

ORGANOMETALLIC REACTIONS

Edited by

Ernest I. Becker

Minoru Tsutsui

VOLUME

3

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Volume 3

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Preface

The primary literature on organometallic chemistry has undergone phenomenal growth. The number of papers published from 1955 to 1970 is about equal to all prior literature. Together with this intense activity there has developed a complexity in the literature. Thus specialized texts and teaching texts, a review journal, an advances series, and a research journal have all appeared during this period. The present series also reflects this growth and recognizes that many categories of organometallic compounds now have numerous representatives in the literature.

The purpose of *Organometallic Reactions* is to provide complete chapters on selected categories of organometallic compounds, describing the methods by which they have been synthesized and the reactions they undergo. The emphasis is on the preparative aspects, although structures of compounds and mechanisms of reactions are briefly discussed and referenced. Tables of all of the compounds prepared in the category under consideration and detailed directions for specific types make these chapters particularly helpful to the preparative chemist. While the specific directions have not been refereed in the same way as are those in *Organic Syntheses* and *Inorganic Syntheses*, the personal experiences of the authors often lend special merit to the procedures and enable the reader to avoid many of the pitfalls frequently encountered in selecting an experimental procedure from the literature.

We acknowledge a debt of gratitude to the contributing authors whose dedication and skill in preparing the manuscripts cannot adequately be rewarded. It has been gratifying to note that virtually all invitations to contribute have been accepted at once. We also owe thanks to the publisher for encouragement and even the "gentle prod" when necessary to see these volumes to their completion.

Ernest I. Becker
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September 1970

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I. INTRODUCTION

In 1959 the Consortium für elektrochemische Industrie GmbH*³⁴² presented a new process for the commercial production of acetaldehyde from ethylene by direct oxidation. This new process not only filled a gap in the availability of basic organic intermediates from petrochemical resources but also, by its intricate catalysis, stimulated elementary investigations in organometallic chemistry.

The reaction between ethylene and oxygen to yield acetaldehyde is effected by an aqueous solution of palladium chloride and cupric chloride, which brought to memory a reaction described by Phillips in 1894:²⁹⁵



At this time Phillips studied the behavior of various hydrocarbons toward oxidizing agents. He observed a black precipitate of palladium metal when he passed ethylene into an aqueous solution of palladium chloride. The olefin was oxidized to acetaldehyde. Evidently, the stoichiometric reaction of a noble metal salt with a scarce olefin found little commercial interest. Phillips' reaction was suggested for analytical application or for the separation of palladium from other noble metals.²⁷⁶

Only the discovery that catalytic quantities of palladium salt could be successfully employed for oxidation reactions in the presence of a suitable oxidant (which prevents the precipitation of the palladium metal) turned broad attention to palladium chemistry and reactions of other noble metals. A variety of new specific reactions performed with PdCl_2 was elaborated: the oxidation of olefinic to carbonyl compounds in aqueous or nonaqueous solutions; the allylic oxidation of olefins; oxidative coupling; as well as a great many specific catalytic reactions without the accompanying oxidation, e.g., hydrolysis of substituted olefins, transvinilation, carbonylations, oligomerization, isomerization, etc.

All of these reactions proceed through organometallic intermediates. In most cases the initial step is formation of a π -complex of an olefin with a noble metal atom. Such complexes have been known since 1831 when Zeise⁴²¹ described a compound $\text{KCl} \cdot \text{PtCl}_2 \cdot \text{C}_2\text{H}_4$, the "sal Kalico Platinicus inflammabilis," which he had obtained by treating a boiling alcoholic solution of hexachloroplatinic acid with potassium chloride. Zeise's salt remained a dubious academic curiosity rather than an inspiring event. It took nearly a century to turn the attention of researchers to such compounds. The first palladium-olefin complex was described in 1938 by Kharasch et al.¹⁹⁰ With the impulse of commercial success, extensive research flared up in this field. The engagement grew worldwide after Moiseev and co-workers²⁵⁰ had reported a synthesis of vinyl acetate from ethylene in acetic acid solution with PdCl_2 .

* Research organization of Wacker-Chemie GmbH, Munich, Germany.

Within a few years a multitude of publications appeared on new reactions with palladium or other noble metal salts; on new complexes, e.g., π -allyl-palladium compounds;³⁴⁰ or on kinetics and mechanisms. These compounds will be critically reviewed in the following chapters.*

