AN INVESTIGATION OF THE FORMATION OF BIS(TOLYL)(CYCLOOCTATETRAENE)PLATINUM(II) COMPLEXES AND THEIR REACTIONS WITH PYRIDINE AND TRIPHENYLARSINE

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ABSTRACT

PROBLEM

The work reported in the following thesis was conducted to study the stabilization of aryl platinum(II) complexes with triphenylarsine, to extend the series of cyclicpolyolefin platinum(II) aryl compounds and to examine the effect organoiodides have on these complexes.

METHOD

Synthesis of the complexes was carried out using the appropriate, predescribed laboratory procedures with modifications.

Complexes were identified by infra-red, carbon, hydrogen and platinum analyses.

RESULTS

Results show that triphenylarsine will stabilize aryl platinum(II) complexes, that halides will be replaced from diiodo(cyclooctatetraene)platinum(II) with m-tolyl groups by use of a Grignard reagent and bis(m-tolyl)platinum(II) is stabilized with pyridine.

Reactions between the prepared platinum complexes and organoiodides could not be induced.

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CHAPTER I

INTRODUCTION

Chatt and Shaw have reported the stabilization of alkyl and aryl platinum(II) complexes with tertiaryphosphines and trialkylarsines.[1,2] They also reported that any ligand capable of producing a large crystal field splitting in the platinum(II) ion should similarly stabilize alkyl and aryl platinum(II) complexes.

Kistner and co-workers have reported alkyl and aryl groups replacing halides from dihalide cyclicpolyolefin platinum(II) complexes by reaction with alkyl and aryl Grignard reagents.[3]

In a more recent study, Kistner and co-workers have reported the reaction of cis-bis(tolyl)bis(pyridine)platinum(II) complexes with organoiodides to yield platinum(IV) complexes.[4]

The following work was conducted to attempt to extend the study of the stabilization of aryl platinum(II) complexes with tertiaryarsine, to extend the series of cyclicpolyolefin platinum(II) aryls and to examine the effect organoiodides have on these complexes.

CHAPTER II

HISTORICAL

The Preparation of Ethylene Platinum(II) Compounds and the Nature of the Platinum Olefin Bond.

The first report of an olefin-platinum bond was presented by Zeise in 1827.[5] By reacting sodium hexachloroplatinate(IV) and ethanol, Zeise's acid $H[(C_2H_4)PtCl_3]\cdot 6H_2O$ can be produced.

In more recent investigations with platinum-ethylene compounds, Chatt reported the platinum-olefin bonds to be an interaction of the d-orbitals of the metal with the olefin.[6,7] A $5d6s6p^2$ hybrid orbital of the platinum ion overlaps the pi bond of the olefin forming a d-pi, sigma type bond. A pi backbond is formed by the overlap of a filled 5d orbital of the platinum ion and the pi antibonding molecular orbitals of the olefin. The double bond of the olefin is, therefore, most favorably oriented perpendicular to the plane of the square planar molecule. (See Figure 1.)

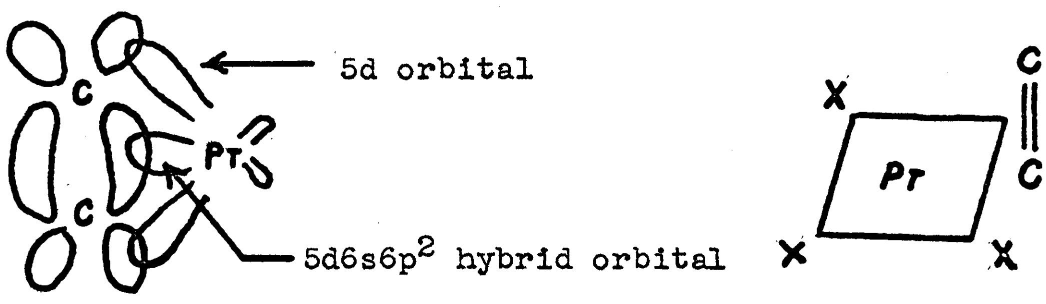

FIGURE 1

THE PLATINUM-OLEFIN BOND

Chatt's explanation is supported by infra-red data which shows a lowering of the C-C double bond stretch frequency when it is coordinated with the platinum ion. This lowering is due to a shift of electron density to the d-pi bond resulting in a weakening of the olefin bond.

Stabilization of Aryl and Alkyl Platinum(II) Compounds with a Phosphine, Amine or Arsine.

Most organo-platinum compounds reported were relatively unstable until Chatt reported the use of a tertiary phosphine, amine and arsine for strong crystal field splitting to stabilize them.[1,2]

As ligands approach on the x and y axes, the dx^2-y^2 and dz^2 orbitals of the metal ion, located on the axes, are activated to a higher energy by electron repulsion. A strong crystal field splitting ligand is used to increase the difference in energy between the highest energy orbital which contains electrons and the lowest energy orbital which is vacant. The triphenylphosphine ligand creates a splitting large enough to stabilize the platinum(II) alkyl and aryl complexes.

By the reaction of dihalo-bis(tertiaryphosphine)-platinum(II) with organo lithium or Grignard reagents, stable alkyl and aryl compounds were obtained. Amines and trialkylarsines were employed in the same manner for stabilization.

