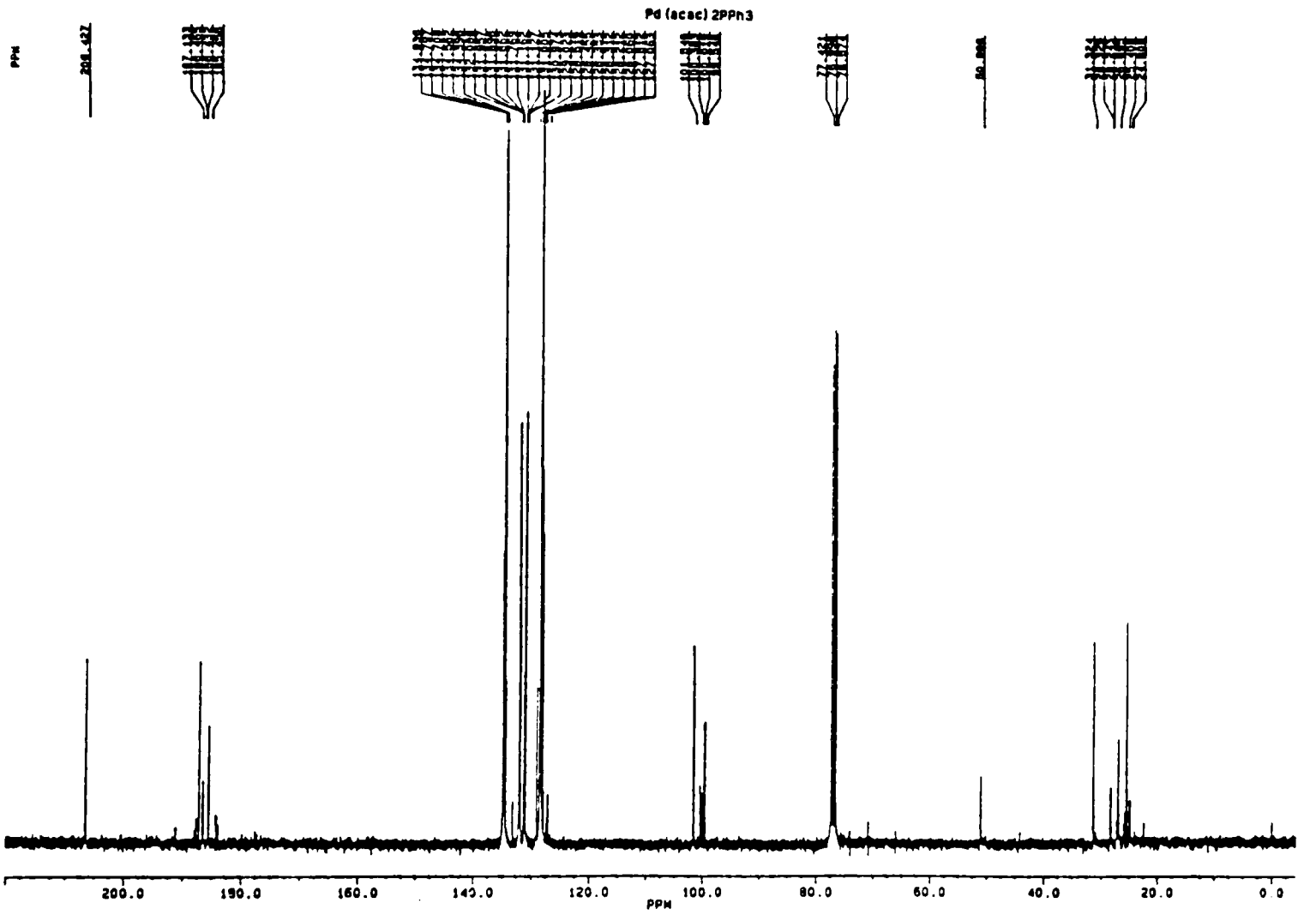


Figure 5

^{13}C NMR Spectrum of $Pd(acac)_2(PPh_3)$

Table 6

^{13}C NMR Chemical Shift Data for
Phosphine Complexes[a]

