ASPECTS OF ZERO-VALENT NICKEL, PALLADIUM AND PLATINUM CHEMISTRY

DEDICATION

To my wife, Ethel, my daughter, Cheryl and my parents, Mr. and Mrs. Robert MacDonald for their continual support and encouragement.

ASPECTS OF ZERO-VALENT NICKEL, PALLADIUM AND PLATINUM CHEMISTRY

By

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
November 1974

MASTER OF SCIENCE (1974) (Chemistry)	McMASTER UNIVERSITY HAMILTON, Ontario

TITLE:	Aspects of Zero-Valent Nickel, Palladium and Platinum Chemistry
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NUMBER OF PAGES:	v, 97

SCOPE AND CONTENTS: The work describes the preparation and properties of some novel dibenzylideneacetone complexes of palladium and platinum. The structure and bonding in these complexes is discussed in view of their infrared and nuclear magnetic resonance spectra. The cyclotrimerization of acetylenes by zero-valent nickel complexes is discussed and the synthesis of a new cyclobutadiene-platinum complex is reported.

ACKNOWLEDGEMENTS

The author is endebted to Dr. P. M. Maitlis for his continuing advice and interest shown in the work.

Thanks are also extended to Dr. M. J. McGlinchey for help and advice in the preparation of this thesis.

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Table of Abbreviations

Abbreviation	Compound
dba	dibenzylideneacetone
dma	dimethyl acetylene dicarboxylate
o-phen	o-phenanthroline
tmedta	tetramethylethylenediamine
py	pyridine
dmg	dimethylglyoxime
dte	1,2-bis(methylthioethane)
badn	biacetyl-dianil
para-methoxyl dba	bis(para-methoxy)dibenzylideneacetone
para-fluoro dba	bis(para-fluoro)dibenzylideneacetone
para-dimethylamino dba	bis(para-dimethylamino)dibenzylideneacetone
para-methyl dba	bis(para-methyl)dibenzylideneacetone
dbh	2,6-dibenzylidenecyclohexanone

INTRODUCTION

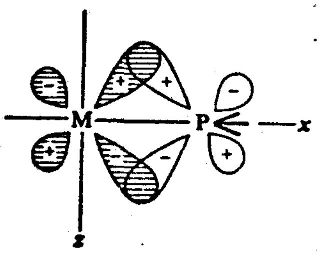
INTRODUCTION

In an effort to rationalize the mechanisms of heterogeneous catalysis, considerable attention has been focussed recently on the chemistry of low valent metal complexes. This presupposes that coordination and chemisorption are interrelated and that the behaviour of low valent metal complexes in solution is essentially that of solvated metal atoms. Zero-valent d^{10} systems are particularly interesting due to their tendency to stabilize coordinatively unsaturated compounds. One series of compounds in particular, the dibenzylideneacetone (dba) complexes of palladium and platinum, has generated widespread interest and the subsequent work helped to elucidate some of the steps involved in the cyclotrimerization of acetylenes. The investigation described in this thesis is devoted to the study of the preparation, properties and reactions of the dba complexes and their products.

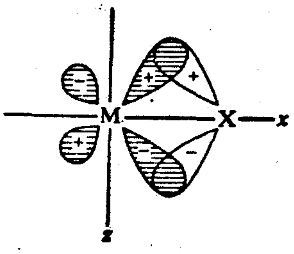
1. Bonding in Zero-valent Complexes

The d-block transition metals are characterized by their ability to form complexes with a wide variety of neutral molecules such as carbon monoxide, isocyanides, substituted phosphines, arsines and stibines, pyridine, 2,2'bipyridyl, etc.. The types of complexes range from simple binary compounds such as $Ni(CO)_4$ to mixed species such as $(Ph_3P)_2Pt(CO)_2$[1] and $(Ph_3P)_2Pd(SbPh_3)_2$.[2]

In many of these complexes, the metal is formally in a zero oxidation state. The metal already has a full complement of electrons and, on bonding to a neutral ligand, must have some mechanism for dissipating the build-up of negative charge which takes place. This charge build-up on the metal from the formation of the coordinate bond is believed to be removed by the back donation of electron density from filled metal d orbitals to vacant ligand π^* or d orbitals by the formation of π-type bonds.[3]



a



b

The bonding in complexes involving trivalent phosphorus arsenic, antimony and bismuth and divalent sulphur and selenium ligands can be explained by back donation to empty d orbitals of correct symmetry as illustrated in figure (a). Back donation from the metal to ligands such as carbon monoxide, bipyridyl, isonitriles, etc. involves the use of vacant ligand π^* orbitals for dissipation of electron density as illustrated in figure (b).

1.1 Bis and Tris (dibenzylideneacetone) Complexes of Palladium and Platinum

The first of these complexes, bis(dibenzylideneacetone) - palladium, $(dba)_2Pd$, was reported in 1970 by Takahashi et al.[4] Previously, the only known zero-valent complexes of palladium involved ligands such as phosphines[5-7], phosphites[5], arsines[5], isocyanides[6] and carbon monoxide[8-10].

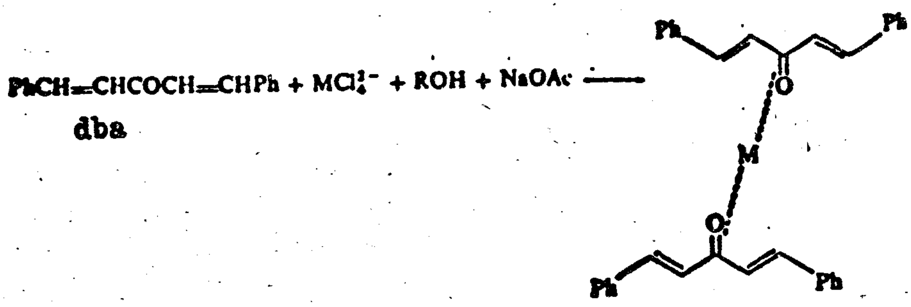
Subsequently, Moseley and Maitlis[11] reported the synthesis of the platinum complexes $(dba)_2Pt$ and $(dba)_3Pt$. Mazza and Pierpont[12] reported the synthesis and crystal structure of the remaining member of this series, $(dba)_3Pd$.

Independently Ishii et al.[13] and Mazza and Pierpont[14] reported the synthesis and crystal structure of an interesting new complex $Pd_2(dba)_3$.solvent . This was the only product recovered from crystallization of a solution of $(dba)_2Pd$ in solvents such as chloroform, methylene chloride, benzene, toluene and THF.

1.2 Properties

There are two divergent opinions as to the actual structure of $(dba)_2Pd$[4,11]. Takahashi suggested that the dba was co-ordinated to the Pd^o mainly through the C=C bonds. This was supported by i.r. evidence; the absorption bands were similar to those of dba, but the bands at 1627 and 983 cm^{-1} (C=C) had disappeared and ν (C=O) had shifted from 1651 (free dba) to 1620 cm^{-1} (co-ordinated dba). In a subsequent spectral comparison of dba, $(dba)_2Pd$ and $(dba)_2Pt$, Moseley and Maitlis[11] proposed that in solution, the metal atoms were bonded to the carbonyl groups rather than the double bonds as originally proposed. They found that in the i.r. spectra in chloroform, ν (C=O) of both complexes had almost disappeared while ν (C=C) remained intense and relatively unchanged. Two new bands at 1544 (Pd) and 1527 (Pt) cm^{-1} were observed and identified as modified ν (C=O) bands.

The electronic spectra of the complexes were similar to dba but had intense charge-transfer bands attributed to metal-ligand (d-π^*) transitions. In addition, the n.m.r. spectrum of $(dba)_2Pt$ was identical to that of dba itself with no evidence of any coupling to ^{195}Pt ($I=\frac{1}{2}$, 34% abundance) by either olefinic or aromatic protons. Although $(dba)_2Pd$ was only slightly soluble in the solvents used, similar results were obtained. The proposed structure is pictured below.



M= Pd, Pt

Most of the spectra quoted in the reports were taken in methylene chloride of chloroform. For this reason, the crystallization product $Pd_2(dba)_3$.solvent [13,14] provides interesting information concerning the nature of the Pd - dba complex in solution.

Mazza and Pierpont[14] recorded the i.r. spectra of both the initial $(dba)_2Pd$ solution and a solution of $Pd_2(dba)_3$.solvent in chloroform and methylene chloride. The spectrum of the initial complex resembled that of Moseley and Maitlis[11]; however, the spectrum of $Pd_2(dba)_3$.solvent resembled that of Takahashi[4] with ν(C=O) at 1618 cm^{-1} and olefinic bands at 1580, 1548 and 1541 cm^{-1}.

Ishii et al.[13] conducted a more detailed study of the complex. Binuclear complexes with the ligands decadeuteriodibenzylideneacetone, $(C_6D_5CH{=}CH)_2CO$, and p,p-dimethoxydibenzylideneacetone were also prepared and studied.

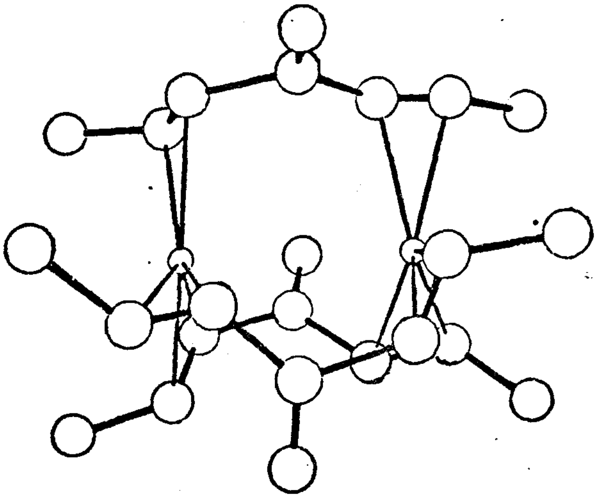
Differences in the i.r. spectra of $Pd_2(dba)_3$.solvent and $Pd_2(dba\text{-}d_{10})_3$.solvent as compared to dba and dba-d_{10} were as follows: a characteristic ν CH(trans) vibration observed at 983 cm^{-1} in the free ligands almost completely disappeared in the complexes, although a broad weak band appeared at a slightly lower frequency (975 cm^{-1}) in both. Also, the ν(C=O) bands were shifted about 40 cm^{-1} to lower frequency. The ν (C-Cl) bands, hidden in the spectrum of $Pd_2(dba)_3$.solvent by the strong ν CH(arom) absorptions, appeared at 766 and 747 cm^{-1} in the deuterated complex.

The electronic spectrum of $Pd_2(dba)_3$.solvent showed bands assigned to $n - \pi^*$ and $\pi - \pi^*$ transitions at 234 and 321 mμ. These remained unchanged from the transitions observed for the free ligand.

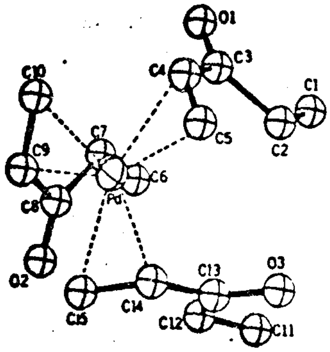
The ^{1}H n.m.r. spectrum showed a multiplet centred at 3.5 τ, identified as the ten-ring proton resonance of the co-ordinated dba. This was confirmed by the disappearance of this multiplet in the n.m.r. spectrum of the complex containing the deuterated ligand. Olefinic proton resonances of the co-ordinated dba were spread over the range from 2.5 to 5.5 τ. The low solubility of the complex necessitated repeated scans in order to obtain a favourable signal-to-noise ratio. During this time part of the co-ordinated dba was liberated and appeared in the spectrum of the complex.

The structure of $Pd_2(dba)_3.CH_2Cl_2$ was determined by x-ray crystallography and the complex was found to consist of two Pd atoms bridged by three dba molecules. Co-ordination of the dba molecules takes place through the C=C olefin portions of the ligands. The co-ordination about each Pd atom is trigonal three co-ordinate if only the centres of the double bonds are considered. The conformations of the three dba ligands vary, with one in the symmetric s-cis, s-cis configuration and the other two in the asymmetric s-cis, s-trans configurations. Each metal in the atom is co-ordinatively unsaturated.'

The structure of $Pd_2(dba)_3.CHCl_3$ was also determined and found to be essentially the same as the CH_2Cl_2 complex, the major difference being that in this case, all three ligands were found to be in the s-cis, s-trans conformation.[14] The change in solvent changes the conformation of one of the ligands. The structure of the chloroform complex is shown below.



The crystal structure of $(dba)_3Pd$ provides additional insight into the nature of the metal-ligand bonding in these complexes.[12] The complex consists of a trigonally co-ordinated Pd atom bonded to olefin groups of three dba ligands. The dba ligands are all in the asymmetric s-cis, s-trans conformation. The structure of the compound is shown below.



Phenyl rings have been omitted for clarity.

Both $(dba)_2Pd$ and $(dba)_2Pt$ were found to be stable in air in the solid state[11], but slowly decomposed in solution to give the metal and dba. The complexes were slightly soluble in methylene chloride, chloroform and benzene, giving deep wine-coloured (Pd) and purple (Pt) solutions.

The complex $(dba)_3Pt$ was also stable in air in the solid state but dissolved in a variety of solvents to give a green solution that rapidly turned purple and from which $(dba)_2Pt$ and dba in a 1:1 molar ratio were recovered. This, together with the observed molecular weight showed that complete dissociation had taken place. Addition of a large excess of dba to $(dba)_2Pt$ did not give the tris complex.

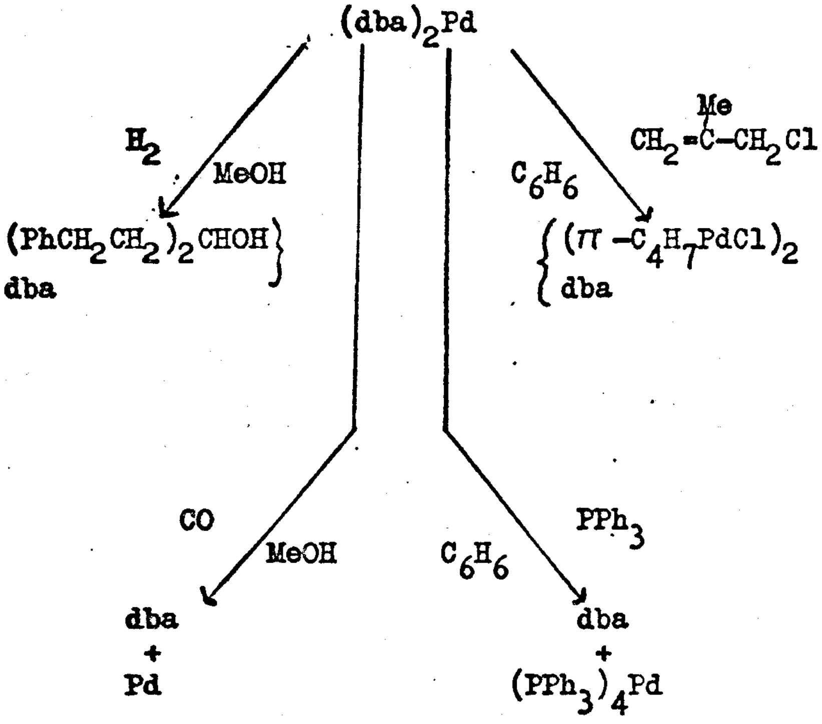
$$(dba)_3Pt \longrightarrow (dba)_2Pt + dba$$

In the case of the complex $(dba)_3Pd$, a state of equilibrium was reported to exist between $(dba)_3Pd$, $(dba)_2Pd$ and dba[12]. In fact $(dba)_3Pd$ was prepared by concentrating a solution of $(dba)_2Pd$ and dba. The $(dba)_3Pd$ readily dissociated in solution in the absence of excess dba giving $(dba)_2Pd$. Attempts to wash the crystals resulted in decomposition.

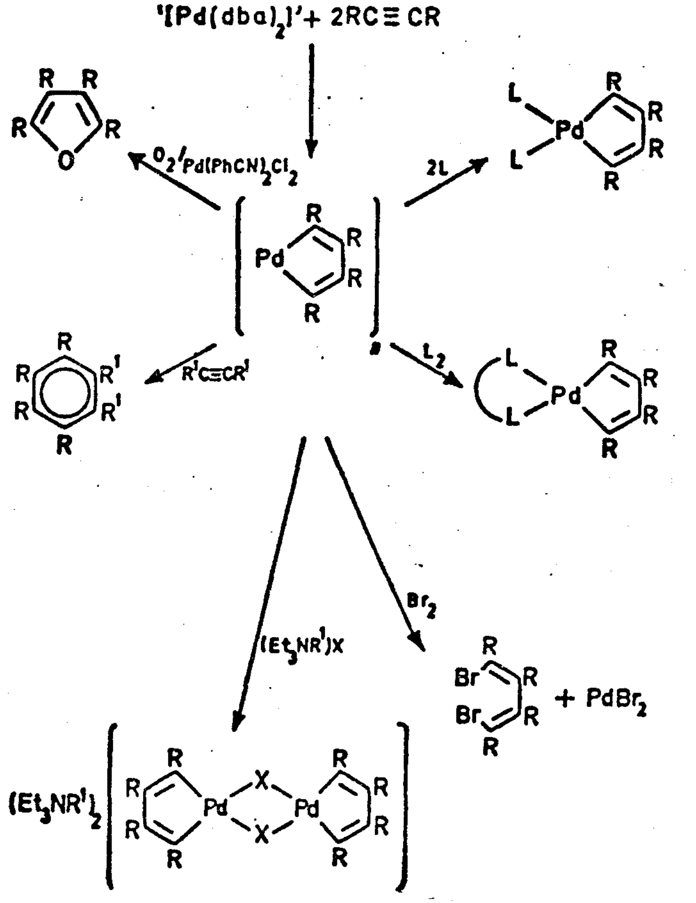
The properties of the binuclear complex $Pd_2(dba)_3$.solvent appear to be similar to those of $(dba)_2Pd$, i.e. a deep wine-red solution in chloroform or methylene chloride which slowly decomposes to dba and metal.[13]

I.3 Reactions

$(dba)_2Pd$ reacted with hydrogen or carbon monoxide in methanol to give a mixture of 1,5-diphenylpentan-3-one and 1,5-diphenylpentan-3-ol in the former case and dibenzylideneacetone, dba, in the latter.[4] Reaction of the complex with triphenylphosphine or methallyl chloride gave the complexes $(Ph_3P)_4Pd$ and bis(π-methallylpalladium chloride) respectively, as shown in the reaction scheme.



(dba)$_2$Pd also reacted with dimethylacetylenedicarboxylate, dma, in a variety of solvents (acetone, benzene, benzonitrile) to give a quantitative yield of the palladiacyclopentadiene complex, $[Pd(CCOOMe)_4]_n$.[15] This complex was characterized by elemental analysis, n.m.r. (two equally intense resonances at τ 6.23 and 6.34 in benzonitrile) and by the reactions outlined below.



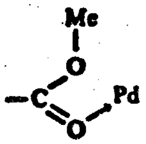
L= Ph_3P, $(PhO)_3P$,
p-toluidine

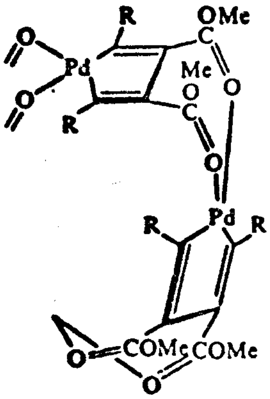
R = COOMe
R' = COOMe
or
Ph

L= $Ph_2PCH_2CH_2PPh_2$,
o-phenanthroline,
bipyridyl

R' = Et, X = I
or R' = H , X = Br

The palladiacyclopentadiene molecules are believed to be associated through the carbonyl groups of the ester functions[11], forming trimeric units. This is supported by the molecular weight determination which is close to that of a trimer.





[R = COOMe]

On warming, the palladiacyclopentadiene complex reacted catalytically with excess dma to form hexamethyl mellitate[15]. Other acetylenes such as diphenyl acetylene also gave benzene, but the reaction was not catalytic[16].

$(dba)_2Pt$ and $(dba)_3Pt$ reacted more slowly[15] (one-sixtieth the rate for palladium) with dma in benzonitrile-benzene to give first, a platinacyclopentadiene complex, isolated and characterized as the bis(triphenylphosphine) adduct $(PPh_3)_2Pt(CCOOMe)_4$, and then hexamethyl mellitate. This implies that the conversion of the metalocyclopentadiene to the benzene occurs more readily for platinum than palladium.

Ishii et al.[19] have reported the preparation of substituted palladiacyclopentadiene complexes, $L_2Pd(CCOOMe)_4$, via a zero-valent π-acetylene-palladium intermediate. On adding dma to an excess of triphenylphosphite and $(dba)_2Pd$ in benzene, the complex $(P(OPh)_3)_2Pd$ (dma) was isolated and characterized. However, the addition of more dma did not give the palladiacyclopentadiene complex in this case. However, with triphenylphosphine as the ligand, the two step synthesis of $(Ph_3P)_2Pd(CCOOMe)_4$ via the formation of $(Ph_3P)_2Pd$ (dma) was observed. Other ligands such as bipyridyl, o-phenanthroline (ophen), tetramethylenediamine (tmedta), pyridine (py), dimethylglyoxime (dmg), 1,2-bis(methylthioethane) (dte) and biacetyl-dianil (badn) gave the corresponding palladiacyclopentadiene complexes directly.

In contrast to this report, Moseley and Maitlis could obtain no evidence for the formation of appreciable amounts of either $Pd(C_4R_4)(PPh_3)_2$ or $\left[Pd(C_4R_4)(PPh_3)\right]_n$ from the monoacetylene complex. They observed that in reactions of the monoacetylene complex with dma an induction period took place which coincided with a reduction of the signal corresponding to the complexed acetylene. Thereafter, during the slow catalytic formation of hexamethyl mellitate, the signal intensity remained constant. This would apparently rule out the intermediacy of a palladiacyclopentadiene-phosphine complex. It was suggested that traces of metal are responsible for the trimerization of the acetylene and the presence of palladiacyclopentadiene complexes.