From studies of the ultraviolet and visible spectra of platinum(II) amine complexes, Chatt proposed the relative energy levels of the platinum d-orbitals.[8] Since the dx^2-y^2 orbital is directed at the ligands, it would be the least stable. The dz^2 orbital was assigned the lowest energy but more recent calculations indicate that the dz^2 energy level is slightly higher than the dxy and dyz orbitals.[9] (See Figure 2.)

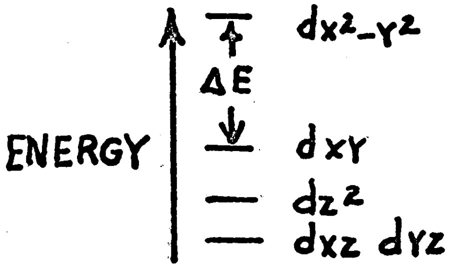

FIGURE 2

ENERGY LEVELS OF THE PLATINUM d-ORBITALS

Chatt and Shaw also reported that phosphine derivatives of platinum(II) containing sigma bonded, o-substituted aryl derivatives had greater stability than the p-substituted analogs.[1,2] Chatt accredited this stability to kinetic and steric effects and proposed that with an o-substituent on an aromatic ring, the free rotation of the ring on the x and y axis is inhibited, keeping the ring perpendicular to the plane of the molecule. This allows a greater overlap of the dxy orbital of the metal ion with the pi electrons of the aryl system, resulting in a lowering of the dxy orbital energy level. This increases the ΔE and the stability of the complex.[10]

Cyclic Polyolefin Platinum(II) Complexes.

A platinum(II) halide cyclic polyolefin, diiodo(cyclooctatetraene)platinum(II) was reported by Jensen in 1953.[11] He proposed a structure for the complex utilizing the "tub" formation of the cyclooctatetraene molecule reported by Karle[12] and confirmed later by Bastiansen and co-workers.[13] The "tub" formation orients the double bonds of the olefin to a favorable position for coordination. (See Figure 3.)

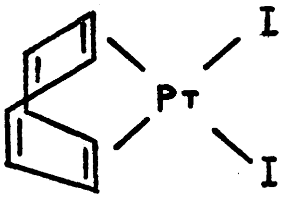

FIGURE 3

DIIODO(CYCLOOCTATETRAENE)PLATINUM(II)

Hoffman and vonNarbutt reported dichloro(dicyclopentadiene)platinum(II),[14] Chatt has reported 1,5-cyclooctadiene-platinum(II) halides[15] and Alexander and co-workers have[16] reported the preparation of diiodo(norbornadiene)platinum(II). More recently, cycloheptatriene and 3-vinylcyclohexene have been reported to stabilize platinum(II) complexes.[17,21]

Reaction of Cyclic Polyolefin Platinum(II) Halide Complexes with Grignard Reagents.

The first example of a cyclic polyolefin stabilizing a transition metal to carbon bond was reported by Calvin and Coates after preparing bis(methyl)1,5-cyclooctadiene-platinum(II).[18]

Binuclear (cyclooctatetraene)platinum(II) methyl and phenyl complexes have been prepared by the reaction of a Grignard reagent with diiodo(cyclooctatetraene)platinum(II) as shown in the equation below.[19,20]

$$2C_8H_8PtI_2 + 4RMgI \longrightarrow R_2PtC_8H_8PtR_2 + C_8H_8 + 4MgI_2$$

R-Me or Ph

Data obtained by X-ray diffraction on the methyl compound indicated a cyclooctatetraene "tub" bridged structure but was not conclusive.

Kistner and co-workers, examining the scope of the cyclic polyolefin complexes, synthesized a series of alkyl and aryl derivatives of platinum(II) containing cyclic diolefins such as norbornadiene, dicyclopentadiene and 1,5-cyclooctadiene.[3]

The reaction of diiodo(norbornadiene)platinum(II) with methylmagnesium iodide produced a mononuclear iodomethyl derivative.

$$C_7H_7PtI_2 + CH_3MgI(\text{excess}) \longrightarrow C_7H_8PtCH_3I$$

The reaction of diiodo(dicyclopentadiene)platinum(II) with the Grignard reagent also produces an iodomethyl derivative but diiodo(1,5-cyclooctadiene)platinum(II) and the Grignard reagent produces a dimethyl derivative.

$$C_8H_{12}PtI_2 + CH_3MgI(\text{excess}) \longrightarrow C_8H_{12}Pt(CH_3)_2$$

In an attempt to extend the series of binuclear cyclooctatetraene derivatives by the use of Grignard reagents derived from p-bromotoluene, 1-bromonapthalene and o-bromotoluene, it was found that mononuclear derivatives with one or both iodo groups replaced were consistently isolated.[3]

Investigation of the products obtained in the preceding reactions showed that the products containing aryl groups have greater stability than those derived from alkyl Grignard reagents, with the exception of the methyl derivatives. Within the aryl series, the order of kinetic stability was shown to be: 1-napthyl > o-tolyl > phenyl > p-tolyl.[3] This order of stability agrees with Chatt's proposal that stability is increased with the limiting of the free rotation of the aromatic ring on the x and y axes. It can be seen that the stability decreases as the substituent moves from the ortho position to the para position on the aromatic ring.