Complex	Primary C-H Signals (C,O-bonded acac, PR_3)	Methine (C-bonded acac)	Methine (O-bonded acac)
$Pd(acac)_2$	25.40		101.52
$Pd(acac)_2PPh_3$	25.41, 26.90, 28.29, 31.32, 50.99	99.55	101.55
$Pd(acac)_2P(p\text{-}CH_3OPh)_3$	25.41, 26.99, 28.27, 31.33, 55.26	99.51	101.56
$Pd(acac)_2P(o\text{-}CH_3OPh)_3$	25.42, 26.45, 26.87, 28.15, 31.23, 55.19	b	b
$Pd(acac)_2P(p\text{-}CH_3Ph)_3$	21.47, 25.43, 26.86, 26.98, 31.34, 51.43	99.51	101.57
$Pd(acac)_2P(p\text{-}Me_2NPh)_3$	25.36, 26.18, 26.91, 31.34, 39.95	99.77	101.56
$Pd(acac)_2P(cyclohexyl)_3$	26.39, 27.48, 27.62, 29.55, 31.59, 32.11, 32.42, 48.31	99.35	101.58
$Pd(acac)_2P(p\text{-}FPh)_3$	25.40, 27.01, 28.29, 31.32, 51.18	99.71	101.53
$Pd(acac)_2P(p\text{-}ClPh)_3$	25.42, 27.10, 28.33, 31.38, 51.04	99.77	101.55

a ^{13}C NMR data recorded at 300 MHz in $CDCl_3$ (δ values given in ppm using $CDCl_3$ as an internal standard).

b Resonances associated with the methine carbons of the C- and O-bonded acetylacetonate linkages are found at 99.00 and 101.57 ppm. Specific assignments were not made due to structural ambiguity (see p. 32).

Table 7

^{13}C NMR Chemical Shift Data for
Phosphine Complexes[a]

Complex	Aromatic Carbon Range (phosphine)	Carbonyl (O-bonded acac)	Carbonyl (C-bonded acac)
$Pd(acac)_2$		187.12	
$Pd(acac)_2PPh_3$	127.06 - 134.94	185.46, 186.45	206.43
$Pd(acac)_2P(p\text{-}CH_3OPh)_3$	113.61 - 162.25	185.36, 186.50	206.47
$Pd(acac)_2P(o\text{-}CH_3OPh)_3$	110.14 - 160.85	b	b
$Pd(acac)_2P(p\text{-}CH_3Ph)_3$	125.36 - 141.46	185.42, 186.45	206.47
$Pd(acac)_2P(p\text{-}Me_2NPh)_3$	110.88 - 151.59	185.24, 186.31	206.50
$Pd(acac)_2P(cyclohexyl)_3$		184.91, 186.67	208.17
$Pd(acac)_2P(p\text{-}FPh)_3{\cdot}H_2O$	115.57 - 166.84	185.46, 186.72	206.26
$Pd(acac)_2P(p\text{-}ClPh)_3$	126.25 - 139.11	185.51, 186.75	206.22

a ^{13}C NMR data recorded at 300 MHz in $CDCl_3$ (δ values given in ppm using $CDCl_3$ as an internal standard).

b Resonances associated with the C-O and C=0 groups of the O- and C-bonded acetylacetonate linkages, respectively, are found at 185.36, 185.92, and 207.17 ppm. Specific assignments were not made due to structural ambiguity (see p. 32).