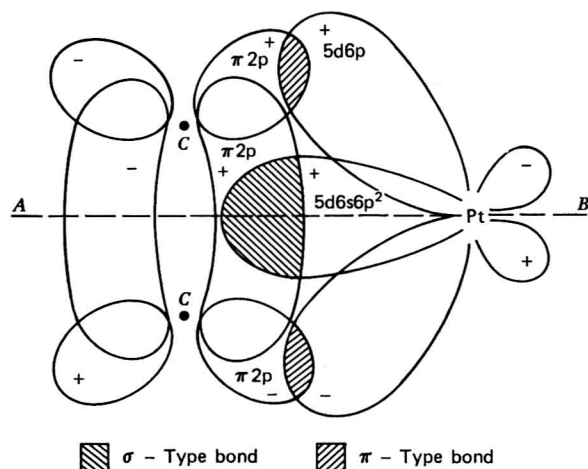
II. BONDS AND STRUCTURES OF π -COMPLEXES

Bonds and structures of π -complexes have been extensively described in summarizing publications, e.g.,^{21,22,99,100,116,124,130} We confine ourselves in this paper to a presentation of the model generally accepted for metal-olefin complexes. It has been shaped by Dewar⁸⁵ for silver-olefin compounds and was applied by Chatt and Duncanson⁴⁷ for the interpretation of platinum-olefin complexes. We use the same model for describing palladium-olefin complexes and their behavior, as well as olefin complexes of other metals of the platinum group. According to this model the olefin should be bonded to the metal by the concerted action of two types of bonds: a σ -type which is brought about by the overlapping of the π -orbital of the olefin with a $5d\ 6s\ 6p^2$ hybrid orbital of the platinum and a π -type by the overlapping of a filled $5d$ orbital of the metal with the antibonding orbitals of the olefin. Since the electron donor property of the olefin prevails, its carbon atoms carry a partial positive charge. See Fig. 1.

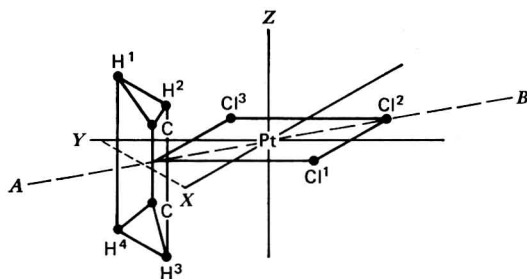
In Zeise's salt the ethylene is symmetrically bonded to the platinum atom, its C—C axis being oriented perpendicular to the plane of the four-coordinated planar complex. The plane of the hydrogen atoms lies parallel to the *cis*-Cl-Z-plane, but the hydrogen atoms are repelled away from the metal behind the olefinic carbon atoms which, therefore, adopt a partial sp^3 character. Nevertheless, the C—C double bond remains almost unchanged.

Coordination of the olefin only causes a lengthening of the C—C distance. This could be demonstrated by the lowering of the C—C stretching frequency for about 100 wave numbers.⁴⁷ Infrared spectroscopic reinvestigation of Zeise's salt—including far infrared, to determine the metal-olefin bond strength—has been published recently.^{127,302} For spectroscopic data on $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ and its deuterio- and palladium-analogues, see Ref. 128. The structure outlined above was essentially confirmed by a crystal structure determination of $\text{K}(\text{PtCl}_3\text{C}_2\text{H}_4) \cdot \text{H}_2\text{O}$.⁴¹⁴ The distances between the platinum atom and the *cis*-chloro atoms are both the same (2.32 Å); only the distance between the platinum atom and the chlorine atom in *trans* position to the olefin was found to be slightly longer (2.42 Å). This lengthening is attributed to the "*trans* effect" of the olefin.^{15,116}

* Patent literature is cited only where examples that have not been published elsewhere are given. But no warranty shall be deduced or construed from the literature cited for priorities.



(a)



(b)

Fig. 1. Orbitals used in the combination of ethylene with platinum. Spatial arrangement of atoms in $C_2H_4PtCl_3^-$. σ -Type bond; π -type bond.

The olefin need not be rigidly fixed to the metal atom, since for rhodium^{62,67a} and platinum³⁰ olefin complexes there is evidence of a rotation of the olefin about its coordination axis with an activation energy of 15 kcal for $[(C_2H_4)_2Rh(C_5H_5)]$.^{67a} An analogous structure was determined by Dempsey and Baenziger⁸³ by X-ray analysis of the binuclear chloro-bridged ethylene palladium chloride complex prepared by Kharasch et al.¹⁹⁰ In this complex the axes of the ethylene molecules are also perpendicular to the plane of the Pd_2Cl_2 system with the planes intersecting in the centers of the ethylenic double bonds.

Substituted ethylenes are asymmetrically bonded to the central metal in analogous complexes. This was found for the corresponding binuclear

styrene palladium chloride complex by Holden and Baenziger.¹⁵⁷ The carbon atoms of the aromatic ring of the complexed styrene are out of plane, whereas free styrene has a planar structure. The C—C axis of the ethylenic group is tipped away from the plane of the chloro-bridges, its bond being off-center and shifted to the terminal carbon atom. Angles and distances can be seen in Fig. 2.