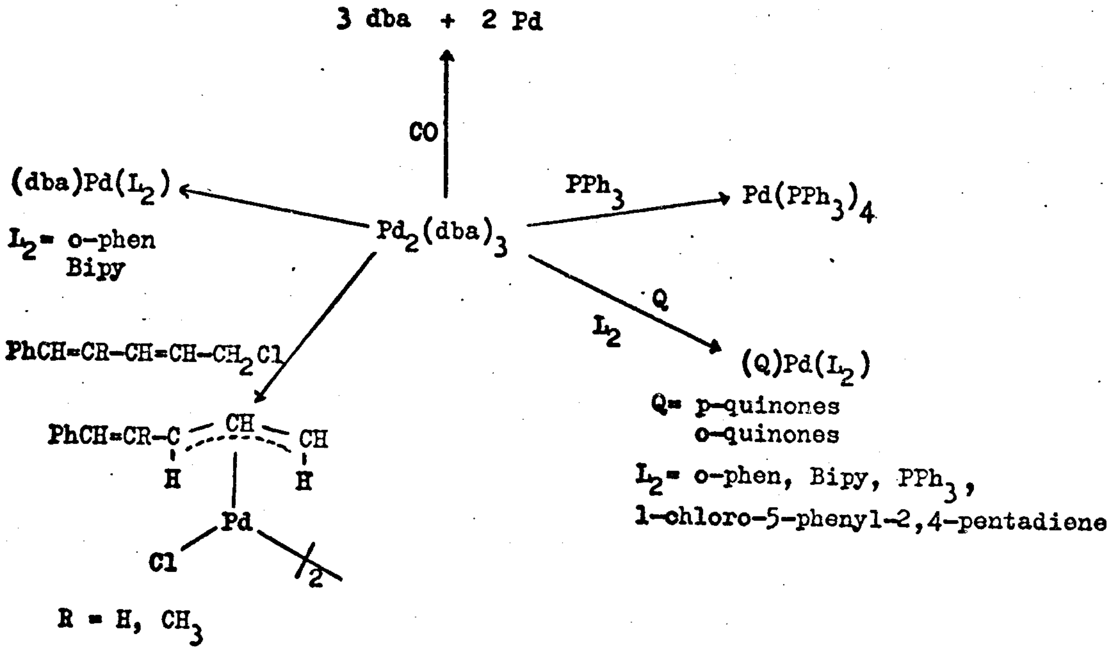
Various zero-valent palladium-olefin complexes have been synthesized via $(dba)_2Pd$. Reaction of olefins with $(dba)_2Pd$ in acetone solution resulted in the decomposition of the complex with the formation of palladium metal and free dba. However, it was found that complexes of the type $(dba)PdL_n$ could be isolated by treating $(dba)_2Pd$ with an excess of the ligand (L-bipyridyl, o-phenanthroline, and pyridine). In the presence of both olefin and ligand, the corresponding olefin-palladium complexes were synthesized, Among the olefins examined, stable complexes were isolated only with acrylonitrile, dimethylfumarate, dimethyl maleate and maleic anhydride. Ligands examined included o-phen, PPh_3, tmeda, $P(Oph)_3$ and $P(OMe)_3$. With tmeda, $P(OPh)_3$ and $P(OMe)_3$, only maleic anhydride formed stable olefin-palladium complexes, and with PPh_3 as the ligand, no olefin-palladium complex was isolated.

Attempts to prepare the platinum analogue[16] of the palladiacyclopentadiene complex were unsuccessful. A material which is probably $[Pt(C_4R_4)]_n$ was isolated from the reaction of $(dba)_2Pt$ and dma in benzene/benzonitrile (5:1). This showed two resonances in the n.m.r. spectrum at 4.0 and 4.08 τ, close to those for the palladiacyclopentadiene complex. On addition of triphenylphosphine, the adduct $Pt(C_4R_4)(PPh_3)_2$ was isolated and fully characterized.

Comparison of the reactions of $(dba)_2Pd$ and $(dba)_2Pt$ with dma under similar conditions showed that $[Pt(C_4R_4)]_n$ formed more slowly than $Pd(C_4R_4)$ but that the platinum complex reacted more readily with further dma to give hexamethyl mellitate.

Reactions of $Pd_2(dba)_3$. solvent

These new binuclear palladium complexes show the same reactivity patterns as was reported for $(dba)_2Pd$.[3] A summary of these reactions is shown on the next page.



$Pd_2(dba)_3$ was found to be an excellent starting material for the preparation of Pd-p-quinone π -coordinated complexes. When an acetone suspension of $Pd_2(dba)_2$ and ligand, L, was treated with p-quinone, Q, (p-benzoquinone, duroquinone, 1,4-napthoquinone and 2-methyl-1, 4-napthoquinone) the complexes $(Q)PdL_2$ crystallized in high yield.

$$Pd_2(dba)_3 + 4L + 2Q \longrightarrow 2(Q)PdL_2 + 3dba$$

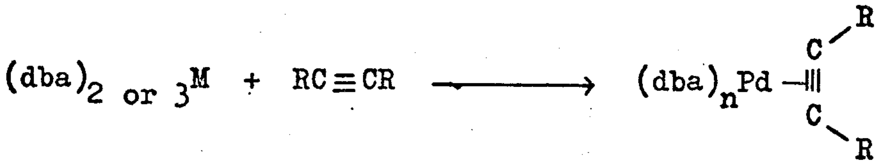
A comparison of the ν (CO) stretching frequencies indicates that the coordination of the p-quinones to the Pd atom takes place through the olefinic double bonds and not through the carbonyl moiety. In addition, the high field shift of the olefin protons in the n.m.r. spectra of the p-benzoquinone complexes are consistent with the coordination of this ligand as a diolefin.

The reactions between $Pd_2(dba)_3$ and o-quinones (9,10-phenanthrenequinone, 1,2-napthoquinone, 4,5-dimethoxy-1,2-benzoquinone, 4-tert-butyl-1,2-benzoquinone) also afforded new quinone-Pd complexes such as $(o\text{-}Q)PdL_2$. In the i.r. spectra of these complexes, the strong ν (CO) bands of the original o-quinones (1650-1700 cm^{-1}) disappear and a characteristic diolato band emerges. This indicates that the two carbonyl oxygen atoms of the o-quinone coordinate to the Pd atom.

1.4 Reaction Mechanism: Oligomerization of Acetylenes by Pd (O) Complexes

The reactions of $(dba)_{2\text{ or }3}M$ (M=Pd, Pt) have been extremely useful in elucidating the mechanism for the cyclic trimerization of acetylenes by zero-valent complexes of the nickel triad. As mentioned previously, the bis and tris(dba) complexes of palladium and platinum react with dimethylacetylene dicarboxylate, dma, either at room termperature (Pt) or on gentle warming (Pd) to give catalytically hexamethyl mellitate.

The first step in this reaction[17,20] is believed to be the replacement of dba by dma to give a monoacetylene complex

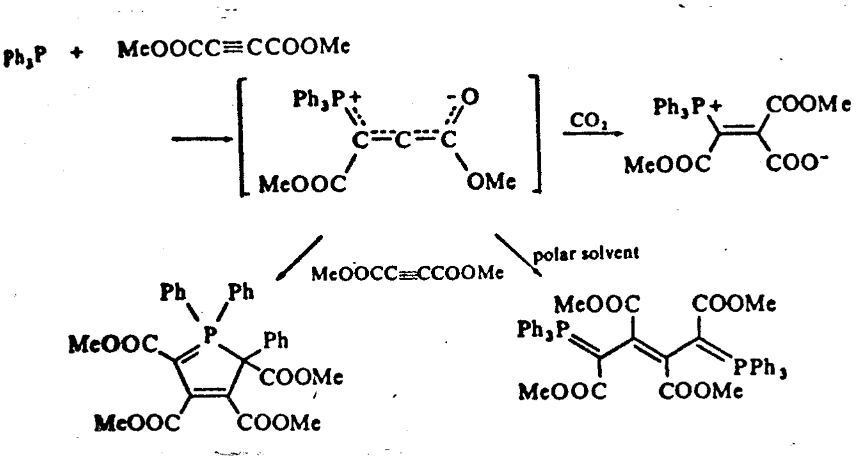


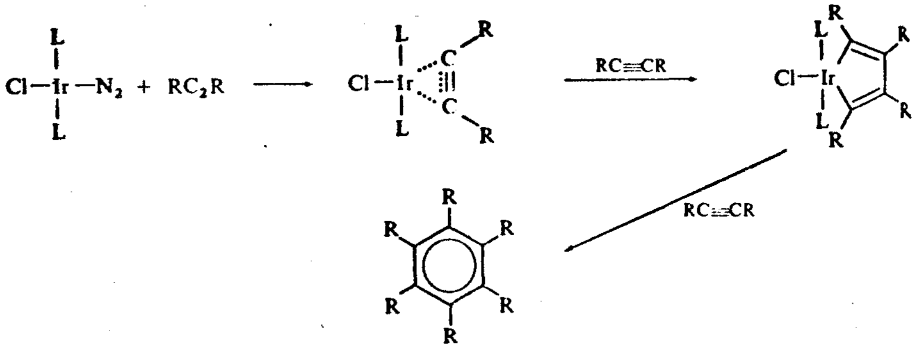
$$(\mathrm{dba})_{2\ \mathrm{or}\ 3}\mathrm{M} + \mathrm{RC{\equiv}CR} \longrightarrow (\mathrm{dba})_n\mathrm{Pd}-\!\!\begin{array}{l}\mathrm{C}-\mathrm{R}\\ \ \vert\vert\vert \\ \mathrm{C}-\mathrm{R}\end{array}$$

M = Pd, Pt

This is supported by the fact that the monoacetylene complexes $L_2Pd(dma)$ ($L=PPh_3$, $P(OPh)_3$) were isolated from the reaction of $(dba)_2Pd$ with the ligand, followed by the addition of dma.[15]

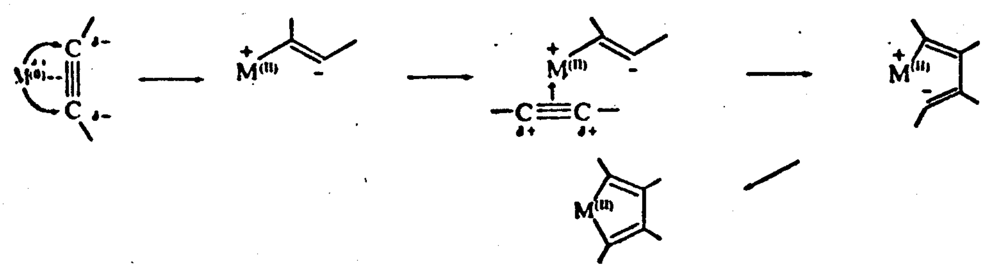
Since dma bears strongly electron-withdrawing groups, it is very susceptible to nucleophilic attack, and dimerization followed by cyclization to give a five membered ring is a very common reaction. For example, Collman et al.[21] prepared rhodia and iridia-cyclopentadiene $M(PPh_3)_2Cl(CCO_2Me)_4$, somewhat analogous to the palladia and platina-cyclopentadienes. Triphenylphosphine will also undergo a similar reaction[22] with dma to give, among other products the phosphole illustrated in the reaction sequence.



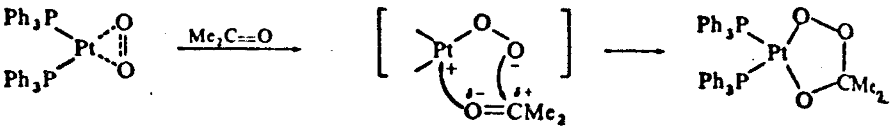


(R = COOMe, L = PPh3)

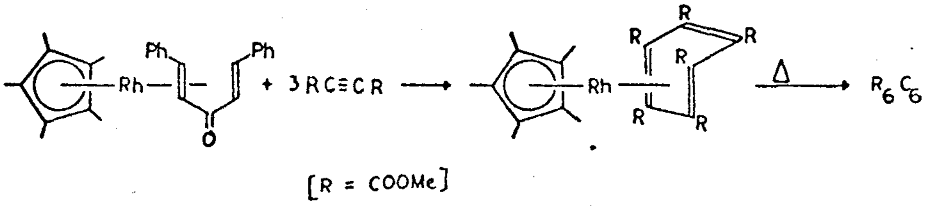
The mono-acetylene complex (PPh3)2Pd(dma) has been reported to react with dma to give the substituted palladiacyclopentadiene, $(PPh_3)_2Pd(CCO_2Me)_4$[19]. If the nucleophilicity of the zero-valent metal complex can be considered to be the driving force of the reaction, then the following mechanism for the second step in the cyclic trimerization of acetylenes can be invoked:



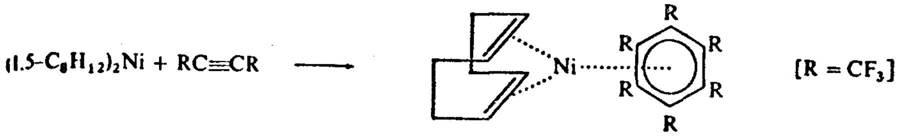
This is analogous to the reaction of $(Ph_3P)_2PtO_2$ with acetone which has also been explained in terms of a dipolar intermediate.[23] Similar mechanisms have also been proposed for the reactions of Fe (O), Ru (O) and Os (O) complexes with fluoro-olefins and fluoro-acetylenes.[24]



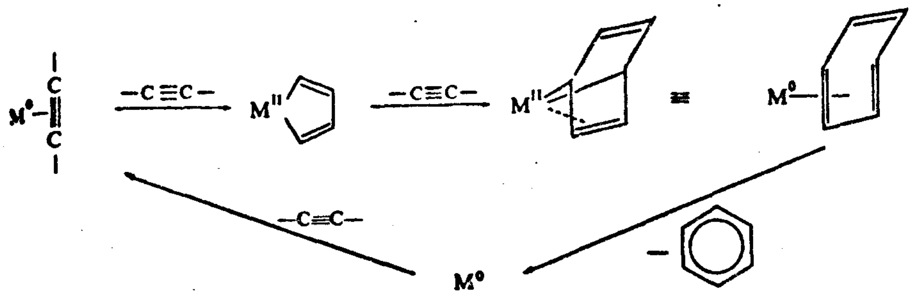
There is no direct evidence for the mechanism of the final step in the cyclic trimerization reaction; however, it is reasonable to expect that it would procede by a π -tetrahaptobenzene ("bent benzene") intermediate. This can be supported by the reaction of $(C_5Me_5)Rh(dba)$ with dma to give a quantitative yield of the tetrahaptobenzene complex.[25,26] On heating, this complex exhibits fluxional behaviour and slowly decomposes to give hexamethyl mellitate.[26]



In addition, Green et al.[27] have reported the isolation of a benzene complex from the reaction of bis(cycloocta-1,5-diene) nickel and hexa-fluorobut-2-yne.



The catalytic cycle for the overall reaction is illustrated below. It gains added significance in view of the catalytic trimerization of dma in a heterogeneous reaction on palladium on charcoal reported by Bryce-Smith.[28]

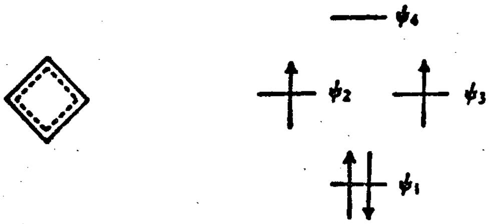


It is believed that the homogeneous and heterogeneous systems proceed via similar mechanisms and the investigation of the homogeneous system has allowed the precise definition of the individual steps in the cyclotrimerization.

2. Cyclobutadiene-Metal Complexes of Nickel, Palladium and Platinum

The cyclobutadiene molecule has intrigued organic chemists for over one hundred years.[29] The instability of this compound is predictable since it does not fulfil the Huckel criterion for aromaticity, 4n + 2 electrons in the valence shell. All attempts to isolate and characterize cyclobutadiene to date have failed, although there is a considerable amount of evidence for its transient existence.

If a square planar geometry is assumed, the ground state of the molecule would be a triplet, as shown in figure 1.

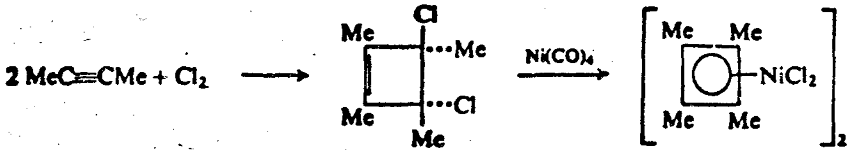


Longuet-Higgins and Orgel[30] noted that the molecular orbitals containing the two non-bonding electrons could readily overlap with two metal orbitals, and predicted that cyclobutadiene would bond strongly to a metal atom. Subsequently, Criegee and Schroder[31] prepared tetramethylcyclobutadienenickel chloride. and Hubel and his co-workers prepared tetraphenylcyclobutadieneiron tricarbonyl. This is one of the few examples in organometallic chemistry of the preparation of a class of compounds based on a theoretical prediction.

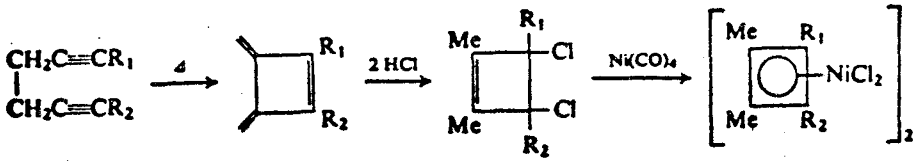
2.1 Preparation:

i) From 3,4-dihalocyclobutenes

The first cyclobutadiene complex was prepared by reacting trans-3,4-dichloro-1,2,3,4-tetramethylcyclobutene and nickel tetracarbonyl to give tetramethylcyclobutadienenickel chloride.[31] This method



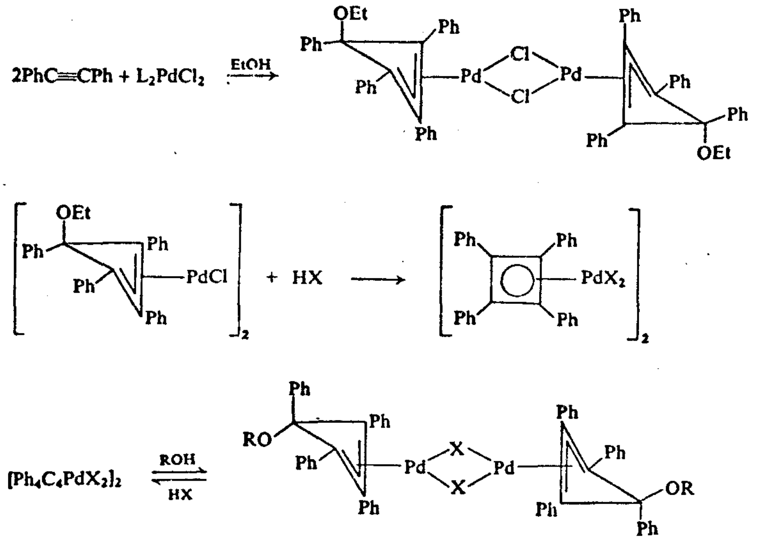
was recently modified[34] to give a nearly quantitative yield of the complex by reacting 3,4-dichloro-tetramethylcyclobutene with a mixture of nickel bromide and sodium naphthalide in THF at low temperatures. The dibromo analog was prepared from nickel tetracarbonyl a diiodotetramethylcyclobutene reacted with Raney nickel to give tetramethylcyclo-butadienenickel iodide.[35] Similar complexes have been prepared from 1,5-hexadiynes.[36,37]



$R_1 = R_2 = H$; $R_1 = H$, $R_2 = Me$; $R_1 = Me$, $R_2 = Et$, Pr^i; $R_1 = R_2 = Et$; $R_1 = H$, $R_2 = Pr^i$

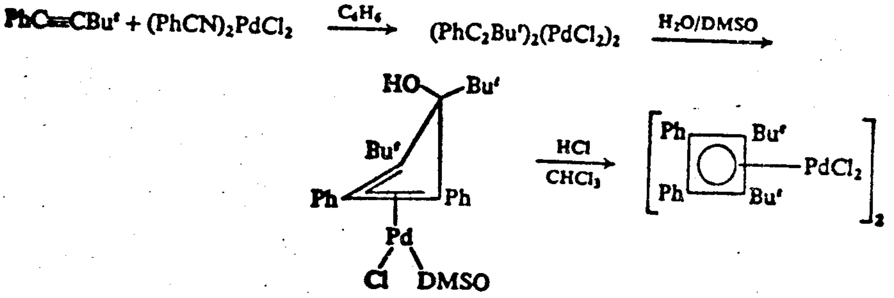
ii) From Acetylenes

The reaction of acetylenes with alcoholic solutions of $(PhCN)_2PdCl_2$, Na_2PdCl_4 and H_2PdCl_4 gave a variety of products depending on the nature of the acetylene and the reaction conditions. Oligomerization and/or cyclotrimerization occurred with acetylenes with no bulky or one bulky substituent. However, diarylacetylenes reacted with $(PhCN)_2PdCl_2$ in ethanol to give the endo-ethoxycyclobutenyl complex[38-43] other alcohols giving analogous complexes.[39]

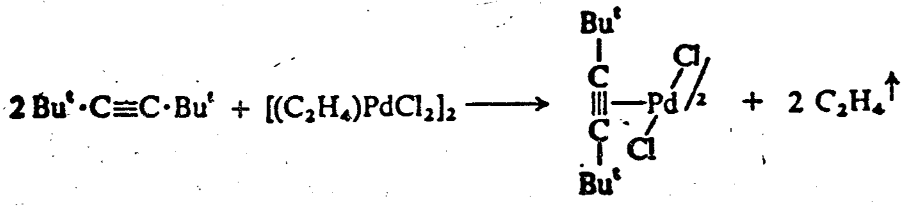


On treatment with hydrogen halides, the alkoxy complex formed tetraphenylcyclobutadiene complexes (X = Cl, Br, I) in high yields. These in turn, reacted reversibly with alcohols to form the exoalkoxycyclobutenylpalladium complexes. Similar reactions were shown to occur with 4,4-ditolylacetylene and bis(4-chlorophenyl)-acetylene.[42]

1,2-di-t-butyl-3,4-diphenylcyclobutadiene palladium chloride has recently been prepared by a similar route.[44] Addition of t-BuC_2Ph

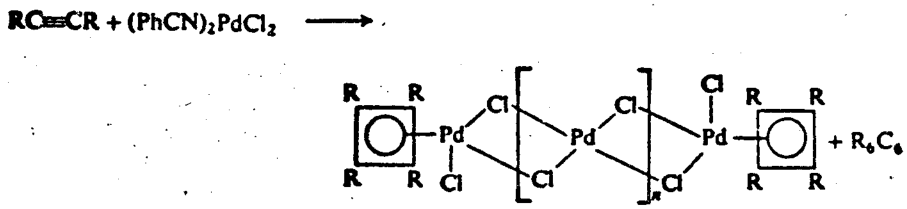


to $(PhCN)_2PdCl_2$ gave the intermediate complex (t-$BuC_2Ph)_2(PdCl_2)_2$ which is assumed to contain a cyclobutadiene group since reduction with $LiAlH_4$ gave 1,2-di-t-butyl-3,4-diphenylcyclobutane. With sterically bulky di-t-butylacetylene, only the stable π -(di-t-butylacetylene) complex was obtained.



$$2\,\mathrm{Bu^t{\cdot}C{\equiv}C{\cdot}Bu^t} + [(\mathrm{C_2H_4})\mathrm{PdCl_2}]_2 \longrightarrow \mathrm{(Bu^tC{\equiv}CBu^t)PdCl_2}/2 + 2\,\mathrm{C_2H_4}\uparrow$$

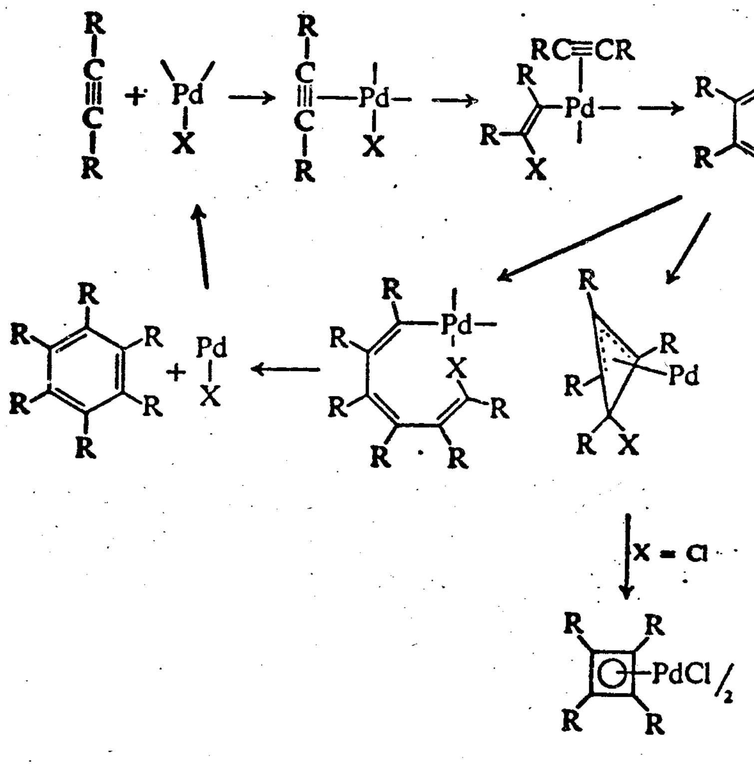
In aprotic solvents, the reaction between diphenylacetylene and $(PhCN)_2PdCl_2$ produced hexaphenylbenzene and a red polmeric cyclobutadiene complex.[43] The structure is not known, but is thought to consist of a chain of $PdCl_2$ units linking the two rings. $Ph_4C_4PdX_2$ can readily



$R = Ph, p\text{-}ClC_6H_4, p\text{-}MeOC_6H_4, p\text{-}MeC_6H_4$

be synthesized by passing HBr through a suspension of the red complex in methylene chloride, or by adding hydrohalic acid to a solution in DMF.