Reactions of Cyclic Polyolefin Alkyl and Aryl Complexes with Pyridine and Triphenylphosphine.

Hutchinson and Doyle have reacted binuclear (cyclooctatetraene)platinum(II) methyl and phenyl compounds with pyridine and triphenylphosphine to replace the olefin and give the corresponding derivatives.[19,20]

$$C_8H_8PtR_4 + 4(Py) \longrightarrow 2(Py)_2PtR_2 + C_8H_8$$

$$C_8H_8PtR_4 + 4(Ph_3P) \longrightarrow 2(Ph_3P)_2PtR_2 + C_8H_8$$

Kistner and co-workers have reported a cyclic diolefin displacement to yield methyliodo, dimethyl, diphenyl, o-tolyl and p-tolyl platinum(II) complexes containing triphenylphosphine and pyridine.[3]

Reactions of Alkyl and Aryl Platinum(II) Derivatives Containing Pyridine and Trialkyl and Triaryl Phosphines with Organo Iodides.

Chatt and Shaw reported methyl iodide reacting with monomethyl platinum(II) derivatives containing trialkylphosphines to yield platinum(IV) compounds of the type $(R_3P)2Pt(CH_3)_2I_2$.[1,2]

Kistner and co-workers found that methyl iodide reacts with bis(o-tolyl)platinum(II) derivatives containing triphenylphosphine, pyridine or 1,5-cyclooctadiene according to the equations:[3]

$$(Ph_3P)_2Pt(o\text{-}tolyl)_2 + CH_3I \xrightarrow{115^\circ} (Ph_3P)_2Pt(CH_3)I_3$$

$$(Py)_2Pt(o\text{-}tolyl)_2 + CH_3I \xrightarrow{42^\circ} (Py)_2Pt(o\text{-}tolyl)(CH_3)I_2$$

$$C_8H_{12}Pt(o\text{-}tolyl)_2 + CH_3I \xrightarrow{115^\circ} C_8H_{12}Pt(o\text{-}tolyl)I$$

Each of the above reactions is accompanied by the displacement of a tolyl group and in the reactions involving the triphenylphosphine and pyridine derivatives, the addition of methyl iodide yields a platinum(IV) complex.

The expansion of this series of reactions to include other organoiodides has been reported.[4] Cis-bis(tolyl)bis(pyridine)platinum(II) was reacted with ethyl iodide, propyl iodide, allyl iodide and iodobenzene. In all of these reactions, at least one tolyl group was displaced and this displacement was usually accompanied by the addition of the organoiodide, resulting in a platinum(IV) complex. The reactions proceed as shown in the following equations.

$$(Py)_2Pt(o\text{-}tolyl)_2 + C_2H_5I \longrightarrow (Py)_2Pt(o\text{-}tolyl)(C_2H_5)I_2$$

$$(Py)_2Pt(p\text{-}tolyl)_2 + C_2H_5I \longrightarrow (Py)_2Pt(p\text{-}tolyl)(C_2H_5)I_2$$

$$(Py)_2Pt(o\text{-}tolyl)_2 + C_3H_7I \longrightarrow (Py)_2Pt(o\text{-}tolyl)(C_3H_7)I_2$$

$$(Py)_2Pt(o\text{-}tolyl)_2 + C_6H_5I \longrightarrow (Py)_2Pt(o\text{-}tolyl)I$$

The reaction of allyl iodide with the o-tolyl and p-tolyl derivatives was of particular interest because a NMR study indicated the allyl group was sigma bonded to the platinum ion and a triiodo ion was present in the complex, shown in the following equations:

$$(Py)_2Pt(o\text{-}tolyl)_2 + C_3H_5I \longrightarrow (Py)_2Pt(C_3H_5)_2(I_3)_2$$
$$(Py)_2Pt(p\text{-}tolyl)_2 + C_3H_5I \longrightarrow (Py)_2Pt(C_3H_5)_2(I_3)_2$$

A reinvestigation of the previously reported $(Ph_3P)_2$-$Pt(CH_3)I_3$ complex showed, through UV analysis that the triiodo ion was also present in that complex.

CHAPTER III

EXPERIMENTAL

I. ANALYSIS

All infra-red analyses were carried out on a Perkins-Elmer, #137 Infra-red Spectrophotometer with a NaCl optic system. Solid samples were prepared in KBr discs.

All carbon-hydrogen analyses were carried out on the Thomas Micro Carbon-Hydrogen Analyzer, model 35.

II. SUPPLIED CHEMICALS

The only olefin used was cyclooctatetraene (C_8H_8) which was used as obtained from Chemical Intermediates and Research, Cuyahoga Falls, Ohio.

The potassium hexachloroplatinate(IV) was prepared in the Inorganic Preparations class at Wisconsin State University La Crosse.

III. GENERAL PROCEDURES

All of the reactions involving a Grignard reagent were carried out in a dry nitrogen atmosphere.