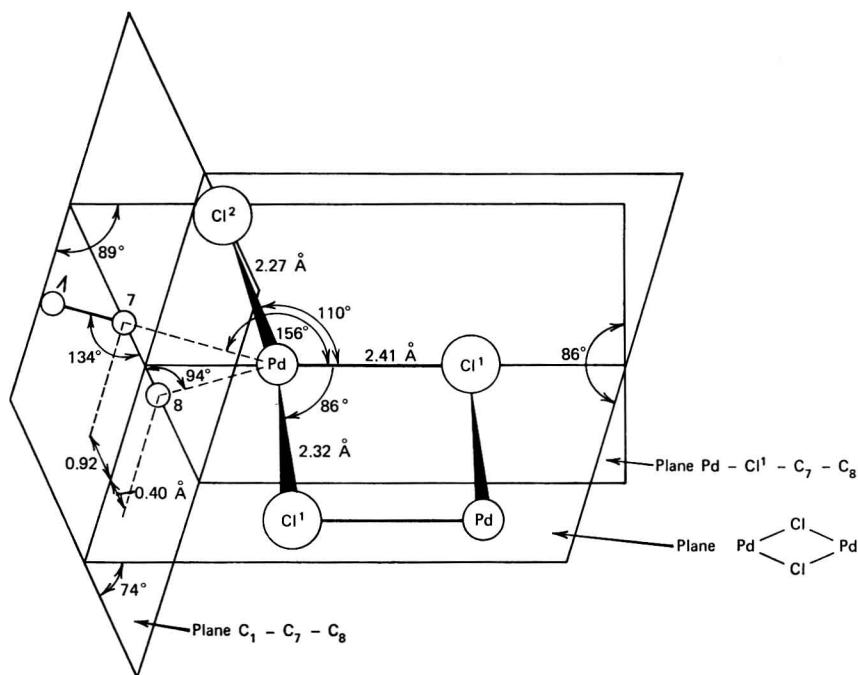


Fig. 2. Detailed sketch of the styrene-palladium chloride complex. The large atoms are chlorine; the medium-size atoms are palladium; and the smallest are the carbon atoms C_1 , C_7 , and C_8 of styrene.

The prototype of π -allyl complexes of palladium $[\text{C}_3\text{H}_5\text{PdCl}]_2$ was first described by Smidt and Hafner.³⁴⁰ The allylic anion is bonded to the palladium atom as a bidentate ligand by two delocalized electron pairs and symmetrically oriented to the $(\text{PdCl})_2$ bridge. Therefore, they occupy two square planar coordination sites. This proposal for a "sandwich-type" bond and structure was confirmed by nuclear magnetic resonance (NMR) studies⁸² and by X-ray analysis.^{272,321,351} According to Oberhansli and Dahl,²⁷² the plane of the three allylic carbon atoms is declined by an angle of 108° to

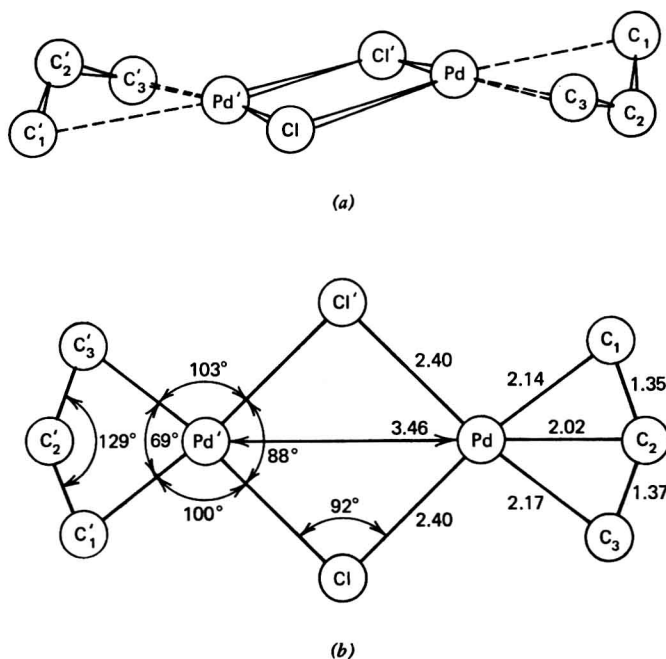


Fig. 3. The molecular configuration of $(C_3H_5)PdCl_2$, intramolecular distances and angles by Smith.

the Pd_2Cl_2 -bridge system with the central carbon atom tipped away from the palladium. The five hydrogen atoms are coplanar with the allylic plane.³⁵¹ Bond angles and distances are shown in Fig. 3.

The allylic carbon atoms are equidistant to the palladium atom;³⁵¹ the $Pd-Cl$ distances agree fairly with the *trans*- $Pd-Cl$ bonds in olefin palladium complexes. This lengthening of the $Pd-Cl$ bonds in $[\pi\text{-allyl } PdCl]_2$ leads to the assumption that beyond a σ -type bond formed by the overlap of the two π -hybrid orbitals of the allylic ligand with unoccupied square planar dsp^2 orbitals of the metal atom, other π -type back bondings—similar to the ones proposed for olefin complexes—are present. The nature of the bonding in π -allyl complexes of transition metal ions was discussed using bonding energy data.¹⁸⁹

Allylic groups in mononuclear complexes of platinum group metals with different ligands that can be obtained, e.g., from bis(π -allyl $PdCl$) complexes by reactions with *tert*-phosphines or arsines are bound unsymmetrically. From NMR spectra three different conformational rearrangements have been discussed:^{402,405}