Based on the ^1H n.m.r. spectra, the reaction of acetylenes with palladium (II) complexes is believed to occur by (i) the initial formation of a complex, (ii) cis insertion of the acetylene into the Pd-X bond, (iii) formation of a new complex and (iv) cis insertion of the acetylene into the Pd-C bond. In this mechanism, the final step is very fast and the overall rate will depend to a large extent on steric factors. For small acetylenic substituents, complex formation and cis insertion is repeated indefinitely. With large substituents, the reaction does not proceed beyond the insertion of three acetylenes with a substantial yield of the two-acetylene insertion product. Rearrangement of these products leads to the formation of benzene and/or the cyclobutadiene complex. For electronic or possibly steric reasons, when X = alkoxy or hydroxy and the acetylenic substituents are very large (phenyl) the reaction effectively ceases after two acetylenes have been inserted.



Cyclobutadiene complexes of platinum are much more scarce than those of palladium. In fact, only two have been reported in the literature. Tetraphenylcyclobutadiene platinum dichloride has been prepared by diphenylacetylene with $Pt(CO)_2Cl_2$ in ether. Reaction with

$$Pt(CO)_2Cl_2 + PhC_2Ph \xrightarrow{Et_2O/\Delta} [Ph_4C_4PtCl_2]_n$$

sodium iodide gave the diiodo derivative and the molecular weight showed it to be dimeric.

Recently a cationic tetramethylcyclobutadiene platinum complex was prepared by Chisholm and Clark.[46]

$$\begin{aligned} &MeC_2Me + \\ &\quad \underline{trans}\ [PtCF_3(acetone)(PMe_2Ph)_2]^+PF_6^- \xrightarrow{CH_2Cl_2} \text{acetone} + \\ &\quad \text{acetylene polymer} + [PtCF_3(C_4Me_4)(PMe_2Ph)_2]^+PF_6^- \end{aligned}$$

iii) <u>From other Cyclobutadiene-Metal Complexes by Ligand-Transfer Reactions</u>

The tetraphenylcyclobutadiene ligand can readily be detached from the complex $Ph_4C_4PdX_2$ by reaction with tertiary phosphines.[47] The products from this reaction were octaphenylcyclooctatetraene and bis(t-phosphine) palladium halide. Since the phosphine ligands on $(R_3P)_2NiX_2$ are labile, reaction of this complex with $Ph_4C_4PdCl_2$ resulted in complete exchange of the ligands.[48] This reaction can be used

$$[R_4C_4PdX_2]_2 + 2(Bu_3P)_2NiX_2 \longrightarrow [R_4C_4Nix_2]_2 + 2(Bu_3P)_2PdX_2$$

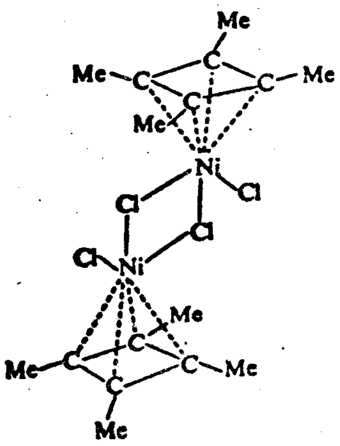
$$R = Ph,\ p\text{-}ClC_6H_4,\ p\text{-}MeC_6H_4,\ \text{and}\ p\text{-}MeOC_6H_4$$

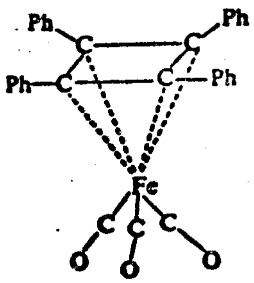
synthetically to prepare tetraphenylcyclobutadienenickel complexes if a phosphine which gives a soluble palladium complex (tri-n-butyl phosphine) is used.

Ligand transfer also occurs between $Ph_4C_4PdX_2$ and a large number of metal carbonyls. ($Co_2(CO)_8$, $Fe(CO)_5$, $Ru_3(CO)_{12}$, $Mo(CO)_6$, $Ni(CO)_4$, etc.).[44-53] In the reaction with nickel carbonyl, two products were obtained[7]; when the reaction was run in refluxing benzene, the major product was tetraphenylcyclopentadienone. At 40°C hardly any of this was formed and the major product was the complex $[Ph_4C_4NiX_2]_2$.

2.2 Properties of Cyclobutadiene-Metal Complexes:

The most detailed x-ray structure determinations were carried out on tetramethylcyclobutadienenickel chloride[55] and tetraphenylcyclobutadieneiron tricarbonyl[55].





In the case of the nickel complex, the molecule exists as a chlorine bridged dimer, with each nickel atom being formally 5-coordinate (assuming that the cyclobutadiene acts as a bidentate ligand). A similar geometry is exhibited by the iron complex. In both cases, the cyclobutadiene ring is square planar with C-C bond lengths of 1.43 Å (Ni) and 1.46 Å (Fe) and the ring substituents are folded back from the plane of the ring. The metal is placed in the four fold axis of the ring and all carbon-metal bond lengths are equal, 2.02 Å for nickel and 2.06 Å for iron. The other three ligands are equally positioned about the four fold axis. In the nickel complex, the solvate benzene molecules are not within bonding distance, but are probably important in determining the state of aggregation of the complex. The molecular weight has been determined in bromoform and corresponds to the formula $[Me_4C_4NiCl_2]$ 10. All of the complexes $R_4C_4MX_2$ where M = Ni, Pd and Pt are associated, making the metals 5-coordinate. Since this is an unusual geometry for palladium, and platinum in particular, cyclobutadiene probably can be viewed as a very small bidentate ligand. No authenticated example of a reaction with a ligand to give the monomeric species $R_4C_4PdX_2L$ has been reported, although several examples are known for the nickel complexes.

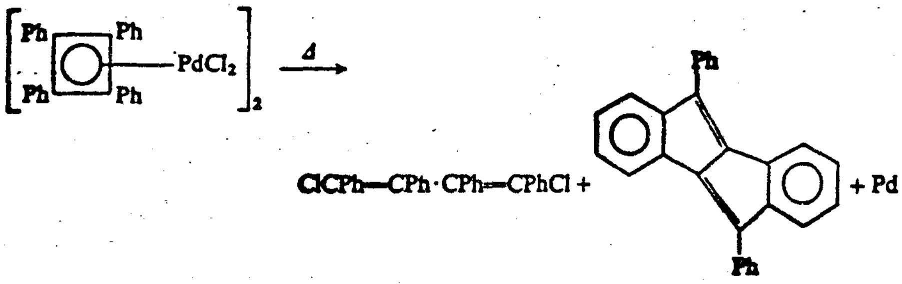
Comparatively little spectroscopic data are available for these complexes. Fritz has measured the i.r. spectra of a number of cyclobutadiene complexes including some of the nickel and palladium complexes. An intense band at 1380 cm^{-1} was observed for these complexes but its origin is not clear. Since all of these complexes were heavily substituted about the C_4 ring, neither i.r. or n.m.r. spectra revealed much structural information.

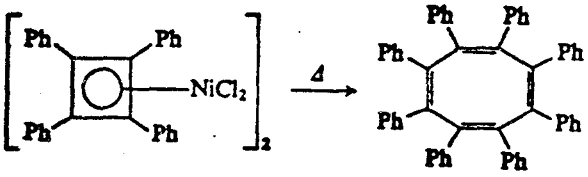
The ^1H n.m.r. spectra of tetramethylcyclobutadiene-and cyclobutadiene complexes exhibited one resonance in solution, indicating the magnetic equivalence of the four groups. This is probably due to rapid rotation about the metal-cyclobutadiene axis.

A peak in the mass spectrum of the pyrolysate of $[Ph_4C_4PdCl_2]_2$ assignable to $Ph_4C_4^+$ has been reported[58]. The formation of this ion could result from either the thermal elimination of the cyclobutadiene or the formation of 1,2-dichloro-1,2,3,4-tetraphenylcyclobutene which undergoes fragmentation in the mass spectrometer to give $Ph_4C_4^+$.

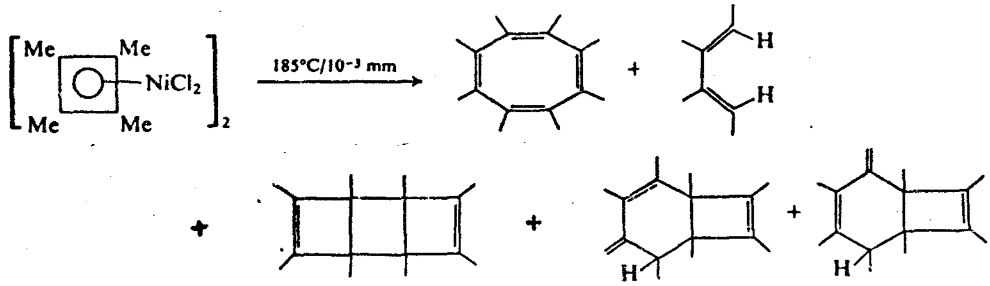
2.3 Reactions of Cyclobutadiene-Metal Complexes:

When $[Ph_4C_4PdCl_2]_2$ was heated above 350°C, two isomers of 1,4-dichlorotetraphenylbutadiene and a small amount of diphenylindenoindene were obtained[40,41]. However, the nickel analog $[Ph_4C_4NiCl_2]_2$ did not lose halogen to the organic ligand and formed octaphenylcyclooctatetraene instead[59-62].



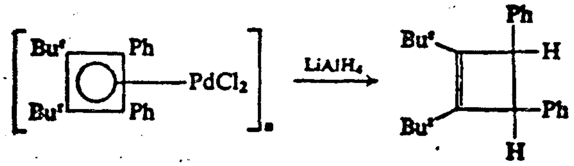


The thermal decomposition of $[Me_4C_4NiCl_2]_2$ gave a wide variety of hydrocarbons, the nature and amount depending on exact conditions[31,35,63]. At 185°C under high vacuum, the main products were the bicyclo (4.2.0.) octadienes. These probably arose from the tricyclo-octadiene as indicated in the reaction scheme.

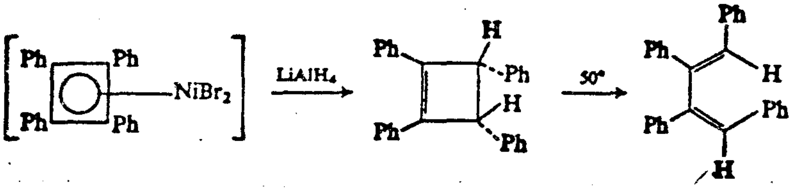


$[Ph_4C_4PdCl_2]_2$ reacted with CO to give 1,2,3,4-tetraphenylcyclopent-2-enone[64]. A similar product was observed in the reaction of $[Ph_4C_4PdCl_2]_2$ with $Ni(CO)_4$[52]. In this case the reaction product was tetraphenylcyclopentadienone.

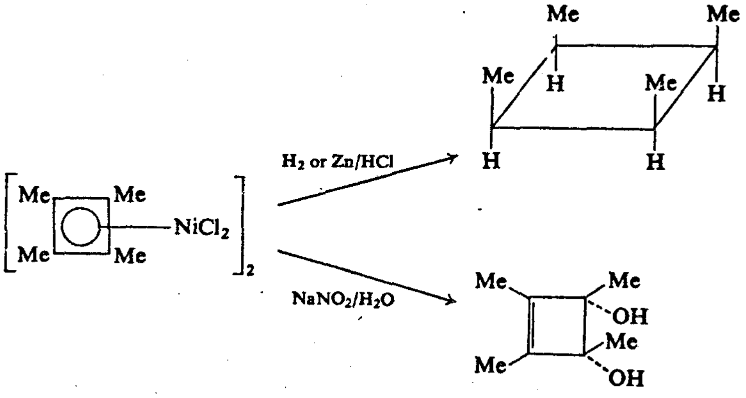
$[Ph_4C_4PdCl_2]_2$ was reduced by $LiAlH_4$ or $NaBH_4$ to give the cis, cis-tetraphenylbutadiene[64-66]. However, the reduction of the complex $Ph_2(Bu^t)_2C_4PdCl_2$ took place without ring opening to give the cyclobutene.



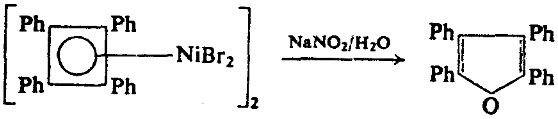
On the other hand, the nickel complex $[Ph_4C_4NiBr_2]_2$ gave the cyclobutene[67] in the same reaction, which isomerized to the cis, trans-tetraphenylbutadiene above 50°C.



On reduction with Zn-HCl or hydrogenation, $[Me_4C_4NiCl_2]_2$ gave the all-cis-tetramethylcyclobutane. Oxidation of the same complex with sodium nitrite gave the cis-3,4-dihydroxyl-1,2,3,4-tetramethylcyclobutene.[35]



However, the tetraphenyl analog, $[Ph_4C_4NiBr_2]_2$, gave tetraphenylfuran in the same reaction[59].



$[Ph_4C_4PdCl_2]_2$ required a more vigorous oxidizer (HNO_3-THF) and gave cis-dibenzoylstilbene as the product[64,65].

The most synthetically useful reactions of the cyclobutadiene-palladium and cyclobutadienenickel halides are the ligand exchange reactions. These reactions are discussed on page 28 .

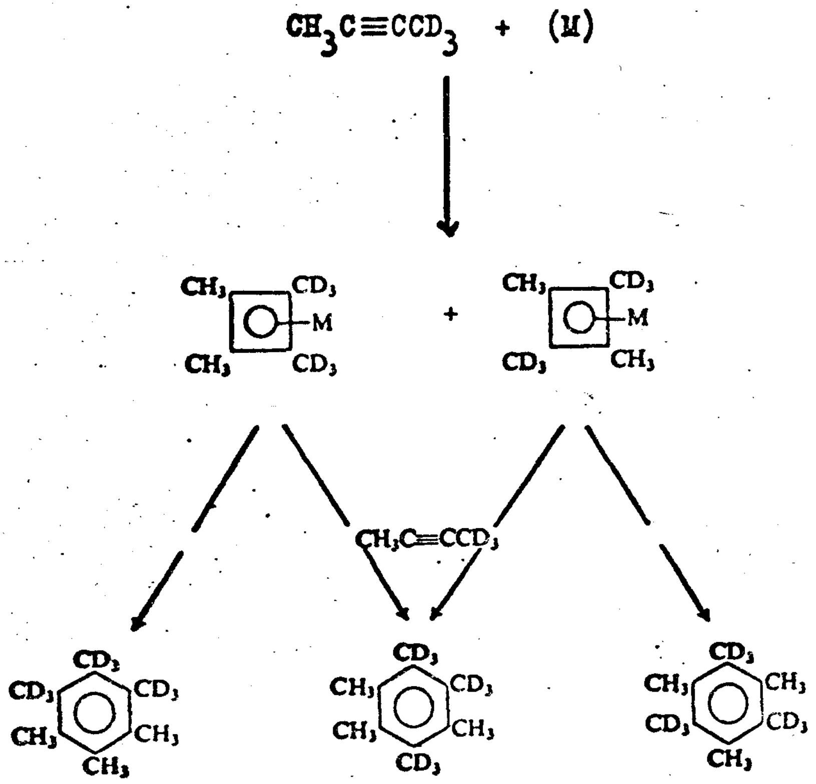
2.4 Cyclobutadiene Complexes as Reaction Intermediates in Cyclotrimerization Reactions

Certain complexes are capable of catalyzing the cyclotrimerization of acetylenes, e.g. $(PhCN)_2PdCl_2$ converted 1-phenylprop-1-yne and but-2-yne into benzene derivatives. Two reaction pathways are well established; they are (a) simultaneous coordination of three molecules of acetylene to the central metal atom, followed by concerted collapse to an arene or a metal-π-arene complex, and (b) formation of metalocyclopentadienes and insertion of the third acetylene molecule[69].

The possibility that the benzene derivative is formed from the reaction of the acetylene with a cyclobutadiene complex has been carefully examined. Blomquist and Maitlis[40] found that although hexaphenyl-benzene and $[Ph_4C_4PdCl_2]_2$ were formed in the reaction of palladium chloride and diphenylacetylene, the cyclobutadiene complex itself did not react with diphenylacetylene to give hexaphenylbenzene. This appeared to be true for most other cyclobutadiene complexes which are rather inert.

Whitesides and Ehmann[70] devised an ingeneous test for the intermediacy of cyclobutadiene-metal complexes in the cyclotrimerization of but-2-yne. They trimerized but-2-yne-1,1,1-d_3 in the presence of triphenyl-tris(tetrahydrofuran)chromium, dimesitylcobalt, dicobalt octacarbonyl, bis(acrylonitrile)nickel, a Ziegler catalyst, bis(benzonitrile)palladium chloride and aluminum chloride. A cyclobutadiene metal intermediate would give a 12.5% yield of 1,2,3-tris (trideuteromethyl)-4,5,6-trimethylbenzene. No established mechanism could explain the presence of this isomer.

None of the above catalysts, except aluminum chloride and $(PhCN)_2PdCl_2$ gave any appreciable amount of this isomer. The aluminum chloride gave exactly 12.5% as predicted, whereas palladium chloride gave 9.5%. However, in both cases there exists the possibility that intermediates which are not cyclobutadienes are present. This method is very useful for establishing the absence of a cyclobutadiene intermediate, but a positive result does not require a mandatory cyclobutadiene.



RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Preparation and Properties of tris(dibenzylideneacetone)palladium and tris(dibenzylideneacetone)platinum

Tris(dibenzylideneacetone)palladium was first prepared by stirring Na_2PdCl_4 and dba (1:4 molar ratio) in 40% aqueous ethanol for two days at room temperature in air. Initially some of the dba remained undissolved and the pale yellow slurry which had formed slowly turned pale brown. This was noticeable after three hours.

The $(dba)_3Pd$ was isolated by filtering off the precipitate and washing it thoroughly with ethanol or methanol until the wash solvent was clear.

The resulting product was virtually insoluble in ethanol. It was slightly soluble in methanol as indicated by the slow appearance of free dba in solution and a darkening of the product (formation of $(dba)_2Pd$). Attempts to dissolve $(dba)_3Pd$ in most other solvents resulted in the loss of one molecule of dba per molecule of complex and the irreversible formation of $(dba)_2Pd$. This occurred instantly in chloroform, methylene chloride, benzene, tetrahydrofuran, diethyl ether and acetone. With diethyl ether and acetone the $(dba)_2Pd$ dropped out as a deep purple precipitate. $(dba)_3Pd$ was slightly soluble and moderately stable in dimethylsulfoxide. When the complex was added to DMSO, a pale brown solution formed, darkened over a period of about thirty minutes, then slowly began to deposit $(dba)_2Pd$. This was complete within two hours. The complex appeared to be more stable in a 50/50 mixture of DMSO and ethanol.

At room temperature, a maximum yield of 75% was obtained after ten days of stirring. The use of a nitrogen, oxygen or argon atmosphere had no effect on the yield, nor did increasing the Na_2PdCl_4/dba ratio to 1:8. The latter attempt only increased the difficulty in removing the excess dba. Similar results were obtained with methanol; however, the product was a darker brown in colour.

The reaction time decreased markedly on increasing the temperature. A 78% yield was obtained on stirring the reaction mixture for two days at 40°C. The application of higher temperatures (even 45°C) resulted in the formation of a dark brown product which was a mixture of the bis and tris complexes.