CHAPTER IV

DISCUSSION

The Chemistry of $Pd(acac)_2(PR_3)$ Complexes

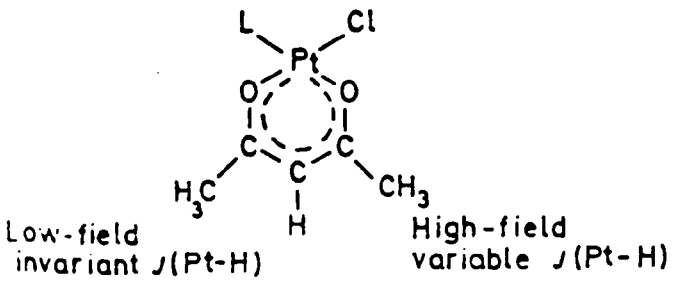
Analysis of Spectral Data

An extensive class of complexes of the form Pd(O-acac)(C-acac)(PR_3) (R = arylphosphine) was successfully isolated throughout the series except for L = P(o-methoxyphenyl)$_3$, where the steric influence of the o-CH_3O substituents apparently prevents isomerization of one of the acac linkages from the oxygen to the carbon-bonded form. The absence of associated C-O and Pd-C stretches in the infrared spectrum of $Pd(acac)_2$P(o-methoxyphenyl)$_3$ supports our claim that the carbon-bonded acetylacetonate linkage is not present in the o-methoxy derivative. Furthermore, the presence of two distinct signals in the proton NMR spectrum of $Pd(acac)_2$P(o-methoxyphenyl)$_3$ attributed to the methine protons of the oxygen-bonded acetylacetonate linkages, in addition to the absence of methyl and methine resonances associated with the carbon-bonded linkage, clearly confirms the absence of the carbon-bonded isomer in this compound. A substantially larger downfield shift of 59.15 ppm was observed in the ^{31}P NMR spectrum of the tris(o-methoxyphenyl)phosphine complex. Finally, the appearance of two methine resonances in the proton NMR spectrum is further substantiated by the presence of two distinct methine carbon resonances associated with the O,O-bonded acetylacetonate linkage in the ^{13}C NMR spectrum of $Pd(acac)_2P(o\text{-}CH_3OPh)_3$. Thus, the spectral data suggest that the o-methoxy derivative actually exists as an intermediate complex of the form $Pd(O\text{-}acac)_2(PR_3)$, where the two oxygen-bonded acetylacetonate ligands are nonequivalent and one of the $acac^-$ linkages is no longer bound equatorially to the Pd(II) center. Specifically, the o-methoxy derivative may exhibit both an equatorially bound,

oxygen-bonded isomer and a second O,O-bonded isomer spanning both axial and equatorial sites and may display a pseudo trigonal bypyramidal geometry. However, the marked similarity between the ^{13}C spectrum of $Pd(acac)_2P(o\text{-}CH_3OPh)_3$ and the $Pd(acac)_2$-$P(p\text{-}CH_3OPh)_3$ complex bearing the carbon-bonded isomer, as well as a ^{13}C resonance at 207.17 ppm attributed to the carbonyl groups of the carbon-bonded linkage, presents an apparent contradiction to this model.

Electronic and infrared spectra of $Pd(acac)_2PPh_3$ and related complexes clearly establish the presence of both the oxygen- and carbon-bonded forms in these complexes. The UV-visible spectra of the $Pd(acac)_2(PR_3)$ complexes generally exhibit two rather intense bands associated with the bidentate, O,O-bonded acetylacetonate linkage, revealing a remarkable ligand-to-metal covalency between the acac- anion chelate and the Pd(II) metal center. Similarily, the infrared spectra showed the presence of both the oxygen- and carbon-bonded isomeric forms (with the exception of L = P(o-methoxyphenyl)3), the carbonyl bands of the carbon-bonded acetylacetonate ligand absorbing at higher frequency than the C-O and C=C stretches of the oxygen-bonded acetylacetonate linkage. Moreover, the NMR spectra served as an additional confirmation of these bonding modes. The well-established work of Lewis and coworkers[44] on the NMR spectra of analogous platinum(II) complexes containing the carbon-bonded acetylacetonate linkage proved invaluable in making assignments of the current NMR spectra. As for the two methyl groups of the oxygen-bonded acetylacetonate ligand in $Pd(acac)_2PPh_3$, the highest field ^1H signal at 1.53 δ was shifted significantly when triphenylphosphine is replaced by other phosphine ligands, while the lower field signal at 2.05 δ did not appear to be sensitive to the nature of the phosphine ligand. Such an observation could be rationalized in terms of an anisotropic shielding effect of the triphenylphosphine ligand, which would exert its greatest influence

on the methyl group in closest proximity to the ligand L and thus the highest-field signal would be attributed to the acetylacetonate methyl group in the cis position to the ligand L.[45] Similar observations have been noted by Lewis and coworkers for PtCl(acac)L complexes containing various phosphines and nitrogen bases as L. From these studies,[46] Lewis et al. found that the high field methyl resonance has a ^{195}Pt-H coupling constant that is sensitive to the nature of the ligand L, while its chemical shift is apparently unaffected. The low-field methyl resonance exhibits a ^{195}Pt-H coupling constant that is relatively invariant to the nature of L and a chemical shift that is very dependent on L. By varying the anisotropic shielding effect of L (e.g., Et_3P to Ph_3P), it becomes evident that the low-field methyl resonance is that of the methyl group in nearest proximity, or cis, to this ligand. The fluctuations in the ^{195}Pt-H coupling to the high-field methyl group are thus explained in terms of a trans-effect (2).