IV. PREPARATIONS

Diiodo(cyclooctatetraene)platinum(II).[11]

A 20 g. (41.1 mmoles) sample of potassium hexachloroplatinate(IV) (K_2PtCl_6) is dissolved in approximately 650 ml. of water in a 1500 ml. flask. The flask is heated until the compound is dissolved, then cooled to room temperature. Another 100 ml. of water is added to keep the solid from precipitating.

An 8 g. (76.9 mmoles) sample of cyclooctatetraene is added to the solution followed by 16.4 g. (98.8 mmoles) of KI, previously dissolved in 25 ml. of warm water. The solution appears red-black.

About 3.5 g. of sodium bisulfite is dissolved in approximately 30 ml. of water and then added to the solution, resulting in the formation of a precipitate, leaving the liquid portion a light yellow color. To ensure a complete reaction, the mixture is stored at ambient conditions for 24 hours.

The precipitate is filtered, washed with approximately 25 ml. each of ethyl alcohol and ethyl ether and allowed to dry on the filter paper. The resulting product is dissolved in approximately one liter of dichloromethane, decolorized with charcoal, filtered through fine (Whattman 50) filter paper and recovered by evaporation of the dichloromethane. The pure diiodo(cyclooctatetrane)platinum(II) appears as bright, red-orange crystals.

18.048 g. (32.65 mmoles) was obtained for a 79.3% yield.

Cis-bis(o-tolyl)(cyclooctatetraene)platinum(II).[3]

All apparatus is thoroughly dried prior to starting the reaction. A Grignard reagent is prepared by placing 1.5 g. of magnesium turnings into a three-neck flask with 50 ml. of anhydrous ethyl ether and an iodine crystal. From a separatory funnel fitted to the flask, a mixture of 6 g. (27.6 mmoles) of o-iodotoluene ($C_6H_4CH_3I$) and 50 ml. of anhydrous ethyl ether is allowed to drop at a slow, steady rate into the flask. (A magnetic stirrer is employed to stir the mixture.) After the ether solution is added, stirring is continued for and additional 15-20 minutes to ensure a complete reaction. During the reaction, the solution turns a cloudy, green-white color.

The contents of the flask are slowly transferred to a second flask containing 5 g. (9.04 mmoles) of diiodo(cyclooctatetraene)platinum(II) and 25 ml. of benzene. This mixture is stirred until all of the platinum is reacted.

The contents of this flask are poured into 25 ml. of a saturated NH_4Cl solution and stirred. The organic layer is separated and the aqueous layer is washed with benzene until all of the product is removed. All organic layers are saved and filtered through cotton. The filtrate is then air evaporated yielding only crystalline product.

The product is purified by dissolving in dichloromethane, decolorized with charcoal, filtered through a fine

(Whattman 50) filter paper and recrystallized using a dichloromethane and hexane solvent pair. (An alternate method of purification which produces a more pure product but a lower yield, consists of washing the crystals in a small amount of benzene.) After normal recrystallization, the pure crystals are a dull, yellow-white color.

In three preparations a total of 5.31 g. of the pure product was recovered for a total yield of 19.6%.

Cis-bis(o-tolyl)bis(triphenylarsine)platinum(II).

A 1.892 g. sample (3.94 mmoles) of bis(o-tolyl)-(cyclooctatetraene)platinum(II), 2.430 g. (7.88 mmoles) of triphenylarsine and 150 ml. of benzene are placed in a 250 ml. flask equipped with a reflux condenser and refluxed for one hour. The resulting solution is decolorized with charcoal, filtered and air evaporated. The pure product is recovered by recrystallization from benzene. The pure crystals are a dull white color.

In two preparations, a total of 2.02 g. of product was recovered for a yield of 24.1%.

Analysis; Calc: Pt, 19.71; C, 60.67; H, 4.48. Found:
Pt, 20.10; C, 57.77; H, 4.52.

Decomposition point: 210°C. Melting point: 217-222°C.

For I. R. spectrum, see appendix, #1.

Reaction of Cis-bis(o-tolyl)bis(triphenylarsine)platinum(II) with Methyl Iodide.

A 0.30 g. (0.32 mmoles) sample of cis-bis(o-tolyl)-bis (triphenylarsine)platinum(II) is placed in a glass test tube containing approximately 3 ml. of methyl iodide. The sample is sealed in the tube and allowed to stand at room temperature for 24 hours. No reaction occured. The sample was then swirled under ultraviolet light for 24 hours, placed in a hot water bath at 60°C. for 24 hours and exposed to gamma rays for 24 hours to try to promote a reaction through a free radical formation.

No visible reaction occured so the sample was removed from the tubes and air evaporated to crystals. I.R. analysis indicated that the starting product, cis-bis(o-tolyl)bis-(cyclooctatetraene)platinum(II) was recovered.

Reaction of Cis-bis(o-tolyl)bis(triphenylarsine)platinum(II) with Ethyl Iodide.

The procedure followed and the amounts of reactants used are the same as those in the preceding section.

After swirling under an ultraviolet light for 24 hours, heating in a hot water bath at 60°C. for 24 hours and air evaporating to crystals, I.R. analysis indicated that the starting product, cis-bis(o-tolyl)bis(triphenylarsine)-platinum(II) was recovered.

Reaction of Cis-bis(o-tolyl)bis(triphenylarsine)platinum(II) with Propyl Iodide.