The synthesis of $(dba)_3Pt$ in 30% yield was first reported by Moseley and Maitlis[11]. This yield was improved by applying the method used to synthesize $(dba)_3Pd$. A yield of 54% was obtained on stirring a 1:4 molar ratio of K_2PtCl_4 and dba in 40% aqueous ethanol for four hours at 40°C. Diethyl ether proved to be the best solvent for washing out the excess dba. $(dba)_3Pt$ was found to be equally soluble with slow decomposition in diethyl ether, ethanol and methanol. The diethyl ether washed out the excess dba more quickly, so less $(dba)_3Pt$ was lost.

$(dba)_2Pd$ was prepared[4] by adding sodium acetate to a hot methanolic solution (60°C) of Na_2PdCl_4 and an excess of dba. The platinum analog, $(dba)_2Pt$, was prepared[11] by a similar route using K_2PtCl_4 and refluxing ethanol. (78.5°C) as the solvent.

$(dba)_3Pd$ was prepared independently by Mazza and Pierpont[12] by heating and taking to dryness a solution of $(dba)_2Pd$ and a four-fold excess of dba. The solution gradually turned from deep red to dark brown and eventually, orange-brown crystals of $(dba)_3Pd \cdot C_6H_6$ were recovered among yellow crystals of dba. The preparation of $(dba)_3Pt$ was similar to those of the bis complexes; however, a refluxing aqueous methanol solution was used in the presence of air or oxygen[11].

The preparation of $(dba)_3Pd$ reported here was somewhat similar to those outlined above, but sodium acetate was not necessary and little or no heat was required for reaction to take place. Also, the presence of air or oxygen had no effect on the reaction.

It has been implied that some type of molecular oxygen complex is involved as an intermediate in the synthesis of $(dba)_3Pt$. A zero-valent platinum complex of molecular oxygen[73], $(PPh_3)_2PtO_2$, has been isolated and reported to be quite stable. Nickel and palladium analogs have also been isolated[72], but are far less stable. Experiments on the optimization of the yield of this complex showed that the synthesis is <u>independent</u> of the atmosphere, that changing from nitrogen to air to oxygen has no effect so an oxygen complex is probably not involved.

Mazza and Pierpont have suggested that a state of equilibrium exists between the bis and tris complexes of palladium and that this equilibrium is involved in the synthesis of $(dba)_3Pd$.

$$(dba)_2Pd + dba \rightleftharpoons (dba)_3Pd$$

At room temperature, the synthesis of $(dba)_3Pd$ appears to be a one-step process without the intermediacy of $(dba)_2Pd$[3]. Indeed, if $(dba)_2Pd$ were formed, it would be expected to drop out of solution since it is completely insoluble in ethanol and methanol. The fact that $(dba)_3Pd$ was observed to rapidly lose one dba molecule at elevated temperatures suggests that these syntheses involve the formation of a tris complex followed by dissociation to $(dba)_2M$ and dba. The increased stability of $(dba)_3Pt$ as compared to $(dba)_3Pd$ can account for the separation of this complex at higher temperatures. The use of aqueous methanol in the synthesis instead of ethanol allows the intermediate complex to precipitate without further reaction.

This state of equilibrium must exist to some degree as indicated by the reported synthesis of $(dba)_3Pd.C_6H_6$; however, this synthesis is probably a result of the relative solubilities of the bis and tris complexes. The $(dba)_3Pd$ could be less soluble in benzene than $(dba)_2Pd$ and the continuous precipitation of the tris complex coupled with the high concentrations involved in taking a solution to dryness would force the equilibrium to the right. The equilibrium must favour $(dba)_2M$ since this complex and free dba can be quantitatively recovered from solutions of $(dba)_3M$.

As mentioned previously, there has been considerable controversy surrounding the nature of the bonding in $(dba)_2Pd$. Moseley and Maitlis[11] suggest that bonding takes place through the oxygen of the carbonyl moiety. This is based on the identification of modified ν (CO) bands in the i.r. spectrum at 1544 cm^{-1} (Pd) and 1527 cm^{-1} (Pt) which represent $\Delta\nu$ (CO) of 112 cm^{-1} and 127 cm^{-1} respectively. These spectra were recorded in chloroform.

The complex precipitated from chloroform or methylene chloride solutions of $(dba)_2Pd$ is the binuclear $Pd_2(dba)_3$.solvent[13]. The crystal structure clearly shows that each Pd atom is bonded to three olefinic groups as does the n.m.r. spectrum. On this basis Ishii et al. suggest that $(dba)_2Pd$ is actually $Pd_2(dba)_3$.dba.

A complex of this type would certainly explain the n.m.r. spectrum reported by Moseley and Maitlis[11], i.e. a spectrum identical to that of free dba. The n.m.r. solutions of $(dba)_2M$ were prepared by stirring an excess of the complex in the solvent, then filtering the saturated solution and recording the spectrum of the filtrate. Displacement of dba of crystallization by the solvent would produce a solution containing a relatively high concentration of free dba as compared to the sparingly soluble $(dba)_2M$. The spectrum of the displaced dba would mask the spectrum of the complex.

Since the spectra supporting the hypothesis of an oxygen bond in $(dba)_2Pd$ were taken in chloroform, the solvent in which $Pd_2(dba)_3$.solvent was crystallized, it is reasonable to assume that the two complexes are one and the same. However there are two points which cloud this assumption. First, although the spectra of the two complexes are similar, the band at 1544 cm^{-1} interpreted as a modified ν (CO) band resulting from bonding through the oxygen, is not reported in the spectrum of $Pd_2(dba)_3$. solvent. Second, Mazza and Pierpont[14] reported that the spectrum of the initial complex was similar to that of Moseley and Maitlis[11] while the spectrum of the crystallization product $Pd_2(dba)_3$.solvent resembled the spectrum first reported by

Ishii et al[4]. for $(dba)_2Pd$. Although the evidence for $(dba)_2Pd$ being an olefin complex is extensive, the actual nature of the complex has not yet been fully resolved.

The i.r. spectrum of $(dba)_3Pd$ shows one ν (CO) absorption at 1645 cm^{-1} and three ν (C=C) absorptions at 1590, 1575 and 1520 cm^{-1} (KBr disc). This varies somewhat from the literature values of 1651, 1598, 1580 and 1531 cm^{-1}; however, the medium in which the spectrum was recorded was not given. The usefulness of this spectrum for structural analysis is diminished by the fact that the strong ν (CO) and aromatic ν (C=C) band mask the region in which the coordinated ν (C=C) would be located.

A strong band at 983 cm^{-1} attributed to ν (CH_{trans}) is observed in this spectrum. This is consistent with coordination of only one olefinic group of the ligand. This band is absent in the spectrum of $Pd_2(dba)_3$ in which every double bond is coordinated to a metal.

The n.m.r. spectrum of $(dba)_3Pd$ could not be recorded as a result of the instability of this complex in solution. However, $(dba)_3Pt$ was sufficiently soluble and stable in d_6-DMSO for the spectrum to be recorded. The most interesting feature of the spectrum is a doublet centred at 5.60 τ (J= 3 Hz). This high field shift of the olefinic resonance is indicative of bonding through the olefin group. The low field portion of the spectrum is identical to that of free dba.

Attempted Preparation of Tris Complexes of Palladium and Platinum Using Para-Substituted dibenzylideneacetone Compounds

Numerous attempts were made to prepare tris complexes, with para-substituted ligands using the preparative method for $(dba)_3Pd$ and $(dba)_3Pt$. The ligands used were bis(para-methoxy)dibenzylideneacetone (para-methoxy dba), bis(para-fluoro)-dibenzylideneacetone (para-fluoro dba), bis(para-dimethylamino)dibenzylideneacetone (para-dimethylamino dba), bis(para-methyl)dibenzylideneacetone (para-methyl dba) and 2,6-dibenzylidenecyclohexanone (dbh). A complex was obtained from the reactions of Na_2PdCl_4 with para-methoxy dba, para-fluoro dba and para-dimethylamino dba but in every case, attempts to separate the complex from the free ligand present resulted in decomposition of the complex and precipitation of metal. The para-substituted complexes appeared to be more soluble than the unsubstituted dba complexes and less stable in solution.

The failure of attempts to isolate these complexes is surprising in view of the bonding involved. Phenyl groups on the dba ligands with electron withdrawing para-substituents would be expected to have some stabilizing influence on the metal-olefin bond and facilitate the synthesis. However, electron withdrawing and electron releasing substituents had no effect, so electronic factors do not appear to play a major role in the bonding. In the cases where complexes were observed to form, the para substituent dictated the solubility of both the free ligand and complex and prevented separation of the two.

In any event, the yield appeared to be very low, and the complexes probably failed to form as a result of steric hindrance of the larger ligands. This was abundantly evident in the case of dbh which structurally is very similar to dba. Since no electronic factors could be involved here, and dbh, dba and metal were recovered from the reaction, the increased size and rigidity of the ligand must have caused decomposition of the dbh complex. The less sterically hindered Pd_2(para-methoxy dba)$_3$ has been synthesized in high yield by the method used to prepare $Pd_2(dba)_3$.

Reactions of Tris(dibenzylideneacetone)palladium and Tris(dibenzylideneacetone) platinum with Triphenylphosphine

A 1:2 molar ratio of $(dba)_3Pd$ and PPh_3 in 95% ethanol produced a clear solution from which red-brown crystals of $(PPh_3)_2Pd(dba)$ were recovered. Attempts to dissolve this complex in other solvents resulted in complete decomposition to the free ligands and metal.

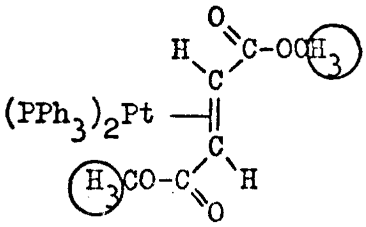
The reaction between $(dba)_3Pt$ and PPh_3 gave a pale yellow precipitate of $(PPh_3)_2Pt(dba)$ which could be filtered off directly. This complex was quite soluble and completely stable in most solvents. The molecular weight was determined in chloroform and found to be 716 as compared to the calculated value of 954. This indicates that considerable dissociation is taking place in solution.

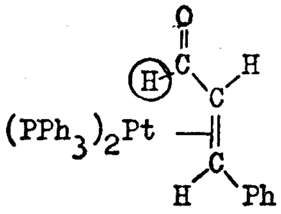
The i.r. spectra of the two complexes are virtually identical indicating that a similar type of bonding occurs in each complex. The most predominent features are a ν (CO) band at 1650 cm^{-1} and two ν (C=C) bands at 1600 and 1575 cm^{-1} (nujoll).

The fact that the ν (CO) absorption remains unchanged on coordination of the ligand clearly indicates that these are metal-olefin complexes. The i.r. spectra of similar zero-valent platinum-olefin complexes show ν (CO) shifts to lower wavenumbers of 40 to 50 cm^{-1} as compared to the free ligands[73]. In complexes where the carbonyl groups participate directly in the bonding with the metal, the shifts are much higher. This characteristic shift can be accounted for by a polarization of the unsaturated electronegative group (-C=O) due to the population of the π * antibonding orbitals of the olefin. The absence of the shift in the ν (CO) of the dba complexes can be attributed to three factors: 1) the weak nature of the metal-olefin bond, 2) the presence of an uncoordinated branch which conjugates with the carbonyl group, and 3) partial loss of conjugation through coordination, a factor which causes a shift to higher wavenumber . This interpretation is supported by the fact that $\Delta\nu$ (CO) in $Pd_2(dba)_3$ is only 30 cm^{-1} although both double bonds of the dba ligand are coordinated to the metal.

The ν (C=C) band at 1600 cm^{-1} can be attributed to the uncoordinated olefin group. In coordinated olefin complexes, there is a shift in ν (C=C) of at least 150 cm^{-1}. This would put the coordinated ν (C=C) band in a region masked by other absorptions.

The ^1H n.m.r. spectrum of $(PPh_3)_2$Ptdba was highly complex. A triplet of doublets centred at 5.90 τ represents a shift to higher field characteristic of the coordination of an olefin group. Coupling is observed between the methine proton and both platinum (J_{Pt-H}=54 Hz) and the trans-phosphorus (J_{P-H}= 5 Hz). Two doublets occur at 2.39 and 4.10 τ as compared to 2.33 and 3.03 τ in the free ligand. In the olefin complex, dimethyl-fumaratebis(triphenylphosphine)platinum, the methyl resonance shifts to higher field by 0.303 ppm and in the cinnamaldehyde analog, the formyl porton shifts by 0.95 ppm[73]. These complexes are shown below and the relevant protons are circled.





On the basis of this information, the two doublets most likely represent the two methine protons of the uncoordinated olefin moiety. The high field shift would arise from interaction between the coordinatively unsaturated platinum and the C_5 proton (farthest from the coordination site).

In an attempt to shed light on the nature of $(PPh_3)_2Pt(dba)$, HCl gas was bubbled through a solution of the complex in $CDCl_3$. When the n.m.r. spectrum was recorded, a weak triplet was observed at 27.27 τ. This is indicative of the formation of the hydrido complex trans-$(PPh_3)_2PtHCl$. The white precipitate which was observed to have formed was isolated and identified as trans-$(PPh_3)_2PtCl_2$ by comparison with an authentic sample. When additional HCl was bubbled through the solution, the hydrido complex reacted to form $(PPh_3)_2PtCl_2$.

A similar reaction has been reported for $(PPh_3)_3Pt$ as outlined below.[74]

$$(PPh_3)_3Pt \overset{HCl}{\underset{KOH}{\rightleftharpoons}} \left[(PPh_3)_3PtH^+\right] Cl^- \overset{-PPh_3}{\underset{+PPh_3}{\rightleftharpoons}} (PPh_3)_2PtHCl$$

The complex which is isolated is dependent on the solvent; polar solvents favour the ionic complex while non-polar solvents favour the covalent complex.

The hydrido complex is formed only when the HCl concentration is low; at high concentrations, only the dichloro complex is observed. The complexes $(PPh_3)_4Ni$ and $(PPh_3)_4Pd$ do not give hydrides in reactions with acids under these conditions, instead the dihalo complexes are isolated and H_2 evolved[74]. The mechanism is believed to be as follows:

$$M(PPh_3)_4 \overset{+PPh_3}{\underset{-PPh_3}{\rightleftharpoons}} M(PPh_3)_3 \overset{+HX,-PPh_3}{\underset{-HX,+PPh_3}{\rightleftharpoons}} (PPh_3)_2MHX$$

$$(PPh_3)_2MHX \overset{+HX}{\underset{-HX}{\rightleftharpoons}} (PPh_3)_2MH_2X_2 \longrightarrow H_2 \quad + \quad (PPh_3)_2MX_2$$

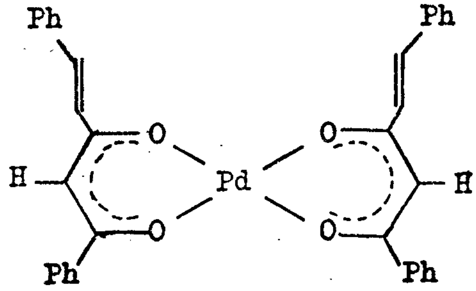
M = Ni, Pd ; X = halide

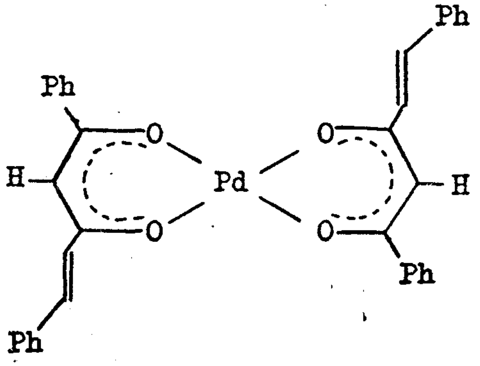
The involvement of both the hydridochloride and dichloro complexes in the same reaction indicates that the platinum system probably goes through the same mechanism.

Synthesis of bis(1,5-diphenyl-1-penten-3,5-dione)palladium, $(C_{17}H_{13}O_2)_2Pd$

The reaction between $(dba)_3Pd$ and dma in ethanol formed a number of products. A yellow precipitate with the formula $C_{34}H_{26}O_4Pd$ was filtered off. When the ethanol solvent was removed and the residue washed with diethyl ether, a red-brown precipitate of tetramethyl palladiacyclopentadiene-tetracarboxylate was removed. The diethyl ether washings were found to contain dba, dma and hexamethyl mellitate.

The yellow precipitate was treated with HCl gas to displace the ligand. The organic product of this reaction was identified as 1,5-diphenyl-1-penten-3,5-dione by n.m.r., i.r. and mixed melting point comparison with an authentic sample. The yellow complex was identified from the n.m.r. spectrum as the β-diketone complex, bis(1,5-diphenyl-1-penten-3,5-dione)-palladium (II). The cis and trans isomers shown below were present in a 50/50 mixture.





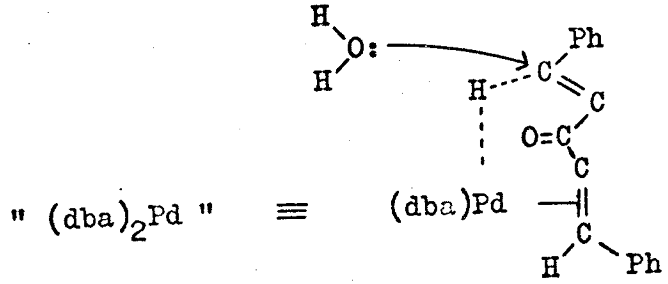
The β -diketone complex represented 10-25% of the palladium, the remainder accounted for by the palladiacyclopentadiene complex. Varying the temperature, molar ratio and nature of the solvent had little or no effect on this yield. A yield of 25% was obtained from 75% aqueous ethanol while a yield of 10% was obtained from freshly prepared absolute ethanol.

The β -diketone complex was not a product of the reaction between $(dba)_2Pd$ and dma. Under the same reaction conditions, a 95% yield of the palladiacyclopentadiene complex was obtained together with dba, dma and hexamethyl mellitate.

The β -diketone complex was obtained in reactions with other organic reagents. A 20% yield of the complex was obtained from the reactions of $(dba)_3Pd$ in ethanol with 1,2-dichloro-1,2,3,4-tetramethylcyclobutene, hexafluoro-but-2-yne and tetracyanoethylene.

The reaction with dichlorotetramethylcyclobutene produced only $(C_{17}H_{13}O_2)_2Pd$, free dba, palladium metal and unreacted cyclobutene. The additional products from the reaction with hexafluorobut-2-yne proved to be highly unstable and decomposed before spectroscopic analysis could be performed. The reaction with tetracyanoethylene produced a red-brown precipitate in high yield, but this proved to be only slightly soluble in all solvents including DMSO and all attempts at identification were unsuccessful.

The presence of $(C_{17}H_{13}O_2)_2Pd$ is somewhat of a mystery, particularly in view of the fact that it appears as a product of a variety of reactions. The presence of a 50/50 mixture of the two isomers indicates that there is no stereochemical or electronic preference for any one mode of attack on the dba ligand. Since the complex occurs as a minor component in the reactions, and does not form in the absence of an olefin or acetylene, synthesis probably takes place after the displacement or dissociation of one dba ligand. The analysis of the n.m.r. spectrum of $(PPh_3)_2Ptdba$ indicates that the terminal proton is activated through interaction with the metal. This weakening of the C-H bond would produce an excellent site for attack by H_2O to produce the enol and H_2. This is indicated in the following diagram.



Subsequent tautomerization and oxidative addition would produce the observed complex.

As mentioned above, the ligand was displaced on reaction with HCl and characterized by comparison with an authentic sample. The reports on this compound in the literature all give the structure as the β -diketone tautomer. However, the n.m.r. spectrum clearly shows a hydroxyl proton resonance at 3.93 τ indicating that the complex prefers the enol form. This is reasonable in view of the extended conjugation exhibited by this tautomer.

Reaction of $(dba)_3Pd$ with other acetylenes

Various attempts were made to prepare an acetylene or palladiacyclopentadiene complex from diphenyl acetylene, 2-butyne and 2-butyne-1,4-diol. The reactions were performed in 95% ethanol at 60°C and in each case, only $(dba)_2Pd$, dba and unreacted acetylene were recovered. The loss of the dba molecule was probably a result of thermal decomposition since the tris complex had previously proved to be unstable at this temperature.

Reactions of $(dba)_2Pd$ and $(dba)_2Pt$

1) Oxidative addition

Oxidative addition reactions represent one of the most interesting and important features of zero-valent nickel, palladium and platinum chemistry. In recent years, a large number of oxidative addition reactions have been reported, particularly with phosphine complexes of platinum. This work has been extensively reviewed[3].

An attempt was made to synthesize a number of oxidative addition products from both $(dba)_2Pd$ and $(dba)_2Pt$. At room temperature, no reaction was observed between $(dba)_2Pt$ and methallyl chloride, benzyl chloride, benzal chloride, benzonitrile and methyl iodide. At elevated temperatures (60°C) decomposition took place.

These experiments were repeated with $(dba)_2Pd$ where the same results were observed, with the exception of methallyl chloride. In this case, the π-methallylpalladium chloride dimer formed as had previously been reported by Ishii et al.

These reagents were selected for the ease with which they oxidatively add to analogous phosphine complexes[3]. The expected product from many of these reactions with X-Y would be trans-$(dba)_2MXY$. Since oxidative addition reactions require ligands which are good σ donors, the two olefinic ligands of the (dba)-Pd (II) complex would not impart sufficient stability for reaction to take place.

Some reagents have been reported to oxidatively add to these complexes, e.g. methallyl chloride, 1-chloro-5-phenyl-2,4-pentadiene and 1-chloro-4-methyl-5-phenyl-2,4-pentadiene. In each case, dimeric π-allyl complexes are formed in which dba has been completely displaced as is seen on page 16 of the introduction. Also, the divalent ortho-quinone complexes require prior displacement of dba by better coordinating ligands such as o-phenanthroline, bipyridyl and triphenylphosphine.

2) Reaction with acetylenes

By reacting $(dba)_2Pd$ with an acetylene with two different electron withdrawing groups, it was believed that a number of isomers of a palladiacyclopentadiene complex could be prepared and isolated. However, the reaction did not go to completion in benzene at room temperature and the product was a dark brown tar from which only dba could be extracted. Changes in solvent and temperature produced only the tar, so the investigation was abandoned.

There have been a number of reports in the literature recently on the reactions of fluoro-olefins and fluoro-acetylenes with zero-valent complexes of palladium and platinum[75]. Consequently, the reactions between hexafluorobut-2-yne and $(dba)_2Pd$ and $(dba)_2Pt$ were studied in some detail. With the palladium complex, the deep purple solution turned pale yellow and contained a fine suspension of metal. The ^{19}F n.m.r. spectrum of the products in solution was extremely complex and contained no information concerning the structures of the compounds. A series of these spectra were recorded at temperatures ranging from room temperature to -90°C and no evidence of fluxional behaviour was observed. In each case, the pale yellow solution of the residue (in chloroform or methylene chloride) slowly turned red and began to deposit a black precipitate. This decomposition accounts for the difficulty experienced in trying to record a meaningful n.m.r. spectrum. It also explains the lack of success in obtaining a pure product by either crystallization or column chromatography.

