from the least squares treatment. A complete list of calculated and observed structure factor values based on the observed electron density map values has been deposited with the American Documentation Institute.[15]

Discussion of the Structure

The arrangement of the palladium and chlorine atoms is quite definitely established; the positions of the carbon atoms may be considered fairly uncertain. The palladium atoms are joined by two bridge chlorine atoms as shown in Figs. 3 and 4. The dimers stack above one another in the *c* direction so that the chlorine atoms are located in the octahedral positions about the palladium atoms above and below the plane of the dimer although too far away for appreciable covalent binding. The two crystallographically different dimers do not have exactly the same dimensions although the angles between the bonds are similar.

The intensity data quite definitely place the ethylene groups in the *trans* position of the dimer. In an earlier stage of refinement an ethylene group and a chlorine atom were interchanged on one of the dimers. Changing them to their present positions caused a very noticeable improvement in the agreement of the calculated and observed structure factors, especially for the non-body-centered type reflections. The carbon atoms of ethylene could not be resolved nor could a choice be made between space groups Pbam and Pba2 since it depends only on the carbon atom positions. The most probable arrangement is to assume that the plane of the ethylene molecule is perpendicular to the line joining the palladium atom and the center of the double bond.

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[15] The list has been deposited as Document number 4604 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints, or $1.75 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Crystal Structure of Styrene–Palladium Chloride

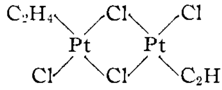
BY J. R. HOLDEN AND N. C. BAENZIGER

RECEIVED MAY 16, 1955

The crystal structure of styrene–palladium chloride has been determined. The unit cell is monoclinic with a = 13.50 Å., b = 4.99 Å., c = 19.19 Å., β = 135.5°. The space group is $P2_1/c$. The molecules are dimers joined by a double chlorine bridge. The atomic configuration indicates that the styrene–palladium bond consists of interaction between the pi orbital of the double bond and a dsp^2 orbital of palladium.

Introduction

Palladium dichloride and platinum dichloride form complexes with olefins containing one molecule of olefin per metal atom. Molecular weight determinations indicate that the compounds usually exist in solution in the form of dimers.[1–3] Anderson[4] and later Chatt[3] proposed the structure to account for the molecular formula, the dimeric nature



and the customary planar square (dsp^2 hybridization) configuration of palladium and platinum. Chatt[5] describes the olefin–metal bond as consisting of an interaction of the pi orbital of the double bond with the dsp^2 orbital of the metal atom. Overlap of these two orbitals requires that a dsp^2 orbital lie approximately in a plane perpendicular to the plane of the ethylene group of the olefin and be directed toward the axis of the double bond.

Although the platinum compounds are more stable than their palladium analogs, the latter are more suitable for X-ray diffraction studies of their structure because of the lower atomic number of palladium. The crystal structure of ethylene–palladium chloride has been studied by Baenziger and Dempsey.[6] Although the ethylene part of the structure was not resolved, the data indicated that the axis of the ethylene group is perpendicular to the plane of the complex, the carbon atoms of the ethylene being equal distances above and below the plane of the complex. A substituted ethylene complex presents the possibility of resolving the carbon atoms and determining the orientation of the double bond. Attempts to obtain crystals of large enough size for X-ray diffraction purposes were successful only for the styrene complex.

Experimental

Styrene–palladium chloride was prepared by the method of Kharasch and Ashford[1] employing bis-benzonitrile–palladium chloride as an intermediate. Single crystals of sufficient size and perfection for diffraction study were grown from a solution of the compound in styrene. The crystals are extremely slender, amber needles.

Single crystal X-ray data were obtained by the Weissenberg and Buerger precession methods. General (*hkl*) intensity data were obtained by the multiple film, equiinclination Weissenberg technique. (*hk*0) and (0*kl*) data were obtained from a Buerger precession camera using the same crystal and several timed exposures. Intensities were estimated by visual comparison of the photographic blackenings with those of a graduated intensity scale.

Structure Determination.—The unit cell of styrene–palladium chloride is monoclinic with the symmetry of space group $P2_1/c$. The dimensions are a' = 13.50 Å., b' = 4.99 Å., c' = 19.19 Å., β' =

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[1] M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1733 (1936).