The procedure followed and results obtained are identical to those presented in the preceding section.

Bis(m-tolyl)(cyclooctatetraene)platinum(II).

The apparatus and proportions used to prepare the complex and the method of purification are the same as those followed in the preparation of bis(o-tolyl)(cyclooctatetraene) platinum(II). M-iodotoluene is substituted for o-iodotoluene in this reaction.

The pure crystals were a light cream color. 0.617 g. of pure product were recovered for a yield of 14.2%.

Analysis; Calc: C, 54.8; H, 4.57. Found: C, 54.30; H, 4.45.
Melting point with decomposition: 143-148°C.
For I.R. spectrum, see appendix, #2.

Reaction of bis(m-tolyl)(cyclooctatetraene)platinum(II) with Triphenylarsine.

A 0.1 g. (0.208 mmoles) sample of bis(m-tolyl)-cyclooctatetraene)platinum(II) is placed in a 25 ml. flask containing 10 ml. of benzene and approximately 0.2 g. of triphenylarsine. The mixture is heated over a steam bath for one hour. A black tar was recovered which yielded no crystalline product.

In a second attempt, a 0.1 g. (0.208 mmoles) sample of bis(m-tolyl)(cyclooctatetraene)platinum(II), 0.2 g. of triphenylarsine and 10 ml. of benzene were placed in a flask attached to a reflux condenser and refluxed for one hour. The black tars again indicated that decomposition of the product had occured.

Reaction of Bis(m-tolyl)(cyclooctatetraene)platinum(II) with Methyl Iodide.

A 0.1 g. (0.208 mmoles) sample of bis(m-tolyl)(cyclooctatetraene)platinum(II) is placed in a test tube with approximately 3 ml. of methyl iodide. The solid dissolves and the tube is sealed. No visible reaction occured after standing at room temperature for 24 hours. Swirling under ultraviolet light and storage in a hot water bath also failed to bring about an obvious reaction. I.R. analysis of the crystals obtained by evaporation of the solution indicated that the starting product was recovered.

Cis-bis(m-tolyl)bis(pyridine)platinum(II).

A 0.1 g. (0.208 mmoles) sample of bis(m-tolyl)(cyclooctatetraene)platinum(II) is placed in a 25 ml. flask with 3 ml. pyridine and 5 ml. benzene and heated over a steam bath for one hour. When a color change occurs, the solution is removed and air evaporated to crystals. The product is purified by washing with benzene. The pure crystals are white. 0.066 g. of the pure product was recovered for a yield of 59.4%.

Analysis; Calc: C, 53.63; H, 4.83. Found: C, 54.7; H, 4.71.

For I.R. spectrum, see appendix, #3.

CHAPTER IV

RESULTS AND DISCUSSION

Production of Bis(m-tolyl)(cyclooctatetraene)platinum(II) using a Grignard Reagent.

It has been reported that organo groups will replace halides in a cyclic polyolefin platinum(II) complex by the reaction of a Grignard reagent with the complex.[19,20]

More recently, Kistner and co-workers have reported mononuclear(cyclooctatetraene)platinum(II) ortho and para-tolyl derivatives produced by reacting diiodo(cyclooctatetraene)platinum(II) with o-tolyl and p-tolyl Grignard reagents.[3]

In this study, extending the series of cyclic polyolefin platinum(II) aryls, a m-tolyl platinum(II) derivative was prepared by reacting diiodo(cyclooctatetraene)platinum(II) with (m-tolylmagnesium iodide) to replace both iodo groups on the complex. The reaction proceeds as shown.

$$C_8H_8PtI_2 + (m\text{-}C_6H_4CH_3)MgI(\text{excess}) \longrightarrow C_8H_8Pt(m\text{-}C_6H_4CH_3)_2$$

From Chatt's proposal[1,2] concerning the stability of ortho and para substituted groups and the report by Kistner and co-workers[3] that complex stability decreased as the substituted groups went from the ortho to para position on the aromatic ring, it would be expected that the stability of bis(m-tolyl)(cyclooctatetraene)platinum(II) would fall somewhere between the corresponding o-tolyl and p-tolyl derivatives. Thermal decomposition of the compound supported this prediction. The compound melted and decomposed at 143-148°C. which fell between the previously reported o-tolyl (171-174°C.) and p-tolyl (137-140°C.) derivatives.[3]

Stabilization of a Bis(aryl)platinum(II) Complex with Triphenylarsine.