These experiments were repeated with $(dba)_2Pt$, and in each case, the only reaction observed was the decomposition of the complex to dba and the metal.

Several reactions between $(dba)_2Pd$ and various acetylenes were attempted without solvent. The compounds used were diphenylacetylene, dimethylacetylene and 2-butyne-1,4-diol. No useful product was obtained in any of these reactions.

The palladiacyclopentadiene complex is reported to form from the reaction of $(dba)_2Pd$ and dma because the electron withdrawing carbomethoxy groups stabilize the intermediate palladium-acetylene complex. If this were the only factor involved, then methyl phenylpropiolate would be expected to react as well. The fact that no product was obtained from this reaction can be understood by examining the bonding in $[PdC_4(COOMe)_4]_{3 \text{ or } 4}$ as seen on page 12. This complex is stable because it forms a trimer through bonding of the Pd atoms to the carbonyl groups of the ester functions. When even one of these carbonyl groups is missing, trimerization is prevented and the complex either will not form or is not sufficiently stable for isolation. This can partly explain the lack of success with other acetylenes as well.

The reactions with hexafluoro-2-butyne gave a complex product which proved to be highly unstable in solution. This is not the case with triphenylphosphine complexes from which $(PPh_3)_2PtC_2(CF_3)_2$ is readily formed. Reaction of $(PEt_3)_2Pt\,C_2(CF_3)_2$ with excess hexafluoro-2-butyne proceeds slowly to give a monophosphine substituted platinacycloheptatriene complex $(PEt_3)PtC_6(CF_3)_6$. In each case, a phosphine ligand is present to stabilize the complex. No such system for stabilization is available with the dba complexes, consequently any complexes which form will rapidly decompose.

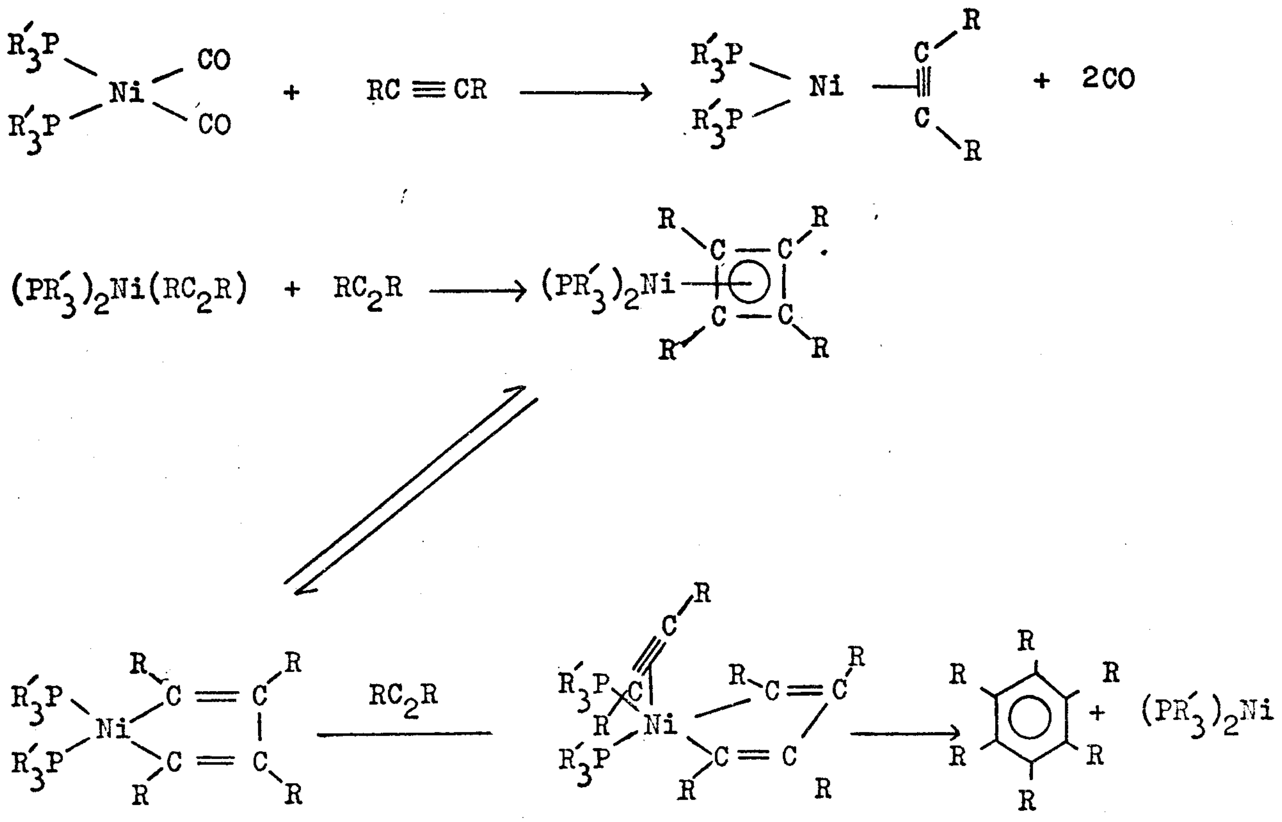
Reaction of Nickel (O) complexes with dimethylacetylenedicarboxylate

Zero-valent carbonyl and phosphine complexes of nickel have also been reported to catalytically cyclotrimerize acetylenes[76]. In an effort to isolate an intermediate complex in the cyclotrimerization reaction, nickel tetracarbonyl and dma were stirred for two hours in benzene and the products identified. After passing nitrogen through the reaction mixture for one hour to remove any nickel tetracarbonyl, the only product remaining was hexamethyl mellitate.

The reaction was repeated in chloroform, using dicarbonylbis(triphenylphosphine) nickel; aliquots were drawn from the reaction mixture at intervals and the i.r. spectra recorded. In the initial mixture, three ν (CO) peaks at 2070, 2005 and 1945 cm^{-1} from the nickel complex and one ν (CO) peak at 1725 cm^{-1} from the dma were observed. After ten minutes, two new peaks appeared at 2045 and 1610 cm^{-1}. Over the next hour, the new peaks increased in intensity while the peak at 1940 cm^{-1} rapidly decreased and finally disappeared. As the reaction progressed, the peaks at 2070, 2045 and 2005 cm^{-1} also decreased and disappeared while the peak at 1610 cm^{-1} continued to grow. After twenty-four hours, only the peaks at 1725 and 1610 cm^{-1} remained of those initially observed. Both of these peaks were attributed to hexamethyl mellitate by comparison with an authentic sample. Unsuccessful attempts were made to isolate the complex responsible for the peak at 2045 cm^{-1} by stripping off the solvent and by passing the reaction mixture through a florisil column. Analogous results were observed with dicarbonyl-bis(triphenylphosphine)nickel.

The bands at 2005 and 1945 cm^{-1} are identical to those reported in the literature for $(PPh3)_2Ni(CO)_2$. The weak band at 2070 cm^{-1} is assigned to the complex $(PPh_3)Ni(CO)_3$ which is present as an impurity. It is interesting to note that during the first hour of the reaction with dma, the bands from $(PPh_3)_2Ni(CO)_2$ rapidly decrease in intensity while the band from $(PPh_3)Ni(CO)_3$ remains relatively constant. This is in complete agreement with previous reports on these two complexes. Since π -back donation to the acetylene is an important feature of the bonding in these reactions, then PPh_3, a stronger σ -donor and weaker π -acceptor than CO would be expected to increase the rate of reaction.

The rapid appearance and slow disappearance of the band at 2045 cm^{-1} indicates that the formation of a transient carbonyl complex is an integral part of the reaction sequence. This contradicts the accepted mechanism for this reaction in which the first step is the formation of a bis(triphenylphosphine)nickel-acetylene complex by displacement of the two CO ligands.

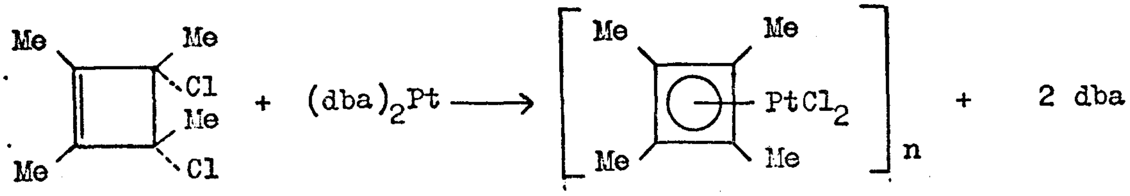


Previous investigations of similar systems involved the application of refluxing solvents (cyclohexane, acetonitrile, etc.) and quenched samples were used for i.r. analysis. The instability of the complex and the high temperatures employed accounts for the fact that the complex had not previously been observed.

When the reaction was repeated with $(PPh_3)Ni(CO)_3$ a transient ν (CO) band at 2045 cm^{-1} was observed. This suggests that the intermediate complex involved in the reaction is the same in both cases. The nature of this complex is as yet unknown.

Preparation of tetramethylcyclobutadieneplatinum dichloride

This complex was prepared by heating a homogeneous blend of $(dba)_2Pt$ and 1,2-dichloro-1,2,3,4,-tetramethylcyclobutene at 80°C for fifteen minutes. This gave a tar from which the complex, $C_4Me_4PtCl_2$ was laboriously extracted in 11% yield.



This yield was not improved by changes in the temperature, molar ratio of the reactants or the atmosphere (nitrogen, oxygen or argon). This corresponded to about 0.060 g of $C_4Me_4PtCl_2$ when 1.0 g of $(dba)_2Pt$ was used. When the reaction was scaled up to 10.0 g of $(dba)_2Pt$, the same quantity of $C_4Me_4PtCl_2$, 0.060 g, was obtained.

Initial attempts to synthesize this complex involved the use of solvents. The solvents applied were chloroform, methylene chloride, methanol, acetone, benzene, tetrahydrofuran, diethyl ether, dimethylsulfoxide and dimethylformamide. In most cases, a tar was obtained from which no useful product could be extracted.

Attempted preparation of tetramethylcyclobutadienepalladium dichloride

Numerous attempts were made to synthesize this complex from $(dba)_2Pd$ and $C_4Me_4Cl_2$. In almost every case, only palladium metal, dba and $C_4Me_4Cl_2$ were recovered. Increasing the temperature or the molar ratio of the two reactants increased the rate at which the metal was deposited. The reaction in dimethylformamide gave a tar from which no useful product could be extracted. The reaction in methanol gave a yellow-green precipitate after fifteen minutes, which proved to be sparingly soluble in most common organic solvents. The ^1H n.m.r. spectrum of this complex showed that it was not a cyclobutadiene complex, so further attempts at characterization were abandoned.

Success in preparing $C_4Me_4PtCl_2$ from a $(dba)_2Pd/C_4Me_4Cl_2$ melt prompted a similar investigation with the palladium system. The black tar which formed in this case was washed with diethyl ether, dissolved in methylene chloride and treated with activated charcoal to give a clear, blue-green solution. The complex in solution proved to be highly unstable and decomposed within minutes. When the solvent was removed, the residue was unstable as well and quickly decomposed. Reactions with $C_4Me_4Br_2$ were also unsuccessful.

The molecular weight was determined in chloroform and found to be 1393 as compared to the formula weight of 555. This tendency for association in solution is shared by the nickel analog of this complex which exhibits a state of aggregation in bromoform of $[C_4Me_4NiCl_2]_{10}$.

The n.m.r. spectrum shows a triplet at 8.37τ in a ratio of 1:4:1. This consists of a single methyl resonance and a doublet due to coupling to ^{195}Pt (natural abundance, 34%; $J_{Pt-H} = 19$ Hz). The magentic equivalence of the methyl protons can be attributed to rapid rotation of the cyclobutadiene ring.

The i.r. spectrum is relatively simple. A number of the bands are very similar to those observed[77] in $C_4Me_4NiCl_2$ as indicated below.

$C_4Me_4NiCl_2$	$C_4Me_4PtCl_2$	Assignment
1541 s	1540 m	ring C-C stretch
1440 ss	1440 s	assym. $C-CH_3$ deformation
1388 w sh	1385 w	sym. $C-CH_3$ deformation
1355 m	1365 w	sym. $C-CH_3$ stretch
1067 s	1078 m	CH_3 rocking
998 ss	1009 s br	$C-CH_3$ stretch
617 m	610 w	$C-CH_3$ stretch
467 m	450 w	metal-ligand deformation

A number of these bands were reported[46] for the spectrum of the cationic complex, $\left[PtCF_3(C_4Me_4)(PMe_2Ph)_2\right]^+ PF_6^-$, i.e. 1540, 1445, 1360, 1070 and 1000 cm^{-1}. These bands are characteristic of a cyclobutadiene complex. The major difference between the spectra of the nickel and platinum analogs is the presence of a strong band in the spectrum of the platinum complex at 1490 cm^{-1}. The nature of this band is unknown.

$C_4Me_4PtCl_2$ is quite stable in the solid state and in solution once it has been isolated (decomposition range 221.5-227.5 °C). Presumably the palladium analog will be equally stable. Unfortunately, the dba complexes do not appear to be the ideal starting materials for the synthesis of this compound.

CONCLUSION

CONCLUSION

The dibenzylideneacetone complexes of palladium and platinum are excellent precursors for other zero-valent complexes via substitution reactions; however, the chemistry of these complexes is somewhat limited due to a tendency to decompose in reactions involving oxidation of the metal.

Bonding in $(dba)_3M$ and $(PPh_3)_2M(dba)$ (M = Pd, Pt) takes place through the olefin moiety of the dba ligand. The n.m.r. spectrum of $(PPh_3)_2Pt(dba)$ shows that there is also interaction between the C5 proton of the uncoordinated olefin and the metal. Attempts to prepare para-substituted dibenzylideneacetone complexes were unsuccessful due to the increased steric hindrance of the larger ligands.

The β -diketone complex $(C_{17}H_{13}O_2)_2Pd$ probably forms through reaction of the activated "$(dba)_2Pd$" and water in the solvent. The weakening of the C-H bond through interaction with the central metal atom (as with $(PPh_3)_2Pt(dba)$) would provide the impetus for the reaction.

The isolation of the metalacyclopentadiene complex $\left[PdC_4(COOMe)_4\right]_n$ is possible since stabilization is achieved by trimerization through the carbonyl groups of the ester functions. Acetylenes without these carbonyl groups did not form complexes sufficiently stable for isolation.

$(PPh_3)_2Ni(CO)_2$ reacts with dimethyl acetylenedicarboxylate to produce a transient intermediate which is sufficiently stable to be observed spectroscopically. Other than the observation that the complex contains a carbonyl group, the nature of the complex is unknown.

$(dba)_2Pt$ was used to prepare $C_4Me_4PtCl_2$ in low yield. Once formed the complex was highly stable. Attempts to prepare the palladium analog were unsuccessful.

EXPERIMENTAL

EXPERIMENTAL

Experimental Procedures

Melting points

These were determined using a Thomas Hoover capilliary melting point apparatus and are uncorrected.

Molecular weight measurements

These were made by Galbraith Laboratories Inc., Knoxville, Tennessee, U.S.A.

Infrared spectra

Most i.r. spectra were recorded using either a Beckman IR-5 or Perkin-Elmer 337 spectrophotometer. The compounds were made up as potassium bromide discs or as nujollmulls between potassium bromide plates. The spectra taken during the reactions involving the nickel complexes were all solution spectra using either chloroform or methylene chloride.

A number of spectra were also recorded on a Perkin-Elmer 521 grating infrared spectophotometer.

Nuclear magnetic resonance spectra

Proton magnetic resonance spectra were recorded on either a Varian A60 or T60 60 Mc sec^{-1} spectrometer or a Varian HA 100 100 Mc sec^{-1} spectrometer. Tetramethylsilane was used as an internal standard in all cases.

Fluorine magnetic resonance spectra were recorded on a Varian DP60 56.4 Mc sec^{-1} spectrometer.

In these spectra, trichlorofluoromethane was used as the internal standard.

Analyses

Analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, and by Gygli Laboratories, Toronto, Ontario.

Reagents

Reagent grade solvents were used at all times and were saturated with nitrogen before use, unless otherwise indicated. Benzene, chloroform, methylene chloride, diethyl ether and tetrahydrofuran were dried over calcium hydride before use. Acetone, t-butanol, methanol, 95% ethanol, absolute ethanol, dimethylformamide and dimethylsulfoxide were used as received. 100% ethanol was prepared according to the method outlined in the literature [78]

Experimental techniques

Most reactions were carried out in 100 ml. three neck round bottom flasks through which a stream of dry nitrogen was continuously passed. A reflux condenser was attached when volatile solvents were used. Solutions were stirred magnetically using $\frac{1}{2}$ inch teflon-coated stirring bars. Most solid products were separated by filtration through Hirsch funnels (65 mm., fine porosity). Liquid reagents were introduced and removed with a hypodermic syringe.

In the case of the phosphine complexes, the reaction, filtration, washing and drying were carried out in a closed system in a continuous stream of dry nitrogen.

The reactions involving hexafluoro-2-butyne were carried out in 125 ml. wash bottles. An apparatus was set up which allowed the collection and re-use of the unreacted hexafluoro-2-butyne.

Preparation of starting materials

Bis(dibenzylideneacetane)palladium(O)[4], bis(dibenzylideneacetone)platinum(O)[11], carbonyltris(triphenylphosphine)nickel(O)[79], dicarbonylbis(triphenylphosphine) nickel(O)[79], dichlorotetramethylcyclobutene[80], and 1,5 diphenyl-1-penten-3,5-dione[81] were prepared according to the methods outlined in the literature.

Preparation and properties of tris(dibenzylideneacetone)palladium and tris(dibenzylideneacetone)platinum

1) $(dba)_3Pd$

Na_2PdCl_4 (0.294 g , 0.001 mole) dissolved in 40 ml. of water was added to a solution of dba (0.936 g , 0.004 mole) in 60 ml. of absolute ethanol. The mixture was stirred at room temperature for two days. The resulting pale brown slurry was filtered and the precipitate washed with 50 ml. of ethanol. This removed all of the excess dba present. It was observed that washing with diethyl ether removed the dba more quickly; however, the precipitate turned dark brown in the process, indicating that some decomposition had occurred. The product was air dried to give the pale brown $(dba)_3Pd$ (0.162 gm., 20% yield). The analysis is as follows: calculated, C, 75.73; H, 5.19; found, C, 75.14; H, 5.36. The melting point was found to be 151°C (dec.).

Additional experimentation on optimizing the yield revealed that a 75% yield could be obtained by stirring the mixture for ten days. A 78% yield was obtained by stirring the reaction mixture for two days at 40°C; however, higher temperatures produced a dark brown product and it was evident that some decomposition had again taken place.

$(dba)_3Pd$ was found to be virtually insoluble in ethanol and methanol. The complex was stable in ethanol, but slowly decomposed in methanol to give a solution of dba and a black precipitate which was identified as $(dba)_2Pd$. Attempts to dissolve the complex in most other common solvents resulted in the immediate loss of one mole of dba and the irreversible formation of $(dba)_2Pd$. This was observed to occur in benzene, chloroform, methylene chloride, acetone, tetrahydrofuran and diethyl ether.

The only solvent in which $(dba)_3Pd$ dissolved without immediate decomposition was dimethylsulfoxide. In this case, a pale brown solution formed which gradually darkened over thirty minutes and began to deposit $(dba)_2Pd$. The decomposition was complete after two hours. $(dba)_3Pd$ was far more stable in a 1:1 solution of DMSO:ethanol. A solution in this solvent remained clear for one hour without any signs of decomposition.

2) $(dba)_3Pt$

$(dba)_3Pt$ was first prepared by K. Moseley in a 30% yield by combining K_2PtCl_4, dba and an excess of sodium acetate in refluxing methanol. Various optimization experiments were carried out and it was found that the complex can be prepared in 54% yield by the following procedure: K_2PtCl_4 (1.00 g , 0.00241 mole) dissolved in 40 ml. of water was added to a solution of dba (4.00 g , 0.0171 mole) and sodium acetate (2.5 g) in 180 ml. of absolute ethanol and the mixture stirred at 40°C for twelve hours. After cooling, filtering and washing with 100 ml. of diethyl ether a dark yellow precipitate of $(dba)_3Pt$ (1.17 g , 54% yield) was collected. It should be noted that diethyl ether is the best wash solvent in this case since $(dba)_3Pt$ is equally soluble with decomposition in diethyl ether, ethanol and methanol. Diethyl ether washed out the excess dba more quickly, so less product was lost.

Attempted preparation of tris complexes of platinum and palladium using para substituted dibenzylideneacetone compounds

Attempted preparation of palladium complexes

1) Bis(para-methoxy)dibenzylideneacetone (para-methoxy dba)

Na_2PdCl_4 (0.294 g , 0.001 mole) dissolved in 40 ml. of water was added to a solution containing para-methoxy dba (0.588 g , 0.002 mole) in 60 ml. of absolute ethanol. After stirring for five days at room temperature in air, the slurry had changed colour from yellow to green. The precipitate was filtered off and attempts were made to separate the complex believed to have formed, from the excess ligand. It was found that the complex and ligand were equally soluble in all solvents used. In solvents such as diethyl ether and methylene chloride, the precipitate dissolved completely giving a purple solution which quickly turned yellow and deposited a black precipitate. The black precipitate was identified as palladium metal.

2) Bis(para-fluoro)dibenzylideneacetone (para-fluoro dba)

Na_2PdCl_4 (0.294 g , 0.001 mole) dissolved in 40 ml. of water was added to a solution of para-fluoro dba (1.080 g , 0.004 mole) in 60 ml. of absolute ethanol. On stirring for five days, the mixture changed from yellow to brown and was filtered to give a brown precipitate and amber filtrate. Attempts to separate the excess ligand from the complex presumed to have formed by washing with ethanol, methanol, diethyl ether, etc. were unsuccessful due to the similar solubility characteristics of the two.

On standing, brown crystals were observed to have formed on the bottom of the flask containing the filtrate. Since the crystals contained black occlusions, attempts were made to obtain a pure product by recrystallization. However, in all solvents, the brown crystals dissolved to form a deep purple solution momentarily, then decomposed to form palladium metal and a solution of the ligand.