(2)

As for the ^{31}P spectral data, the magnitude of the coordination chemical shifts of these $Pd(acac)_2PR_3$ complexes is an indirect measure of the σ-donating ability of the phosphine ligand. A very interesting linear correlation exists between the ^{31}P coordination chemical shift ($\delta_{complex} - \delta_{ligand}$) and the corresponding Hammett p-substituent constant (see Figure 6). Similar Hammett σ_p correlations with infrared, proton NMR, and ^{13}C NMR data were not found to exist. Triarylphosphine donor ligands typically underwent a downfield shift of about 40 ppm upon coordination to the $Pd(acac)_2$ moiety, suggesting that there is significant polarization of phosphorus 3p electron density towards the

electrophilic Pd(II) center. For instance, the bis(acetylacetonato)triphenylphosphine P atom exhibited a downfield shift of 38.01 ppm upon coordination.

Unfortunately, a direct correlation between the phosphorus coordination chemical shifts and the ^{13}C chemical shift data could not be obtained. The methyl, methine, and carbonyl ^{13}C resonances appeared to be relatively insensitive to the electronic nature of the phosphine ligand L. This observation may imply that the electron density of the phosphine ligand is poorly transmitted to the Pd-C bond of the carbon-bonded linkage if it is transmitted at all. It is remarkable, in fact, that the σ-donating ability of the phosphine does not exhibit a more profound effect on either the oxygen-bonded chelating or carbon-bonded linkages. Phosphorus electron density is transmitted poorly to the bidentate, O,O-bonded acac linkage via back-bonding and therefore appears to be largely localized on the central Pd atom. The observation that excess phosphine does not displace the remaining bidentate, O,O-bonded acac linkage in the $Pd(acac)_2PR_3$ complexes suggests that this unit is stabilized within the PCO_2 coordination sphere of palladium. Thus, while it is not yet clear why the palladium(II) complex bearing multiple arylphosphine ligands cannot be isolated, several plausible explanations exist to explain why the second O,O-bonded acetylacetonate linkage fails to undergo linkage isomerization:

(1) The electronic effect of the phosphine ligand may actually have a stabilizing influence on the oxygen-bonded acetylacetonate chelate ring, which may lend additional stability to the carbon-bonded mode of the other acetylacetonate linkage. This observation may especially hold true for the series of $Pd(acac)_2(PR_3)$ complexes, where extensive conjugation exists throughout the molecule.

(2) Although the carbon-bonded acetylacetonate linkage is not a good enough σ-donor ligand in its own right, the presence of the strongly σ-donating phosphine ligand may induce a synergistic effect which maximizes covalency between these two competing σ-donor ligands. This synergistic effect may, in turn, lend additional thermodynamic stability to the oxygen-bonded acetylacetonate chelate ring with an accompanying strengthening of the Pd-C and Pd-P bonds. Such a system is entirely analogous to that of Jeong et al.,[47] where the unanticipated hydrolysis of the $[Pd(C\text{-}CA)Cl_2]^{2-}$ complex is believed to be thermodynamically driven by a strengthening of the Pd-chloranilate C bonds as a result of the departure of the competing sigma donor chloride ligands.

Future Work

In conclusion, the next stage of our research will entail the use of extensive kinetic studies in order to more fully elucidate the isomerization process of the acetylacetonate linkage from the bidentate, oxygen-bonded to the monodentate, carbon-bonded form. Specifically, the emphasis will be upon understanding the mechanism by which this trans-formation occurs and determining the degree to which both Pd-P bond-making and Pd-O bond-breaking contribute to the rate-determining step. Additionally, we wish to explore the role the phosphine substituents play in influencing the rate of isomerization of the coordinated acetylacetonate linkage, as well as the phosphine substituent's influence upon the mechanism of Pd-C bond formation. Ultimately, the goal of our investigation will be to more fully understand the mechanisms by which palladium(II)-σ-alkyl carbon bonds form and rupture in simpler systems in an effort to develop new catalytic applications of palladium(II) compounds in modern industrial organometallic syntheses.