[2] M. S. Kharasch and R. C. Seyler, *ibid.*, **60**, 884 (1938).

[3] J. Chatt, *J. Chem. Soc.*, 3340 (1949).

[4] J. S. Anderson, *ibid.*, 970 (1934).

[5] J. Chatt and L. A. Duncanson, *ibid.*, 2939 (1953).

[6] N. C. Baenziger and J. N. Dempsey, THIS JOURNAL, **77**, 4984 (1955).

135.5°, $Z = 4$, $V = 922$ Å.^{3}, $D_x = 2.02$ g./cc. A more convenient cell can be chosen, for which β is nearly equal to 90 degrees, by designating the short diagonal of the oblique face of the above cell as the new c-axis. This cell requires a new space group designation, $P2_1/n$, which does not appear explicitly in the "International Tables for X-ray Crystallography." Its dimensions are: $a = 13.50$ Å. $b = 4.99$ Å., $c = 13.69$ Å., $\beta = 90.4°$. The coördinates of equivalent positions for the "right-angled" cell (unprimed symbols) are x,y,z; $\bar{x},\bar{y},\bar{z}$; $^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$; $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$. The conversion formulas relating the two cells are

$$\begin{array}{lll} a' = a & h' = h & x' = x + z \\ b' = b & k' = k & y' = y \\ c' = c - a & l' = l - h & z' = z \end{array}$$

All plane indices are given in terms of the "right-angled" cell; the final positions of the atoms are given in terms of both cells.

The x and z coördinates of the palladium and chlorine atoms were obtained from a Patterson projection on the (010) plane. Structure factor signs obtained from these positions were used in the calculation of an (010) electron density projection. This projection, shown in Fig. 1, contains peaks for all atoms of the cell except the hydrogen. The y parameter, 0.125, was assigned to the palladium atom to account for the fact that reflection (020) is absent. The ($hk0$) structure factor signs obtained from this palladium position were used in the calculation of an (001) electron density projection. The resolution in this projection is limited by the fact that only about thirty ($hk0$) reflections lie within the range of observation. The projection contains peaks for the chlorine atoms but no resolved peaks for the carbon atoms.

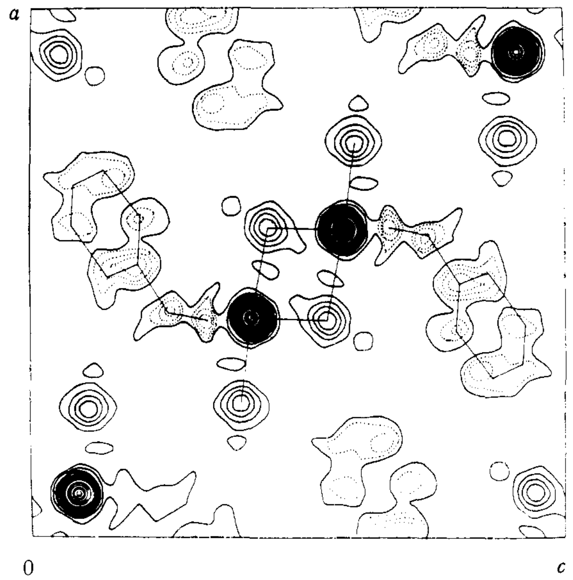

Fig. 1.—Projection of the electron density of styrene-palladium chloride on to (010).

Signs for the observed (hkl) structure factors obtained from the palladium and chlorine contributions based on positions found from the (010) and (001) electron density projection were used to evaluate the electron density in three dimensions. The observed intensities from the upper layer films were scaled to correspond to those of the zero layer by comparing the observed intensities of the ($0kl$) reflections with those obtained from the ($0kl$) precession camera films. The electron density was calculated, at intervals of one sixtieth of the cell length in all three directions, within cylinders parallel to the b-axis and including the positions of the peaks on the ($h0l$) projection. The positions of the electron density maxima were then located by a three dimensional adaptation of Booth's[7] extrapolation method. Well defined maxima were observed for all of the atoms of the compound. The coördinates of the atoms obtained from this three-dimensional determination of electron density are listed in Table I. All Patterson projections, electron density determinations and (hkl) structure factors were computed by means of International Business Machines punched card equipment.