3) 2,6-dibenzylidenecyclohexanone (dbh)

Na_2PdCl_4 (0.294 g 0.001 mole) dissolved in 40 ml. of water was added to a solution of dbh (1.096 g , 0.004 mole) in 60 ml. of absolute ethanol. The mixture was stirred for five days and gradually changed colour from yellow to green, after which it was filtered and washed with ethanol.

The black precipitate which remained was identified as palladium metal.

4) Bis(para-dimethylamino)dibenzylideneacetone (para-dimethylamino dba)

Na_2PdCl_4 (0.294 g , 0.001 mole) dissolved in 40 ml. of water was added to a solution of para-dimethylamino dba (1.176 g , 0.004 mole) in 60 ml. of absolute ethanol. The mixture was stirred for five days and gradually changed colour from orange-red to dark brown. Filtration, and washing left a black precipitate which was identified as palladium metal.

Attempted preparation of platinum complexes

The experiments described in the above section were repeated using solutions of K_2PtCl_4 and were all unsuccessful. In each case, no apparent reaction had taken place.

An attempt was also made to prepare a platinum complex from bis(para-methyl) dibenzylideneacetone (para-methyl dba). K_2PtCl_4 (0.208 g , 0.0005 mole) dissolved in 20 ml. of water was added to a solution of para-methyl dba (0.524 g , 0.002 mole) in 30 ml. of absolute ethanol to form a clear amber solution. This was stirred for twelve hours and gradually turned dark brown, depositing a black precipitate. The precipitate was identified as platinum metal.

Reactions of $(dba)_3Pd$ and $(dba)_3Pt$ with triphenylphosphine

1) $(dba)_3Pd$

$(dba)_3Pd$ (0.404 g , 0.0005 mole) was added to a solution of PPh_3 (0.262 g , 0.001 mole) in 50 ml. of 95% ethanol heated to 65°C. Within two minutes, a clear red solution had formed which was filtered hot, concentrated and then cooled in the refrigerator. There was approximately three milligrams of metal contained in the frit used in the filtration. After two days, orange-red crystals had formed in the filtrate. These were recovered and an attempt was made to record the n.m.r. spectrum of the complex. The complex was found to be completely unstable in solution, decomposing within seconds to deposit the metal. Elemental analysis revealed that the complex was $(PPh_3)_2Pd(dba)$. The results are as follows: calculated, C, 73.57; H, 5.13; P, 7.16; found, C, 73.45; H, 5.15; P, 7.22.

2) $(dba)_3Pt$

PPh_3 (0.262 g , 0.001 mole) was added to a slurry of $(dba)_3Pt$ (0.449 g , 0.0005 mole) in 10 ml. of 95% ethanol. After stirring for forty-eight hours, a canary yellow precipitate had formed, which was filtered off, washed with 25 ml. of cold 95% ethanol and dried to give dibenzylideneacetonebis (triphenylphosphine)platinum (0.310 g , 65% yield). The analysis of the product is as follows: calculated, C, 66.73; H, 4.65; P, 6.49; found, C, 66.67; H, 4.83; P, 6.36; molecular weight, calculated, 954; found, 716 (chloroform). The n.m.r. spectrum of the complex was also recorded (appendix 2).

Reaction of $(PPh_3)_2Pt$ dba with HCl

A 0.100 g sample of the complex dissolved in $CDCl_3$ was placed in an n.m.r. tube and HCl gas bubbled through for two minutes. The yellow-brown solution momentarily turned dark brown, then resumed its original colour. Argon was bubbled through to remove the excess HCl and a white precipitate was observed to form. The n.m.r. spectrum was recorded and a weak triplet centred at 27.27 τ was observed. The white precipitate platinum by IR spectral comparison with an authentic sample.

A second n.m.r. solution was prepared, $CDCl_3$ saturated with HCl was added drop-wise, and the n.m.r. spectrum recorded at intervals. The peaks at 4.10, 4.16, 5.92 and 6.08 τ gradually decreased in intensity with the simultaneous deposition of the white precipitate identified as $(PPh_3)_2PtCl_2$. No high field resonance attributable to a hydride complex was observed at any time.

Reaction of $(dba)_3Pd$ with dimethylacetylenedicarboxylate

$(dba)_3Pd$ (0.808 g , 0.001 mole) was added to a solution of dma (0.426 g , 0.003 mole) in 25 ml. of 95% ethanol. The initial brown slurry gradually turned yellow, the change being complete after three hours. The yellow precipitate was filtered off, washed with 25 ml. of ethanol and set aside for further investigation.

The filtrate was taken to dryness, the residue collected and washed with 200 ml. of diethyl ether to give a pale yellow-brown precipitate (0.300 g). This was identified as tetramethylpalladiacyclopentadienetetracarboxylate by n.m.r. and i.r. spectral comparison with an authentic sample. This represents a 77% yield. The diethyl ether washings were also taken to dryness and an n.m.r. spectrum taken of the residue. This was found to contain dba, dma and hexamethyl mellitate.

The yellow precipitate originally recovered from the reaction mixture (melting range, 222-227°C) was found to be slightly soluble in ethanol, methanol, acetone and moderately soluble in chloroform, methylene chloride and benzene.

HCl gas was bubbled through a solution of the complex in methylene chloride. A red-brown precipitate immediately was formed and filtered off to give a pale yellow solution. The n.m.r. spectrum was recorded and the compound in solution tentatively identified as 1,5-diphenyl-1-penten-3,5-dione. This was confirmed by n.m.r., i.r. and mixed melting point comparison with an authentic sample. It was observed that the n.m.r. spectrum was consistent with the enol rather than the keto tautomer.

The palladium complex recovered initially was identified from the n.m.r. spectrum as the cis and trans isomers of bis(1,5-diphenyl-1-penten-3,5-dione)palladium (II). The analysis for this complex is as follows: calculated, C, 67.49; H, 4.38; 0, 10.59; found, C, 67.22; H, 4.47; 0, 10.75.

The yield of the product was not affected by performing the reaction in an oxygen atmosphere. Increasing the molar ratio of dma: $(dba)_3Pd$ or the temperature had a dramatic effect on the rate of the reaction, but not the yield. For example, $(dba)_3Pd$ (0.808 g , 0.001 mole) was added to a solution of dma (0.426 g , 0.003 mole) in 25 ml. of 95% ethanol heated to 80°C. The reaction was complete as soon as the reactants were mixed, and gave the same number and distribution of products as the reaction at room temperature. The reaction was repeated at room temperature using $(dba)_3Pd$ (0.808 g , 0.001 mole) and dma (1.42 g , 0.010 mole) and was found to be complete in 20 minutes.

The yield of the β -diketone complex did vary slightly with the solvent as indicated in the following table:

Solvent	Yield (%)	Reaction time (hours)
Absolute ethanol (reagent)	10	3
Absolute ethanol (100%)	10	3
95% ethanol (reagent)	20	3
75% ethanol-water	25	3
Absolute methanol (reagent)	20	3
2:1 THF:water	20	0.1

In each reaction, $(dba)_3Pd$ (0.808 g , 0.001 mole) was added to a solution of dma (0.426 g , 0.003 mole) in 25 ml. of the solvent and the mixture stirred at room temperature.

The possibility that the β -diketone complex had been formed but not observed in the reaction between $(dba)_2Pd$ and dma was investigated. $(dba)_2Pd$ (0.575 g , 0.001 mole) was added to a solution of dma (0.426 g , 0.003 mole) in 25 ml. of 95% ethanol to give a clear pale brown solution after one hour. The solvent was removed, the residue collected and washed with 200 ml. of diethyl ether to give a pale brown precipitate identified as the palladia-cyclopentadiene complex (0.370 g , 95% yield). The solvent was removed from the ether washings and the residue found by n.m.r. to contain dba, dma and hexamethyl mellitate.

Formation of $(C_{17}H_{13}O_2)_2Pd$ in other reactions

$(dba)_3Pd$ (0.808 g , 0.001 mole) was added to a solution of 1,2-dichloro-1,2,3,4-tetramethylcyclobutene, $C_4Me_4Cl_2$, (0.537 g , 0.003 mole) in 25 ml. of 95% ethanol. Within thirty minutes, a dark green precipitate had formed. The mixture was filtered, the solvent removed from the filtrate and the products in the residue identified by n.m.r. as dba and $C_4Me_4Cl_2$. The precipitate was washed with 100 ml. of methylene chloride to give a black residue and yellow filtrate. The black residue was identified as palladium metal. The solvent was removed from the filtrate and the yellow residue identified by n.m.r. as $(C_{17}H_{13}O_2)Pd$ (0.120 gm., 20% yield).

1) Hexafluoro-2-butyne

$(dba)_3Pd$ (0.808 g , 0.001 mole) was suspended in 25 ml. of 95% ethanol and a cold condenser attached to the reaction vessel. Hexafluoro-2-butyne was admitted into the flask until refluxing was observed and the mixture stirred for twelve hours. A yellow precipitate was observed, filtered off and identified by n.m.r. as $(C_{17}H_{13}O_2)Pd$ (0.120 g , 20% yield). The filtrate from this reaction was pale yellow and clear. There was no evidence of metal or other decomposition products observed in the reaction with $(dba)_2Pd$. The ethanol was removed from the filtrate and an attempt was made to wash out the dba in the residue. However, the entire reaction product was soluble in 2 ml. of diethyl ether. The solution of the product slowly began to turn red and a black precipitate formed, so further attempts to isolate and identify the products were abandoned.

2) Tetracyanoethylene

(dba)$_3$Pd (0.404 gm., 0.0005 mole) was added to a solution of TCNE (0.198 gm., 0.0015 mole) in 25 ml. of 95% ethanol. After thirty minutes, a yellow precipitate had formed which was filtered off and identified by n.m.r. as $(C_{17}H_{13}O_2)_2Pd$ (0.060 gm., 20% yield). The ethanol was removed from the filtrate, the residue collected and washed with diethyl ether, and finally methylene chloride. This gave an orange-red precipitate which was very sparingly soluble in all organic solvents, including dimethylsulfoxide. No n.m.r. spectrum could be obtained, but the i.r. spectrum was recorded. No further attempts were made to identify this complex.

Reaction of (dba)$_3$Pd with other acetylenes

(dba)$_3$Pd (0.404 gm., 0.0005 mole) was added to a solution of diphenylacetylene (0.267 gm., 0.0015 mole) in 25 ml. of 95% ethanol. On stirring for one hour at 60°C, the reaction mixture turned black. The mixture was filtered and the black precipitate identified by IR as (dba)$_2$Pd. The solvent was removed from the filtrate and the products identified by n.m.r. as dba and diphenylacetylene.

The reaction was repeated using 2-butyne and the results were identical.

The reaction was again repeated using 2-butyne-1,4-diol. In this case the black precipitate was found to be a mixture of metal and (dba)$_2$Pd.

Reactions of $(dba)_2Pd$ and $(dba)_2Pt$

1) Methallyl chloride, benzyl chloride, benzal chloride, benzonitrile, and methyl iodide

An attempt was made to establish a series of oxidative addition reactions involving both $(dba)_2Pd$ and $(dba)_2Pt$. $(dba)_2Pt$ (0.332 g , 0.0005 mole) was added to a solution of methallyl chloride (0.056 g ., 0.00065 mole) in 50 ml. of benzene. After stirring for twenty-four hours at room temperature, no reaction was observed to have taken place. The mixture was stirred an additional twenty-four hours at 60°C and gave a yellow solution and black precipitate. The precipitate was identified as platinum metal, and the solution found by n.m.r. analysis to contain only dba and methallyl chloride.

This reaction was repeated using benzyl chloride (0.082 g , 0.00065 mole), benzal chloride (0.105 g ., 0.00065 mole), benzonitrile (0.067 g , 0.00065 mole) and methyl iodide (0.092 g ., 0.00065 mole) and the results were the same in each case, i.e. no reaction at room temperature and decomposition at higher temperatures.

This series of reactions, with the exception of methallyl chloride, was repeated using $(dba)_2Pd$ (0.288 g , 0.0005 mole) and in each case, only decomposition was observed to have occurred.

2) Methyl phenylpropiolate

Methyl phenylpropiolate (0.320 g , 0.002 mole) was added drop-wise over a fifteen minute period to a slurry of $(dba)_2Pd$ (0.575 g , 0.001 mole) in 25 ml. of benzene. The mixture was stirred at room temperature for twenty-four hours, filtered, and 0.190 g of unreacted $(dba)_2Pd$ recovered. The dark brown tarry filtrate was treated with activated charcoal powder to give a pale yellow solution. The solvent was removed and the n.m.r. spectrum showed that only dba and methyl phenylpropiolate were present.

The reaction was repeated and the brown filtrate concentrated to 10 ml. and passed through a column of kieselguhr prepared in deaerated benzene. No separation took place and the dark brown product was absorbed over the length of the column.

The reaction was repeated using various solvents (chloroform, methylene chloride, diethyl ether) but since no identifiable complex could be isolated, the investigation was abandoned.

3) Hexafluoro-2-butyne

Hexafluoro-2-butyne was bubbled through a solution of $(dba)_2Pd$ (0.288 g , 0.0005 mole) in 100 ml. of benzene for three hours at room temperature. This gave a yellow solution containing a fine suspension of black precipitate. On filtration, the precipitate was found to be palladium metal. The solvent was removed and the ^{19}F n.m.r. spectrum of the residue recorded. Attempts were made to purify the product by recrystallization from methylene chloride/petroleum ether and by column chromatography (florisil in methylene chloride); however, the ^{19}F n.m.r. spectrum of the "purified" product was identical to that of the crude product. In addition, the solution of the product gradually turned red over several hours and began to deposit a black precipitate, an indication that some decomposition was taking place. A series of low temperature ^{19}F n.m.r. spectra were recorded, ranging from room temperature to -90°C. No evidence of fluxional behaviour was observed.

The reaction was repeated in methylene chloride and tetrahydrofuran, and in both cases, a small amount of metal and a dark brown filtrate formed. When the solvent was removed and the ^{19}F n.m.r. spectrum recorded, an additional product was observed as a quartet in the spectrum. All attempts at obtaining a single pure product by either crystallization or chromatography were unsuccessful, so the investigation was abandoned.

Hexafluoro-2-butyne was bubbled through a solution of $(dba)_2Pt$ (0.332 g , 0.0005 mole) in 100 ml. of benzene for one hour at room temperature. A copious amount of black precipitate in a yellow solution was observed. On filtration, the black precipitate was identified as platinum metal. At this point further investigation was discontinued.

4) Other acetylenes

A blend of $(dba)_2Pd$ (0.575 g , 0.001 mole) and diphenylacetylene (0.891 g , 0.005 mole) was prepared in a mortar and pestle, transferred to a round bottom flask and heated in a nitrogen atmosphere at 80°C for one hour. The product was removed from the heat, quenched with 25 ml. of diethyl ether, filtered and washed with an additional 100 ml. of ether. The residue was found to contain only unreacted $(dba)_2Pd$. The ether was removed from the filtrate, the n.m.r. spectrum recorded and the products identified as dba and diphenylacetylene.

The reaction was repeated using dimethylacetylene (2 ml.) and a black tar formed from which no useful product could be recovered.

$(dba)_2Pd$ (0.288 g , 0.0005 mole) and 2-butyne-1,4-diol (0.172 g , 0.002 mole) were added to 250 ml. of acetone and the mixture stirred at 60°C for thirty minutes. A large amount of black precipitate formed which, on filtration, was identified as palladium metal. Further investigation was abandoned.

Reaction of nickel (O) complexes with dimethylacetylenedicarboxylate

Nickel tetracarbonyl (2.25 g , 0.015 mole) and dma (4.26 g , 0.03 mole) were added to 50 ml. of benzene and the resulting solution stirred at room temperature for two hours. On mixing the solution immediately turned yellow and a white precipitate began to form. At the end of the reaction, this precipitate was filtered off and identified by n.m.r. and i.r. spectral comparison with an authentic sample as hexamethylmellitate. Nitrogen was bubbled through the filtrate to remove any $Ni(CO)_4$ present and, on removing the solvent, it was found that only hexamethyl mellitate was present.

The reaction was repeated in chloroform, using dicarbonyl bis(triphenylphosphine) nickel as the starting complex, aliquots were drawn from the reaction mixture at intervals and the i.r. spectra recorded. In the initial mixture, three -CO absorptions attributed to the nickel complex were observed at 2070, 2005 and 1945 cm^{-1}, and one peak at 1725 cm^{-1} attributed to dma. After ten minutes, two new peaks were observed at 2045 cm^{-1} and 1610 cm^{-1}. Over the next hour, these two peaks increased in intensity while the peak at 1945 cm^{-1} decreased rapidly and finally disappeared. Subsequently, the peaks at 2070 cm^{-1}, 2045 cm^{-1} and 2005 cm^{-1} gradually decreased in intensity and finally disappeared while the peak at 1610 cm^{-1} continued to grow. The only peaks in the 2100 to 1500 cm^{-1} region observed in the final spectrum, taken after twenty-two hours were at 1725 cm^{-1} and 1610 cm^{-1}. Both of these peaks were attributed to hexamethyl mellitate by comparison with an authentic sample.

The reaction was repeated in both chloroform and methylene chloride using triphenylphosphinenickel tricarbonyl as the starting complex. The results were analogous to these observed for dicarbonylbis(triphenylphosphine)nickel. Attempts to isolate the complex responsible for the peak at 2045 cm^{-1} were unsuccessful.

<u>Preparation of tetramethylcyclobutadieneplatinum dichloride</u>

$(dba)_2Pt$ (0.995 g , 0.0015 mole) and $C_4Me_4Cl_2$ (0.806 g , 0.0045 mole) were blended in a mortar and pestle, transferred to a 50 ml. round bottom flask and heated in a nitrogen atmosphere at 80°C for fifteen minutes. The resulting dark brown melt was removed from the heat and immediately quenched with 25 ml. of diethyl ether. The granular precipitate was removed by filtration and washed with 200 ml. of diethyl ether to remove the excess $C_4Me_4Cl_2$ and dba. The washed product was dissolved in 50 ml. of methylene chloride to give a clear, deep brown solution which was treated three times with activated charcoal powder. The solvent was removed from the resulting pale yellow solution and the product recrystallized from methylene chloride/diethyl ether to give orange hexagonal crystals of $C_4Me_4PtCl_2$ (0.061 g , 11% yield). The analysis of the product is as follows: calculated, C, 25.68; H, 3.23; Cl, 18.95; found, C, 25.85; H, 3.21; Cl, 18.84; molecular weight, calculated, 555; found, 1393 (chloroform). Both i.r. and n.m.r. spectra were recorded and the J_{Pt-H} was observed to be 19 hertz.

Numerous attempts were made to improve the yield; however, no product was isolated from the reactions performed in chloroform; methylene chloride, methanol, acetone, diethyl ether, tetrahydrofuran, dimethylformamide and dimethyl sulfoxide. As far as the neat reaction was concerned, no increase or decrease in the yield was observed on increasing the ratio of $C_4Me_4Cl_2$: $(dba)_2Pt$ from 3:1 to 10:1, on performing the reaction in an atmosphere of oxygen or on heating the blend to 120°C.

Attempted preparation of tetramethylcyclobutadienepalladium dichloride

Various attempts were made to synthesize this compound from $(dba)_2Pd$ and $C_4Me_4Cl_2$. In a typical reaction, $(dba)_2Pd$ (0.150 g , 0.000261 mole) and $C_4Me_4Cl_2$ (0.047 g , 0.000261 mole) were added to 25 ml. of methylene chloride to form a deep purple slurry, and stirred at room temperature. After five minutes, a mirror of palladium metal had formed on the surface of the reaction vessel and, within thirty minutes a pale yellow solution had formed. The products in solution were identified from their n.m.r. and i.r. spectra as dba and $C_4Me_4Cl_2$.

A wide variety of reaction conditions was used in attempting to synthesize $C_4Me_4PdCl_2$. The following is a summary of the conditions used:

1) Solvent

The following solvents were used in addition to methylene chloride in an attempt to synthesize the desired compound: benzene, chloroform, diethyl ether, tetrahydrofuran, acetone, dimethylformamide, t-butanol and methanol. In all but the last case, the result was the same as with methylene chloride. The only variation was the length of time required for $(dba)_2Pd$ to decompose. For example, the decomposition reaction in benzene took twelve hours to go to completion as compared to thirty minutes in methylene chloride.

Only when methanol was used as a solvent was there any indication that reaction was taking place to form a new complex. In this reaction, $(dba)_2Pd$ (0.150 g , 0.000261 mole) and $C_4Me_4Cl_2$ (0.047 g , 0.000261 mole) were added to 15 ml. of anhydrous methanol cooled to -15°C. The $(dba)_2Pd$ is completely insoluble in methanol, so no colour change was observed in the solvent. The mixture was allowed to warm to room temperature and within fifteen minutes a yellow-green precipitate was observed. This was removed by filtration.

The precipitate was found to be insoluble in most common organic solvents with the exceptions of dimethylformamide and dimethylsulfoxide, in which it was sparingly soluble. The n.m.r. and i.r. spectra taken clearly indicated that the complex was not $C_4Me_4PdCl_2$, so further investigation was discontinued.

2) Temperature

The reactions in the different solvents were repeated at various temperatures ranging from -50°C in methylene chloride to 80°C in benzene (refluxing temperature). In every case, only the decomposition of the $(dba)_2Pd$ was observed. The reaction took several days at -50°C as compared to five minutes in refluxing benzene.