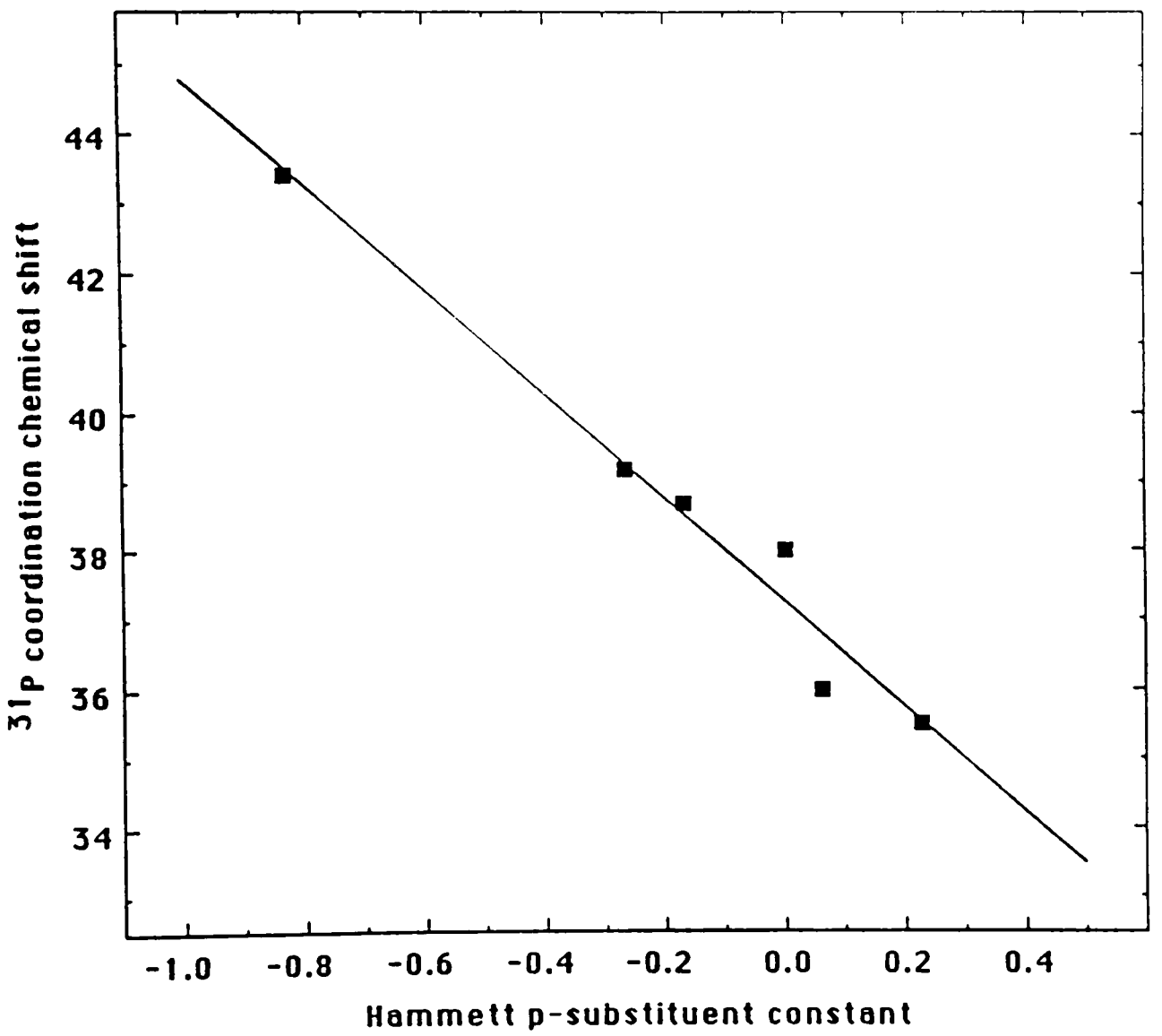


Figure 6

Linear Relationship between ^{31}P Coordination Chemical Shift (ppm) and Hammett p-Substituent Constant for Phosphine Ligands

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