Chatt and Shaw have reported the stabilization of aryl and alkyl platinum(II) complexes with strong crystal field splitting phosphines, amines and arsines.[1,2]

More recently, Kistner and co-workers have reported using triphenylphosphine as a strong crystal field splitting ligand to produce cis-bis(o-tolyl)bis(triphenylphosphine)-platinum(II).[3]

To expand the group of substituents which would stabilize the aryl platinum(II) complexes, triphenylarsine was used to replace the diolefin from bis(o-tolyl)(cyclooctatetraene)platinum(II). The reaction proceeds as shown.

$$C_8H_8Pt(o\text{-}C_6H_4CH_3)_2 + 2\ (C_6H_5)_3As \xrightarrow{C_6H_6} \left[(C_6H_5)_3As\right]_2Pt(o\text{-}C_6H_4CH_3)_2 + C_8H_8$$

As expected, the triphenylarsine ligand produces a strong enough crystal field splitting to stabilize the complex. This idea was supported by melting point data which showed that cis-bis(o-tolyl)bis(triphenylarsine)platinum(II) darkened and decomposed at 210°C. and melted at 217-222°C. This value is higher than the melting point previously reported for cis-bis(o-tolyl)bis(triphenylphosphine)platinum(II). (179-189°C.)[3]

The higher melting point may be due to the relative sizes of the d-orbitals in the phosphine and arsine ligands. The 4d orbitals of the arsine are larger and should overlap with the 5d orbitals of the platinum to a greater extent than the 3d orbitals of the phosphine. The greater backbond overlap should result in a more stable complex.

It is believed that the arsine provides an electron pair to sigma bond with an overlapping, empty $5d6s6p^2$ hybrid orbital of the platinum ion while an overlap of the filled 5d orbital of the platinum ion and the empty 4d orbital of the arsine provides a backbond through a shift in electron density to strengthen metal-ligand bonding, providing greater stability to the complex.

The concept of backbond formation is reinforced by the previously reported melting point of cis-bis(o-tolyl)bis-(pyridine)platinum(II) which, at 155-158°C.[3] is lower than the triphenylarsine and triphenylphosphine derivatives. Although the N in pyridine is a stronger Lewis base than phosphine or arsine, the possibility of a backbond does not exist.

Stabilization of a Bis(m-tolyl)platinum(II) Derivative with Pyridine.

In an attempt to characterize the bis(m-tolyl)(cyclooctatetraene)platinum(II) complex, the complex was reacted with triphenylarsine. A black tar resulted that could not be identified.

Kistner and co-workers have reported pyridine replacing a cyclic diolefin from bis(o-tolyl)(cyclooctatetraene)platinum(II) to yield bis(o-tolyl)bis(pyridine)platinum(II).[3] In this study, the same reaction was attempted with bis(m-tolyl)(cyclooctatetraene)platinum(II), resulting in a displacement of the diolefin by pyridine. The reaction proceeds as shown.

$$C_8H_8Pt(m\text{-}C_6H_4CH_3)_2 + 2C_5H_5N(\text{excess}) \longrightarrow (C_5H_5N)_2Pt(m\text{-}C_6H_4CH_3)_2$$

Reactions with Organo-Iodides.

Attempts were made to react cis-bis(o-tolyl)bis(triphenylarsine)platinum(II) with methyl, ethyl and propyl iodide and to react bis(m-tolyl)(cyclooctatetraene)platinum(II) with methyl iodide.

In previous studies it was reported that o-tolyl platinum(II) derivatives containing triphenylphosphine and cyclic diolefins usually reacted with methyl iodide to replace one or both o-tolyl groups, coupled with a methyl iodide addition yielding a platinum(IV) complex.[3,4]

Cis-bis(tolyl)bis(pyridine)platinum(II) complexes have been reacted with organoiodides to yield platinum(IV) complexes and reactions with allyl iodides have produced compounds in which a triiodide ion occupies a position in the coordination sphere.[4]

In this study, reactions between the platinum complexes and organoiodides could not be induced.