3) Molar ratio

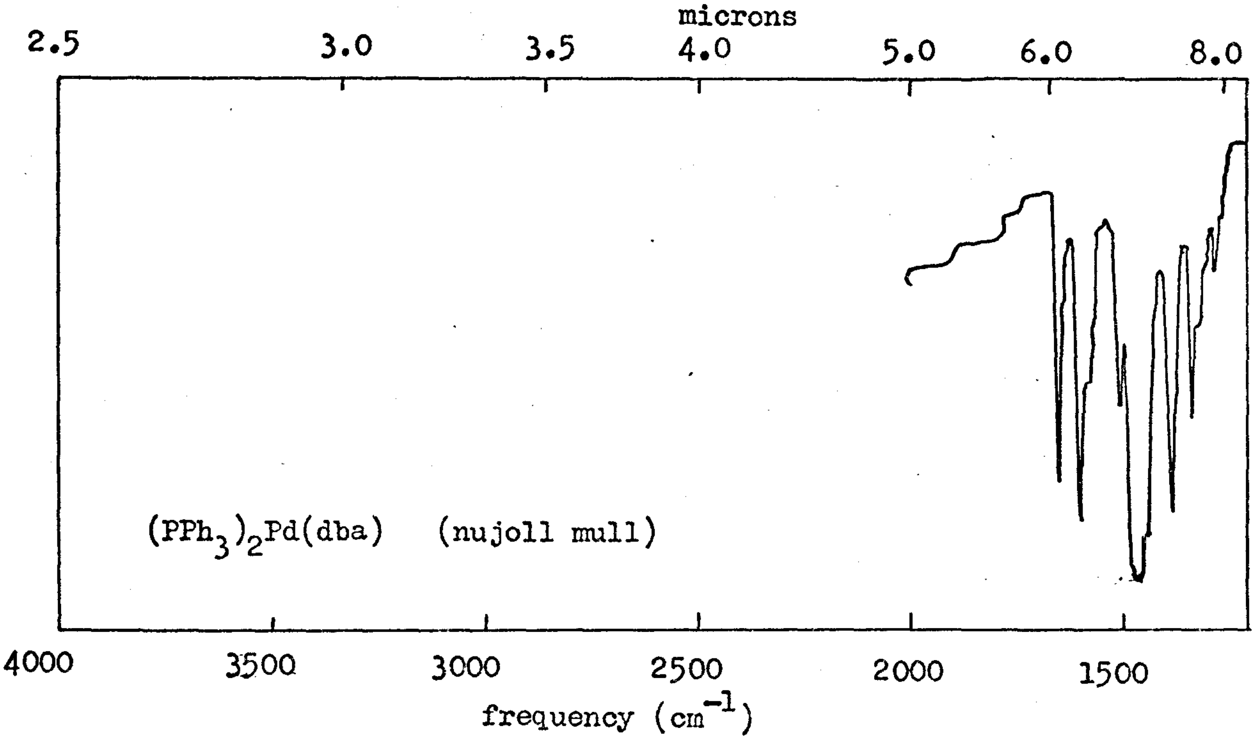
The molar ratio of $C_4Me_4Cl_2$: $(dba)_2Pd$ was varied from 1:1 to 10:1. It was observed that the higher the molar ratio used, the faster the rate of decomposition of the $(dba)_2Pd$.

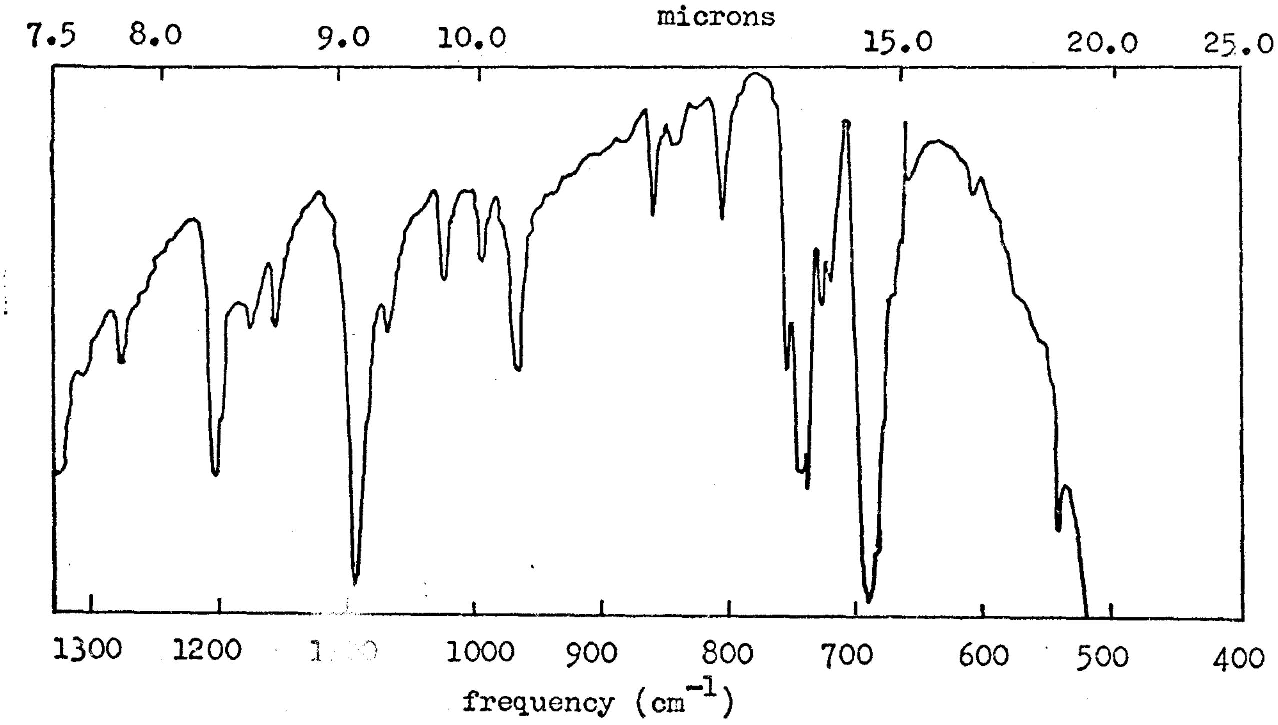
Other variations were also employed, including the addition of sodium iodide to the reactions in dimethylformamide and acetone, and the heating of a blend of $(dba)_2Pd$ and $C_4Me_4Cl_2$ without solvent to 80°C. All of these attempts were unsuccessful, and, in most cases, gave only palladium metal, dba and $C_4Me_4Cl_2$.