Structure factors corresponding to the atomic positions obtained from the electron density determination were calculated for all reflections within the range of observation. Sign changes resulted for only a few weak reflections. A temperature factor was computed and applied to the calculated structure factors. The discrepancy factor, defined as

$$R = \frac{\Sigma\,||F_{\text{calcd}}| - |F_{\text{obsd}}||}{\Sigma\,|F_{\text{obsd}}|}$$

is equal to 0.168 including only the observed reflections. The temperature factor, B, is equal to 4.35 Å.^{2}. A complete list of calculated and observed structure factors has been deposited with the American Documentation Institute.[8] The observed atomic positions were corrected for series termination errors and the minor sign errors by the "back-shift" method.

The shifts of the observed maxima from the positions for which the corresponding atoms had been calculated are listed in Table I along with the corrected atomic coördinates. The standard deviations listed in this table were obtained by Cruickshank's method[9] and account only for random errors in the F_{obsd} data.

Discussion

The important interatomic distances within the styrene–palladium chloride molecule are listed in Table II. Figure 2, which is a projection of the structure on the (010) plane, gives the numbering system, the distance of closest approach of adjacent molecules, and the Pd–Cl bond angles. The distances of closest approach between molecules in the b direction are C_3–$C_5{}' = 3.64$ Å. and Pd–$Cl_1{}' = 3.99$ Å.

The best plane through the observed positions of the atoms of the benzene ring was determined by a

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(7) A. D. Booth, "Fourier Techniques in X-Ray Organic Structure Analysis," Cambridge University Press, Cambridge, England, 1948, pp. 63.

(8) The list has been deposited as Document number 4605 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints, or $1.75 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(9) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

TABLE I

STRUCTURE REFINEMENT AND FINAL POSITIONS

x,y,z—positions in space group P2_1/n, (β = 90°27′); x',y,z—positions in space group $P2_1$/c, (β' = 135°).

Atom		Obsd position	Shift	Final position	Standard dev.
Pd	x	0.0825	0.0007	0.082	0.0002
	y	.1257	.0013	.124	.0008
	z	.0863	.0000	.086	.0002
	x'			.168	
Cl_1	x	0.0842	−0.0010	0.085	0.001
	y	.8345	.0067	.828	.003
	z	.9450	− .0020	.947	.001
	x'			.032	
Cl_2	x	0.2480	0.0002	0.248	0.001
	y	.0987	.0162	.083	.003
	z	.1057	− .0007	.106	.001
	x'			.354	
C_1	x	0.0148	0.0007	0.014	0.002
	y	.8740	.0138	.860	.010
	z	.6980	− .0015	.700	.002
	x'			.714	
C_2	x	0.0118	0.0068	0.005	0.003
	y	.9288	− .0107	.940	.008
	z	.3627	.0060	.357	.004
	x'			.362	
C_3	x	0.0842	−0.0028	0.087	0.002
	y	.1708	− .0055	.176	.011
	z	.5782	.0022	.576	.005
	x'			.663	
C_4	x	0.1680	0.0020	0.166	0.003
	y	.0437	.0163	.027	.013
	z	.5697	− .0095	.579	.005
	x'			.745	
C_5	x	0.2002	0.0062	0.194	0.002
	y	.8243	− .0012	.826	.010
	z	.6338	− .0020	.636	.003
	x'			.830	
C_6	x	0.1117	0.0052	0.107	0.003
	y	.7078	− .0188	.727	.012
	z	.7018	− .0042	.706	.003
	x'			.813	
C_7	x	0.0672	−0.0052	0.072	0.003
	y	.2693	.0267	.243	.035
	z	.2550	.0085	.247	.006
	x'			.319	
C_8	x	0.0780	−0.0062	0.084	0.001
	y	.3763	− .0207	.397	.007
	z	.1675	− .0025	.170	.001
	x'			.254	

least-squares fit. The distances of the observed positions of the atoms from this plane are

C_1, 0.008 Å. C_4, 0.050 Å.
C_2, 0.029 Å. C_5, −0.005 Å.
C_3, −0.054 Å. C_6, −0.025 Å.