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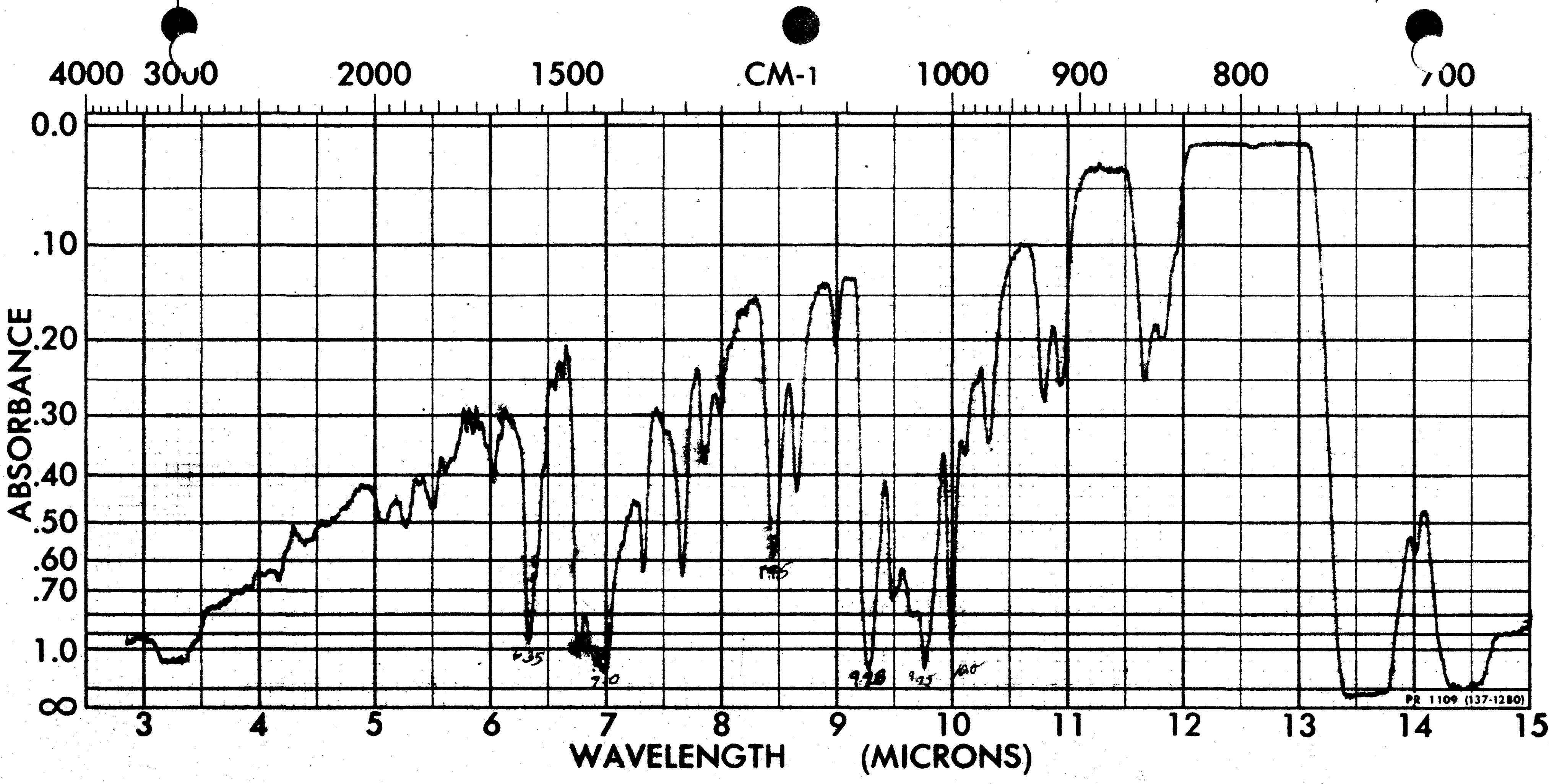
APPENDIX



SPECTRUM NO. 1

SAMPLE

$(\phi_3As)_2Pt(OT)_2$

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

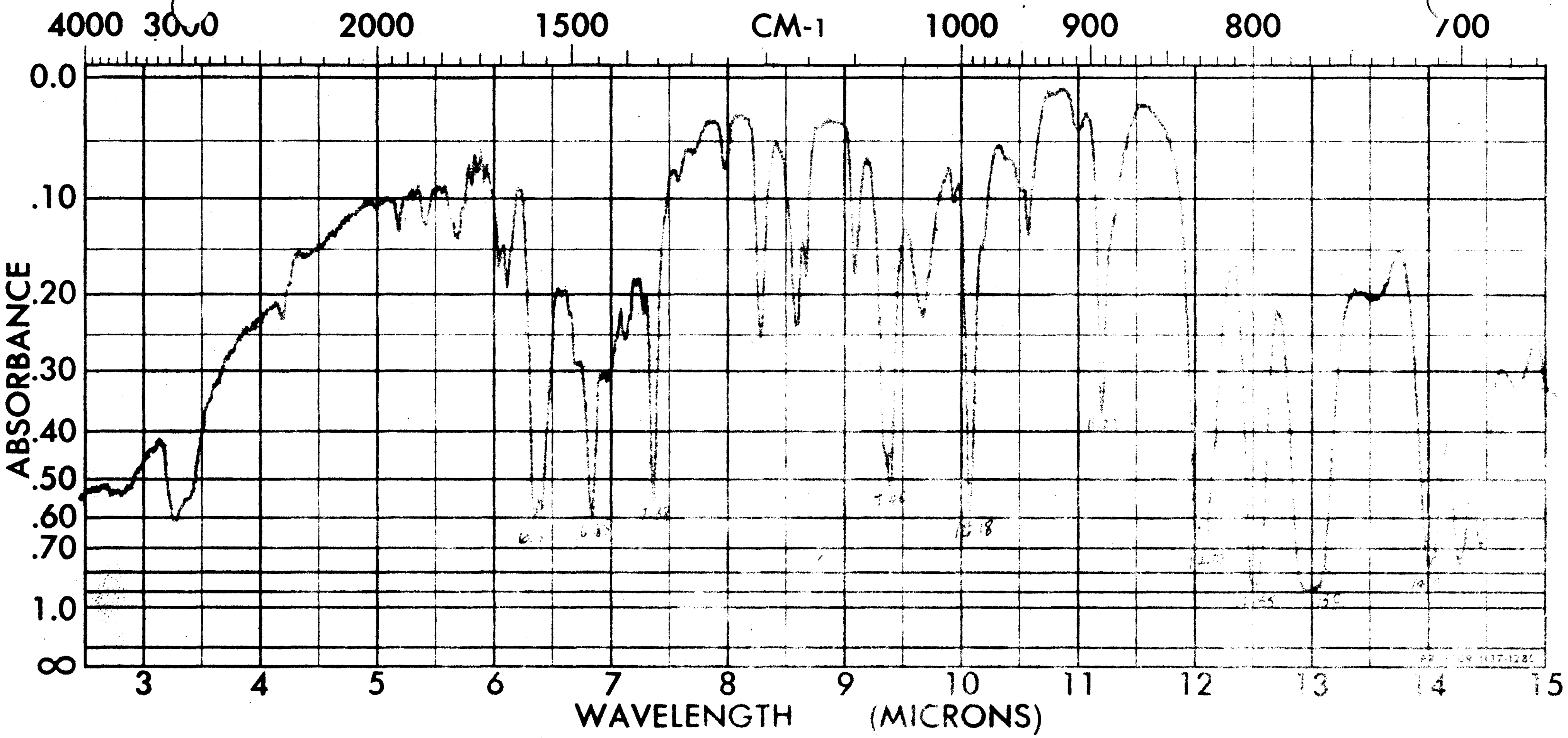
2.