APPENDIX

APPENDIX I

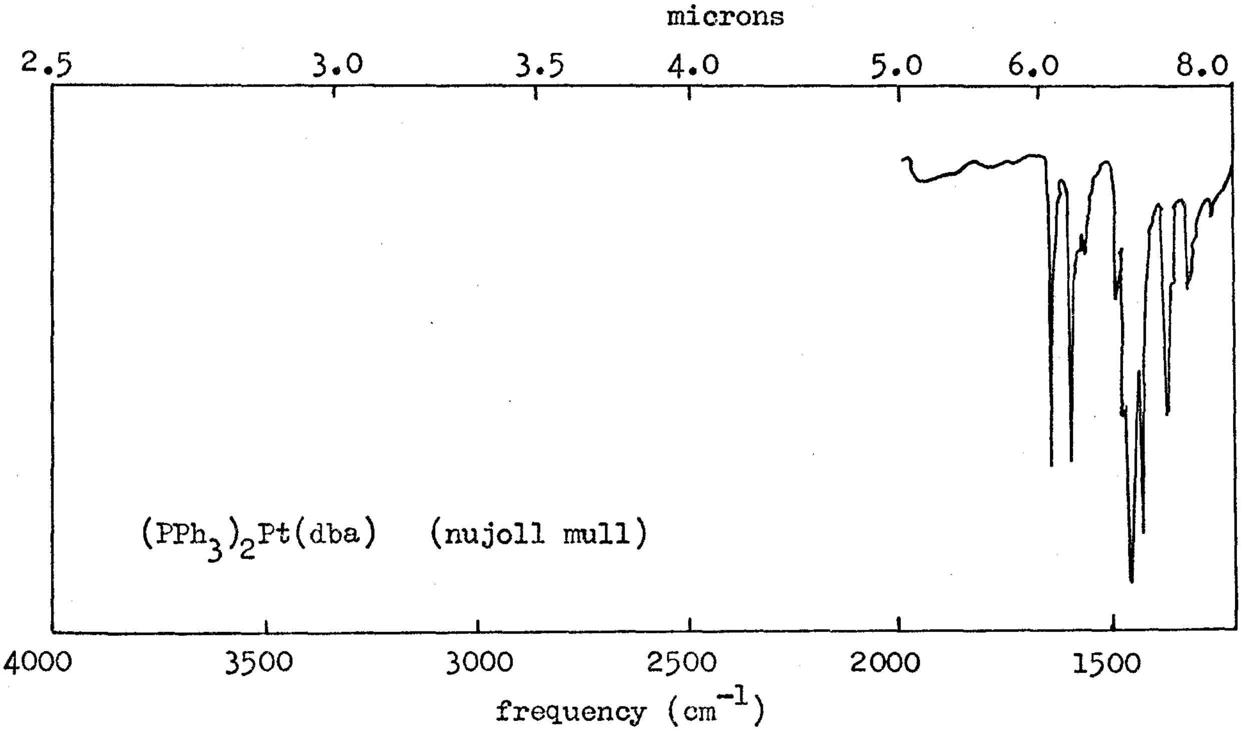
Infrared Spectra

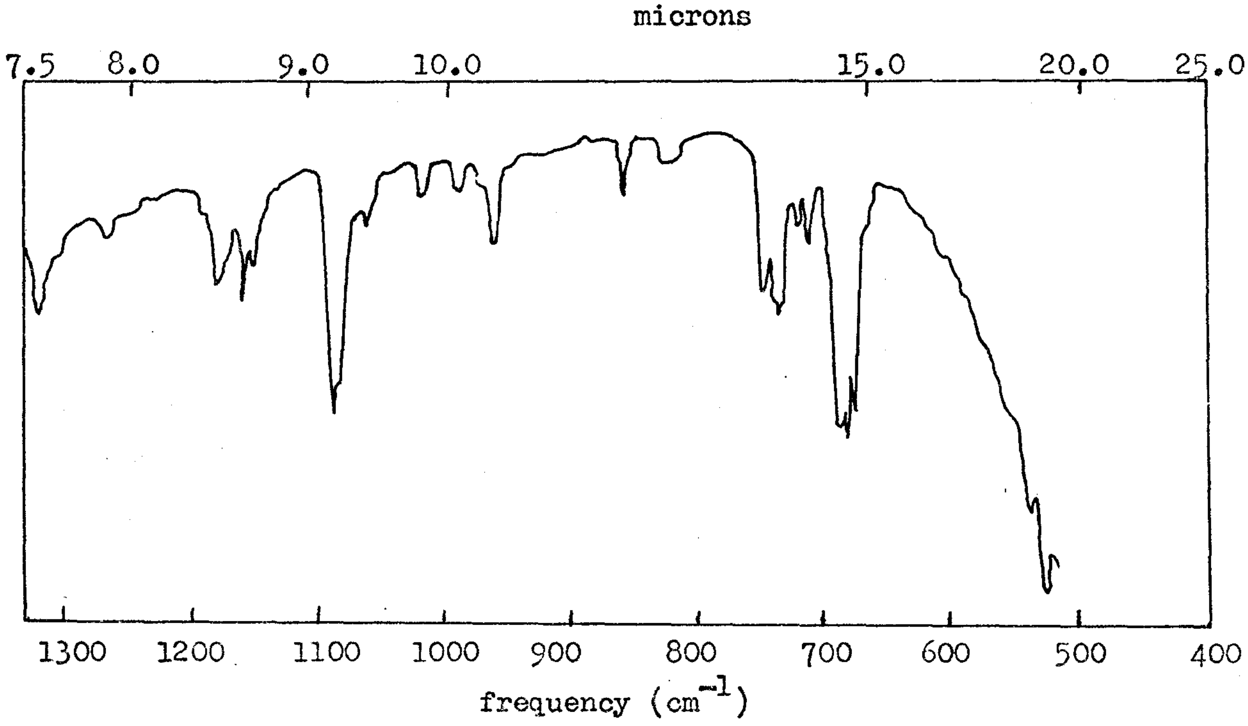




APPENDIX I

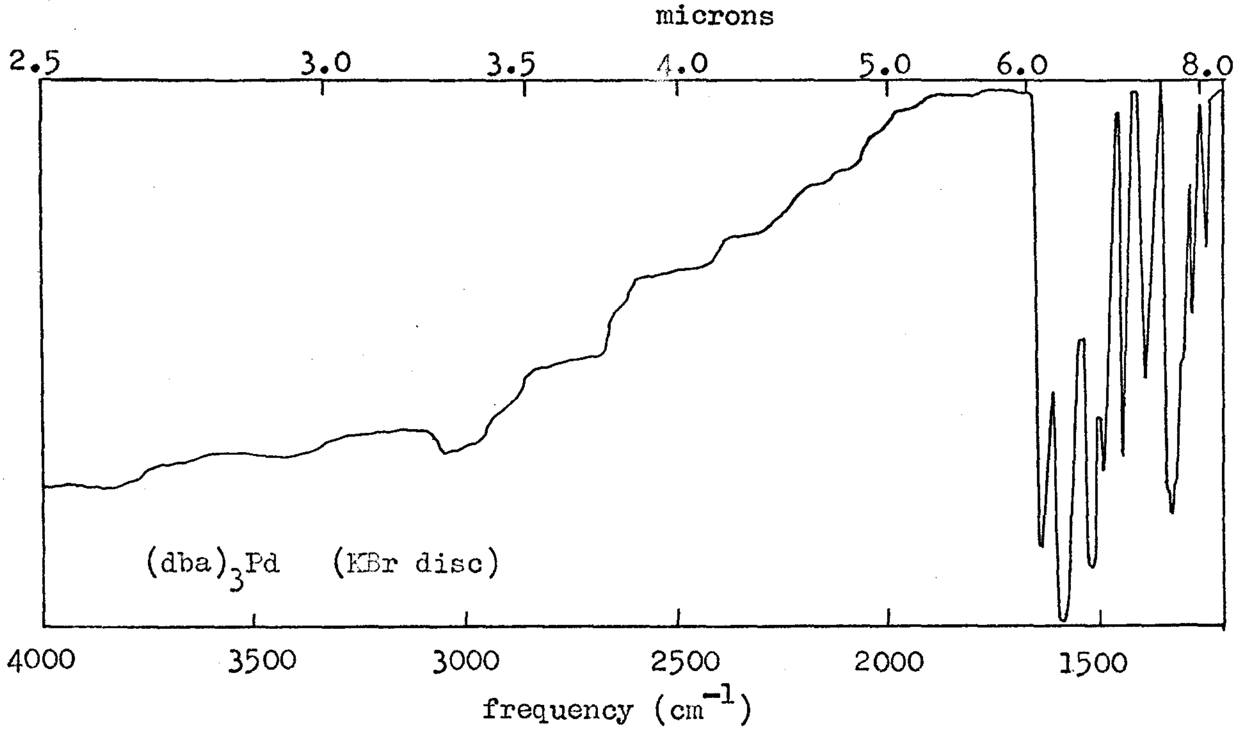
Infrared Spectra

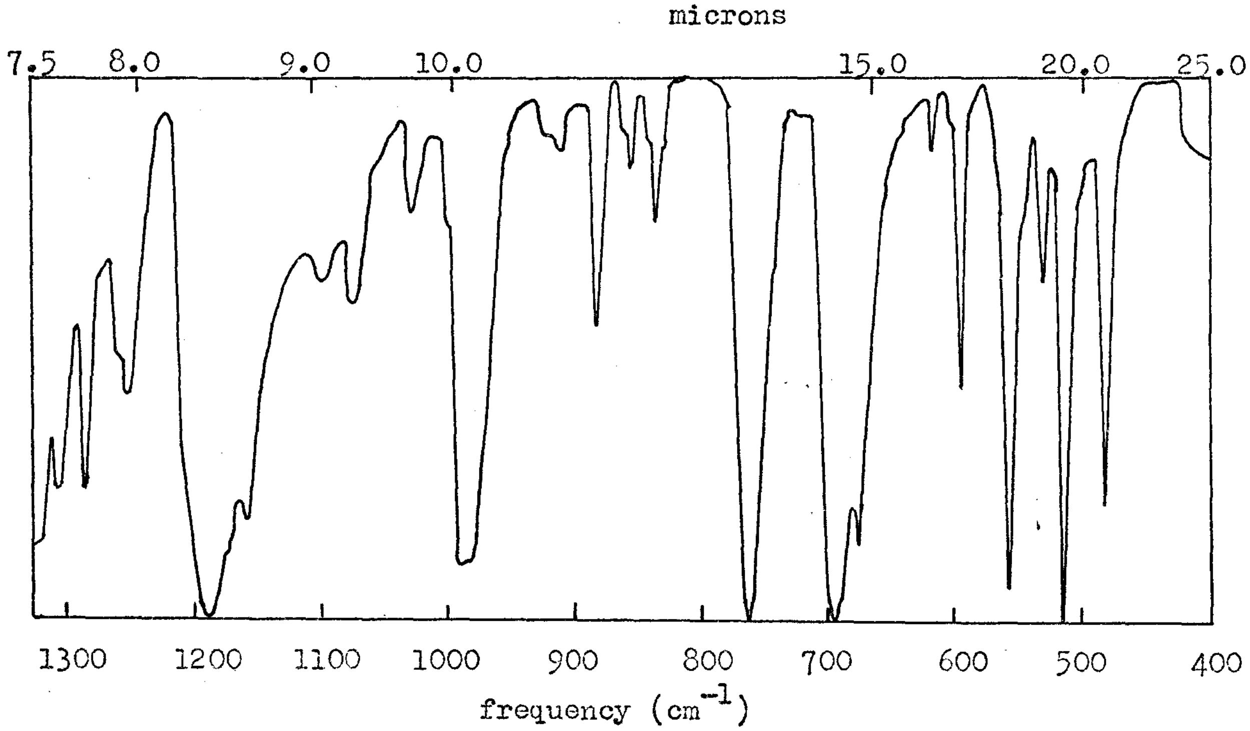




APPENDIX I

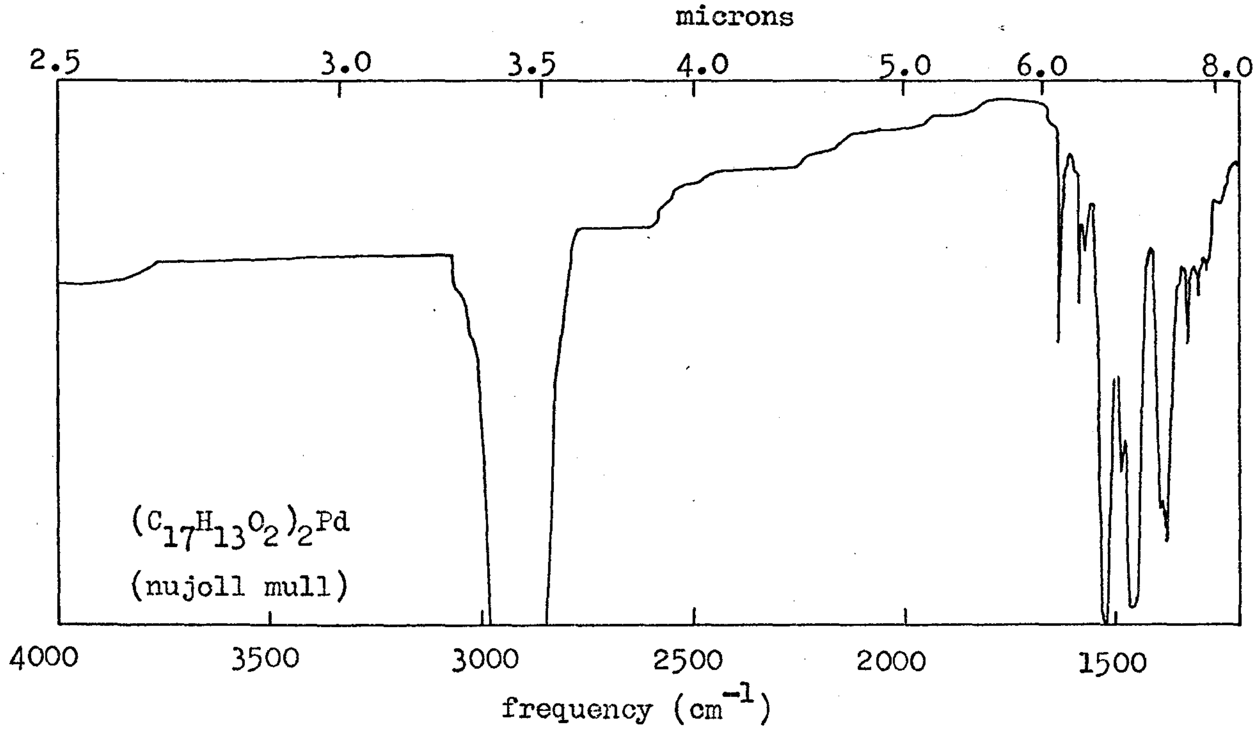
Infrared Spectra

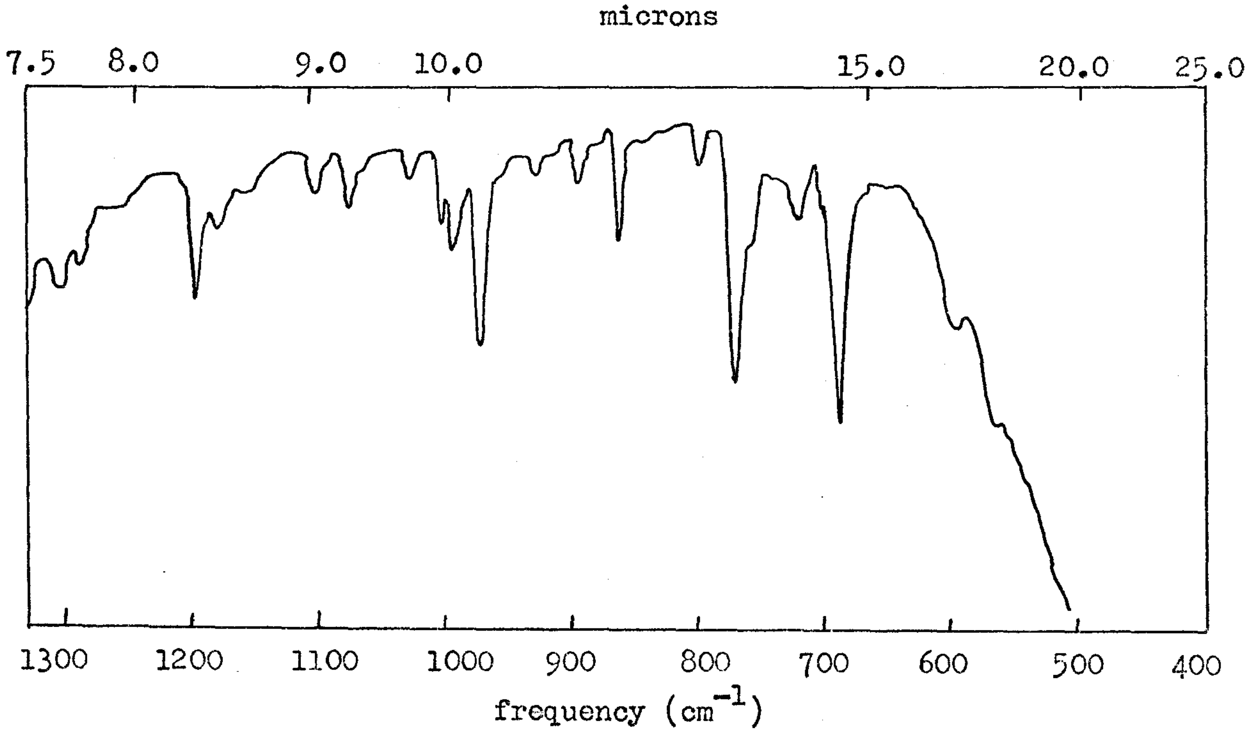




APPENDIX I

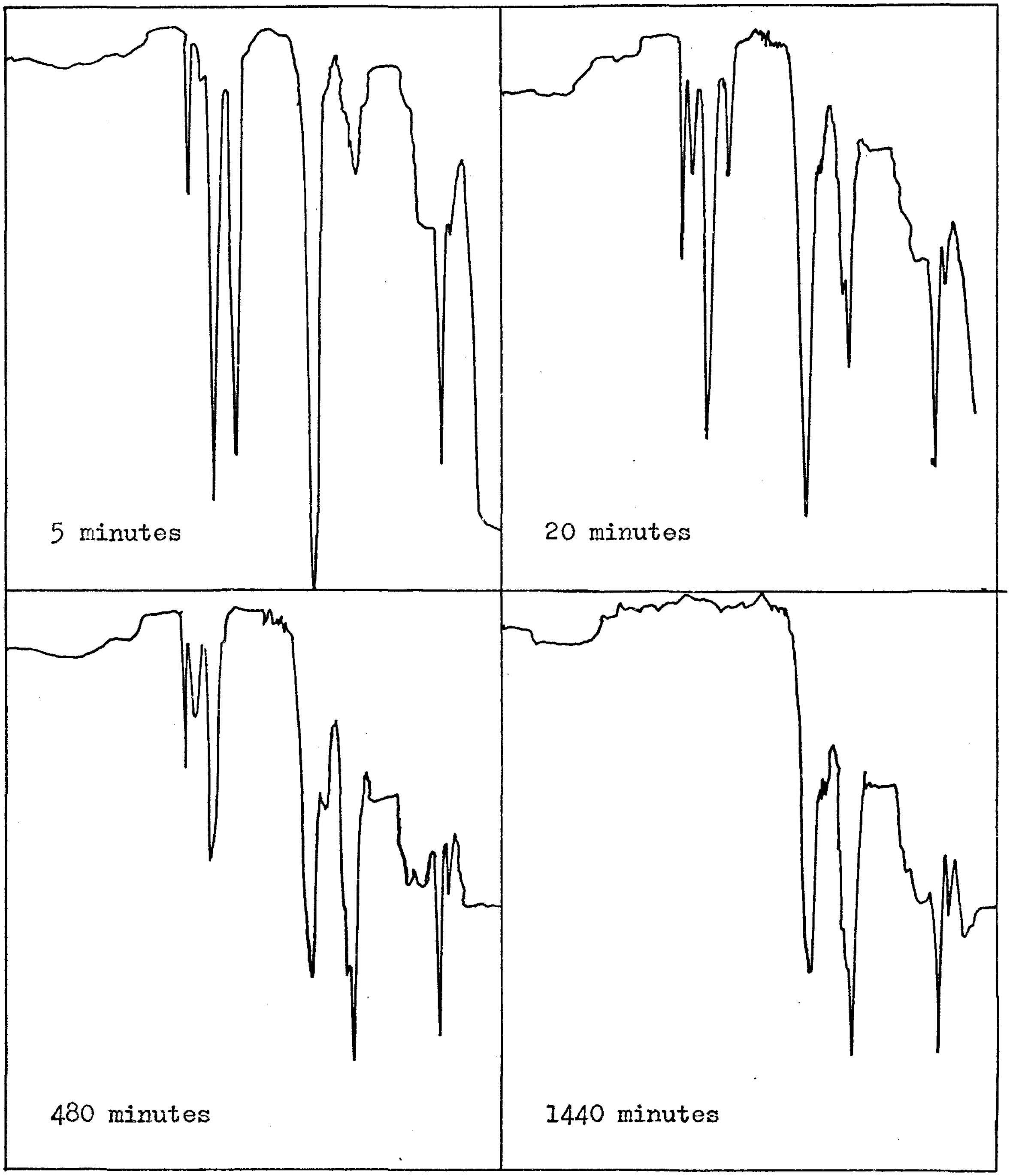
Infrared Spectra





APPENDIX I

Infrared Spectra

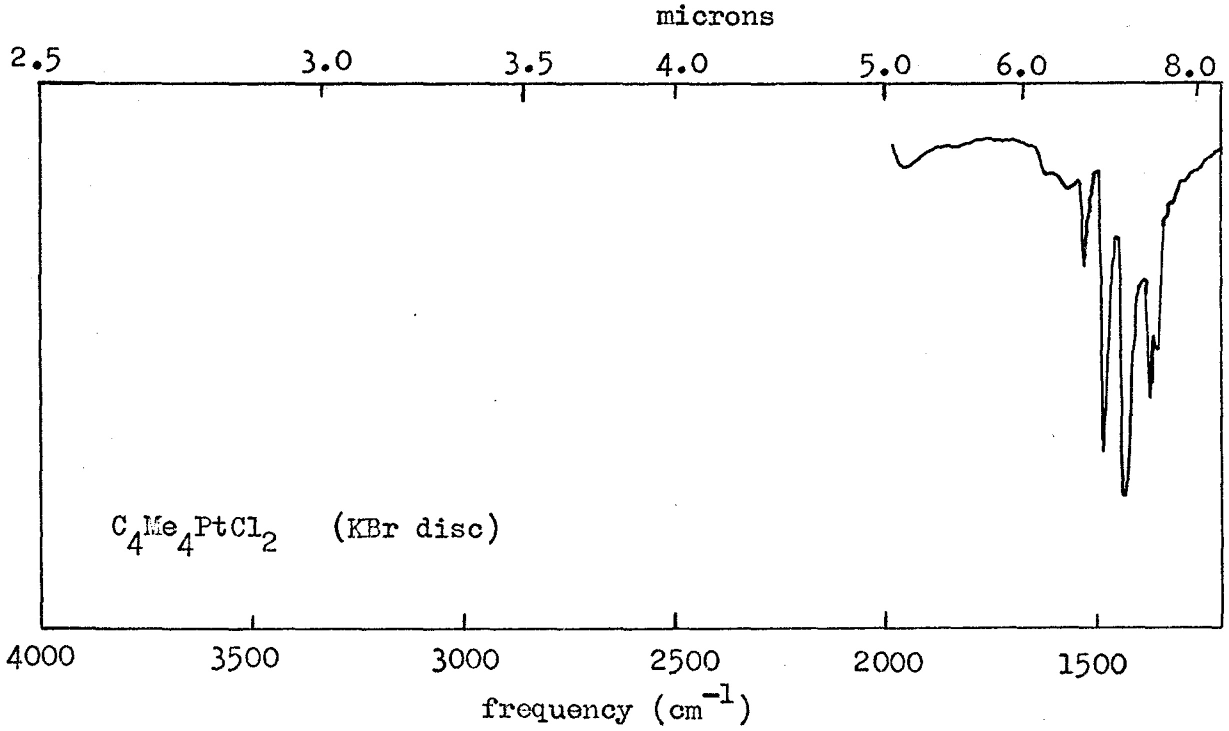


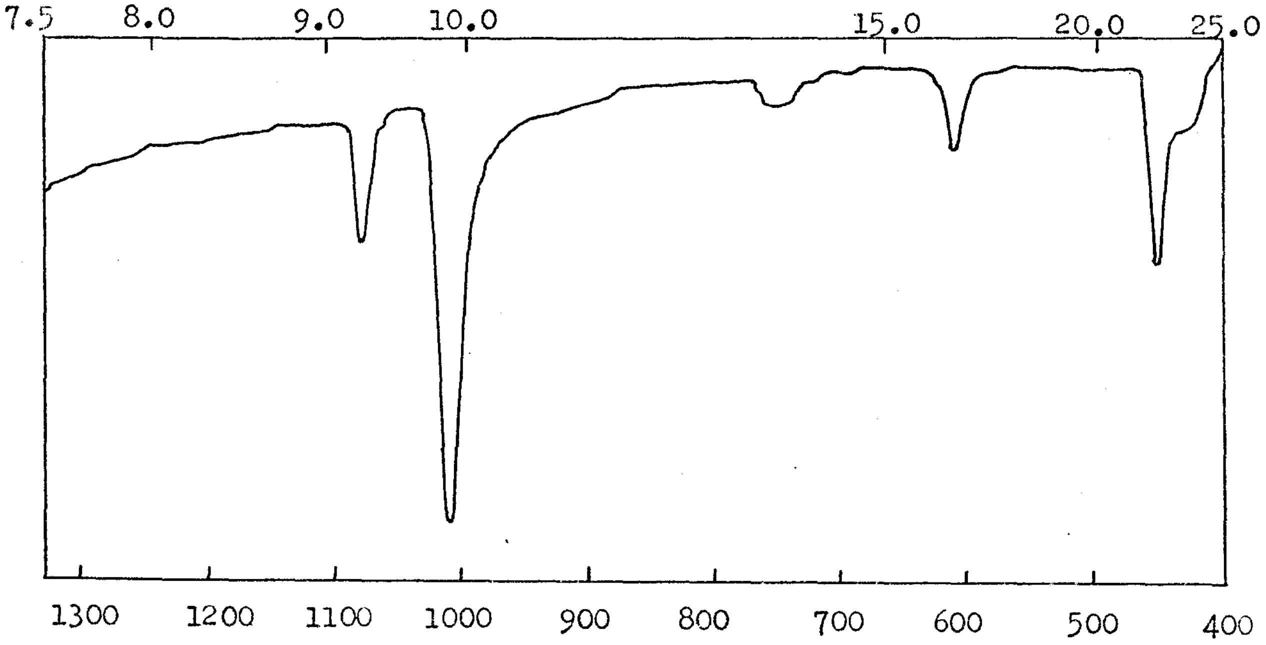
$(PPh_3)_2Ni(CO)_2$ + $CH_3O_2CC{\equiv}CCO_2CH_3$ in chloroform

Infrared spectra in the 2500 to 1200 cm^{-1} region

APPENDIX I

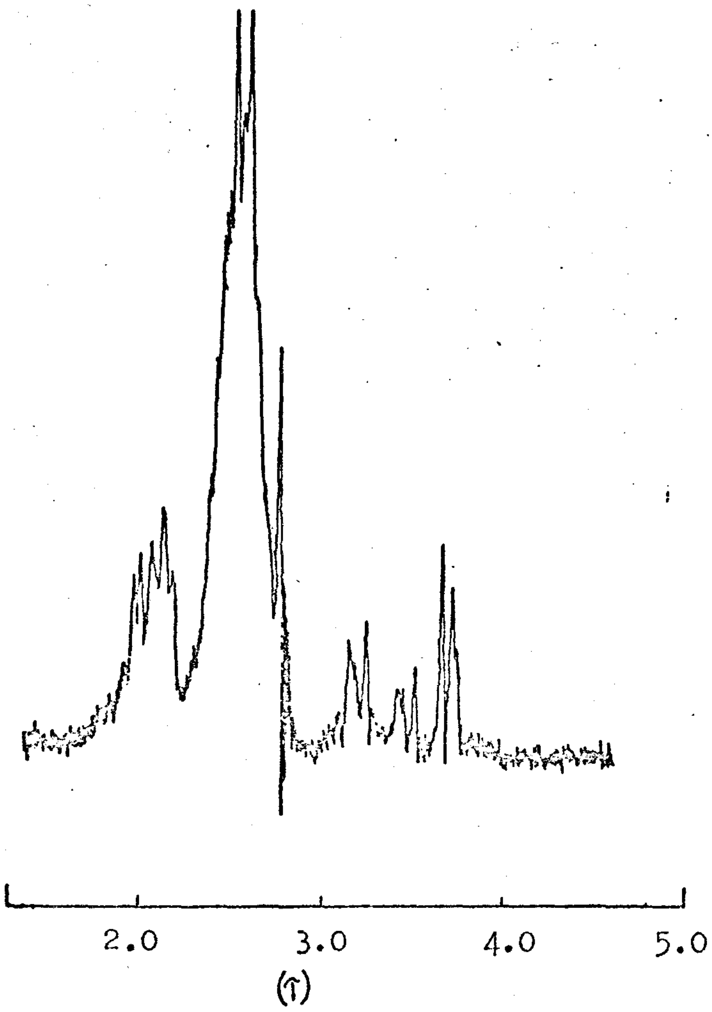
Infrared Spectra



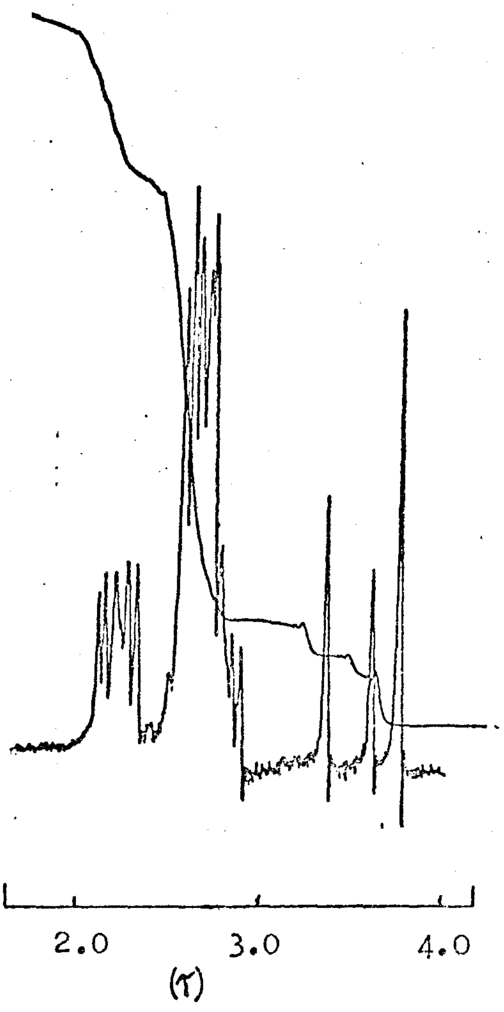


APPENDIX II

Nuclear Magnetic Resonance Spectra



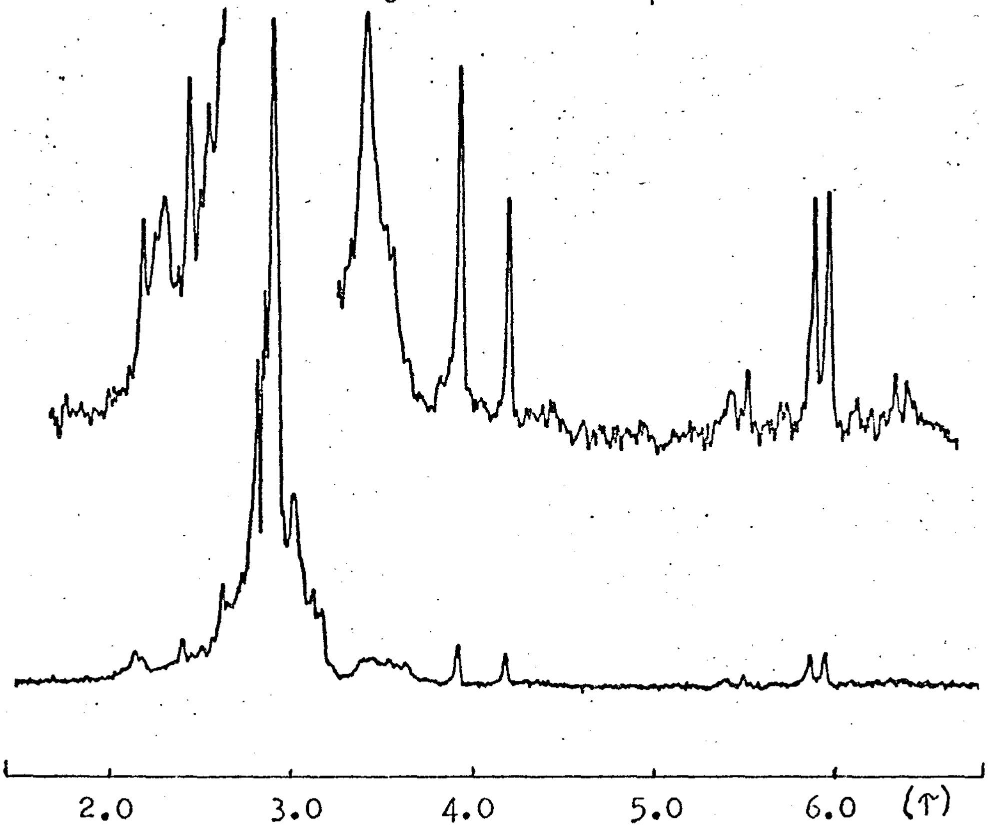
$(C_{17}H_{13}O_2)_2Pd$



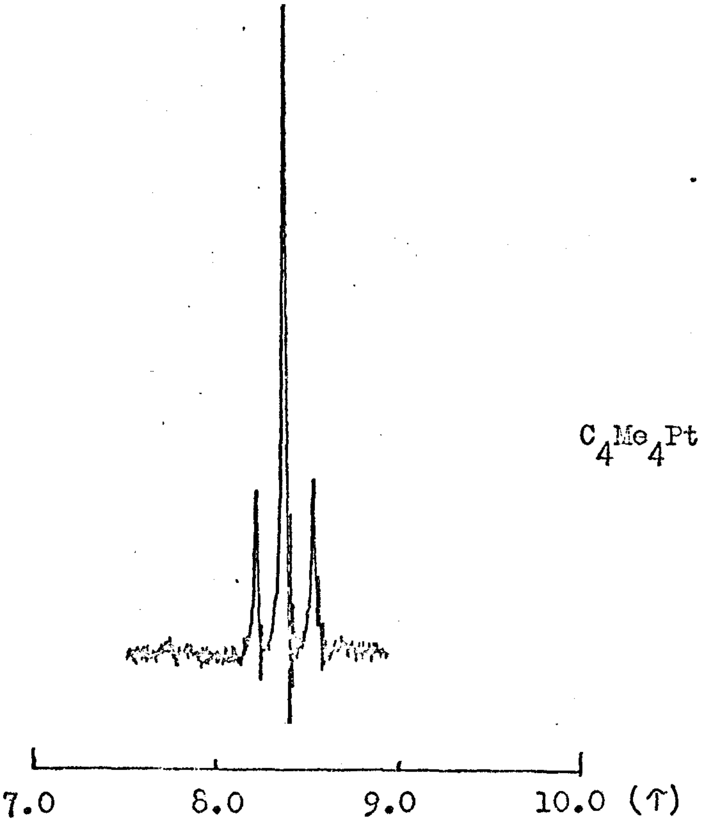
$C_{17}H_{14}O_2$

APPENDIX II

Nuclear Magnetic Resonance Spectra



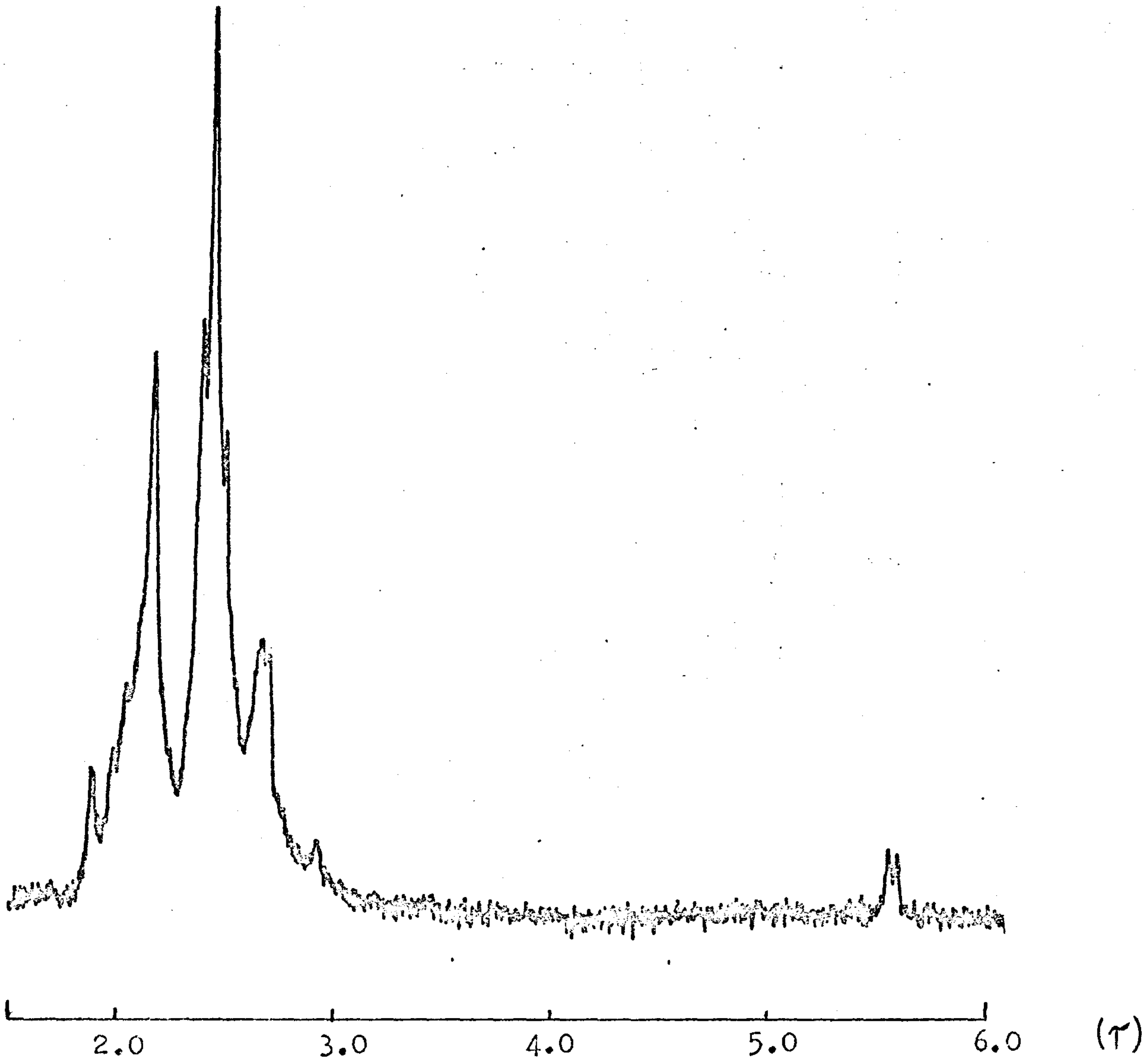
$(PPh_3)_2Pt(dba)$



$C_4Me_4PtCl_2$

APPENDIX II

Nuclear Magnetic Resonance Spectra



(dba)$_3$Pt in d_6-DMSO

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