The free styrene molecule is presumed to be planar due to resonance interaction of the side-chain double bond with the benzene ring. In this structure, the side chain carbon atoms, C_7 and C_8, are observed to be out of the plane of the benzene ring by 0.16 and 0.07 Å., respectively.

The styrene–palladium chloride dimer is held together by a double chlorine bridge as was observed in ethylene palladium chloride.[6] The palladium bonds are approximately in the expected planar square configuration, which requires that all of the palladium and chlorine atoms of the molecule be coplanar. The two Cl_2 atoms are, however, found to be 0.13 Å. out of the plane of the chlorine bridge. The Pd–Cl bond distances within the bridge are found to be significantly different. Those which are opposite the palladium–olefin bonds are longer (2.41 Å.) than those which are opposite the bonds to the outer chlorine atoms (2.32 Å.). Lengthening of the metal–chlorine bond opposite an olefin linkage is also observed in the structure of Zeise's salt which has been determined by Wunderlich and Mellor.[10]

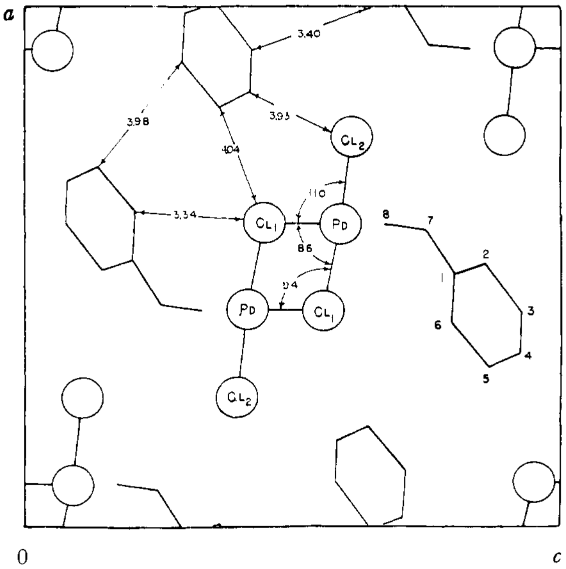

Fig. 2.—Projection of the structure of the styrene–palladium chloride dimer on to (010) showing intermolecular distances.

TABLE II

INTERATOMIC DISTANCES WITHIN THE MOLECULE

Atoms	Distance, Å.	Standard dev.
Pd–Cl_1	2.41	0.02
Pd–Cl_1	2.32	.02
Pd–Cl_2	2.27	.02
Pd–Pd	3.46	.01
Cl_1–Cl_1	3.21	.03

The plane of the ethylene group of the styrene molecule is established by the positions of C_1, C_7 and C_8. The palladium atom lies in the direction of the pi orbital of the double bond if the plane of Pd, C_8 and C_7 is perpendicular to this plane. The calculated value of the angle between these two planes is 89 degrees. The indicated direction of the dsp^2 orbital is into the pi bond if the plane of the chlorine bridge cuts the double bond axis and if one of the Cl_1 atoms lies in the plane of Pd, C_8 and C_7. These relations are illustrated in Fig. 3. The observed position of Cl_1 is only 0.01 Å. out of the plane of Pd, C_8 and C_7, and the plane of the chlorine bridge cuts the double bond axis $^3/_{10}$ of the interatomic distance away from C_8.

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[10] J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, **7**, 130 (1954).