DATE

OPERATOR

REMARKS

SAMPLE $(\phi_3As)_2 Pt(O$



SPECTRUM NO. 2

SAMPLE C_8H_8

Pt(m-I)$_2$

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

DATE

OPERATOR

REMARKS

SPECTRUM NO. 2
SAMPLE C_8H_8 Pt(m-I)$_2$

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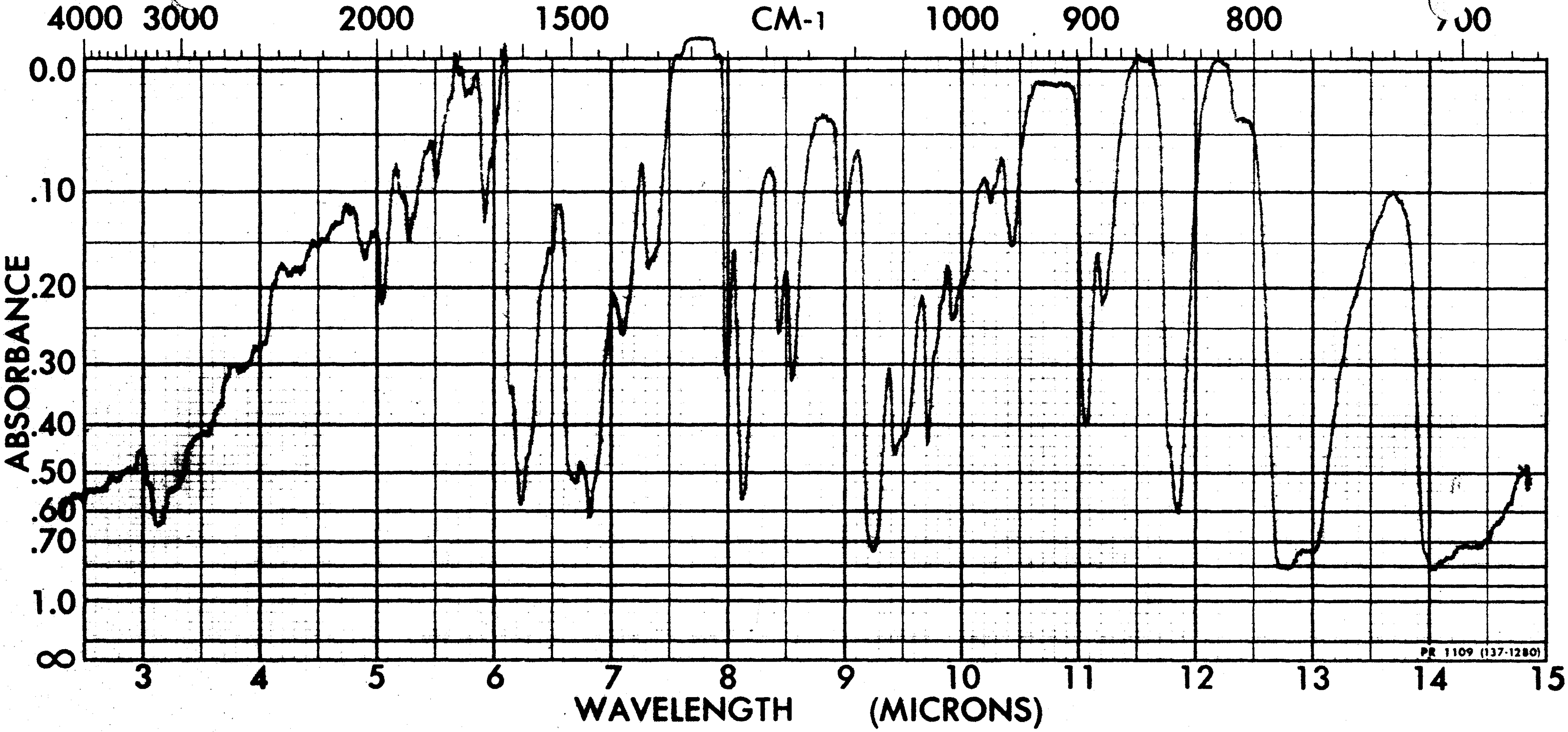

SPECTRUM NO. 3	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
$(Py)_2Pt(m\text{-}T)_2$	PURITY	2.	
	PHASE	DATE	
	THICKNESS	OPERATOR	

SPECTRUM NO. 3
SAMPLE $(Py)_2Pt(m\text{-}T)_2$

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