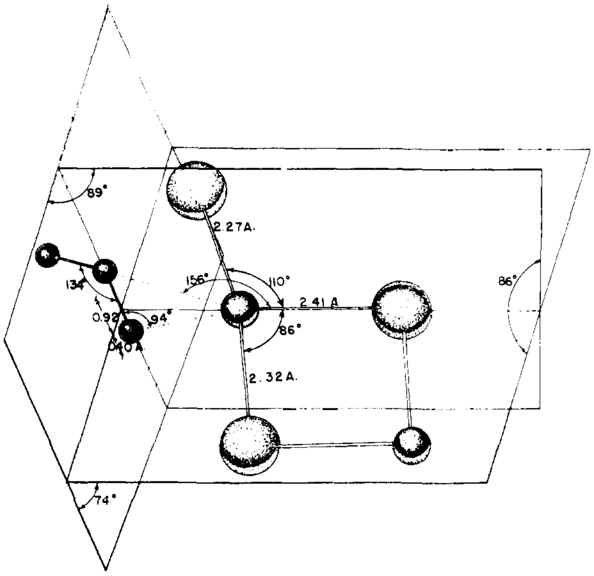

Fig. 3.—Detail sketch of the styrene–palladium chloride complex. The large atoms are chlorine, the medium size atoms are palladium, and the smallest are the carbon atoms, C_1, C_7 and C_8 of styrene. The intersection of the three planes lies at 0.40 Å. from carbon atom C_8.

The configuration of the atoms in styrene–palladium chloride is, therefore, entirely consistent with the theory that the palladium–olefin bond consists of interaction between one of the dsp^2 hybrid orbitals of palladium and the pi orbital of the double bond. The palladium orbital enters the pi bond off center and forms an angle of 74 degrees with the double bond axis. The structure of ethylene–palladium chloride indicates, however, that the palladium orbital enters the ethylene pi bond at its center and forms an angle of 90 degrees with the double bond axis. The ethylene molecule is symmetrical about its double bond; whereas, in styrene, where one of the carbons of the double bond is attached to the large phenyl group, the bond from palladium is off center. There are several possible causes for the displacement of the palladium bond toward the end carbon of the styrene molecule. (1) There may be an asymmetrical distribution of electrons in the pi bond of the ethylene side-chain, the carbon atom C_8 being more negative. (2) Rotation of the ethylene group into a position such that the carbon atoms are equidistant from the palladium atom requires, either that the ethylene side chain be twisted far out of the plane of the benzene ring, or that the molecules assume an entirely new packing arrangement in the solid. Either alternative could increase the crystal energy.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

The Thermodynamic Functions of Bis-cyclopentadienyl Iron, Bis-cyclopentadienylnickel and Bis-cyclopentadienylruthenium

BY ELLIS R. LIPPINCOTT* AND RICHARD D. NELSON

RECEIVED APRIL 29, 1955

The thermodynamic quantities C_p^0, $(H^0 - E_0^0)/T$, $-(F^0 - E_0^0)/T$ and S^0 have been calculated from 298.16 to 1500°K. for bis-cyclopentadienyliron(II), nickel(II) and ruthenium(II) from an assignment of frequencies based on infrared and Raman spectroscopic studies. The quantities ΔH_f^0, ΔF_f^0 and ΔS_f^0 have been calculated for $Fe(C_5H_5)_2$ and $Ni(C_5H_5)_2$ from 298.16 to 1500°K. Thermodynamically $Ru(C_5H_5)_2$ is the most stable and $Ni(C_5H_5)_2$ the least stable of these three compounds.

Introduction

The unusual sandwich structures of a number of the transition metal dicyclopentadienyl compounds have stimulated a wide range of studies concerning their chemical and physical properties.[1–8] The structures of these compounds have been demonstrated conclusively and the aromatic nature of the cyclopentadienyl rings established.[9–13] However the nature of the forces binding the rings to the metal atom is only partially understood and there is no complete agreement as to how best to describe the type of bonding involved. A tabulation of the calculated thermodynamic functions for some representative examples of this interesting series of compounds is then desirable for a comparison with their other properties. We are carrying out a detailed spectroscopic study of a number of metal cyclopentadienyl compounds. The results of the vibrational analysis on $Fe(C_5H_5)_2$, $Ru(C_5H_5)_2$ and $Ni(C_5H_5)_2$ are nearly complete and permit a reliable assignment of frequencies to be made to the fundamental modes of vibration for these molecules. We wish to present here tabulations of a number of thermodynamics functions at 100° intervals from 300 to 1500°K. for these three molecules based on this assignment. At this time no heat capacity or entropy measurements are available for comparison. When such thermal measurements are available a comparison of the experimental and calculated thermodynamic quantities will furnish information concerning the possible existence of a barrier preventing free internal rotation of the cyclopentadi-

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* Department of Chemistry, University of Maryland, College Park, Maryland.

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