THE CRYSTAL STRUCTURE OF A COMPOUND WITH A TRIANGULAR PALLADIUM CLUSTER

by

PEARSE MORONEY

B.A., Dublin University, 1974

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Chemistry

We accept this thesis as conforming
to the required standard

[redacted]

UNIVERSITY OF VICTORIA

July 1977

Joint Supervisors: Drs. G. W. Bushnell and K. R. Dixon

ABSTRACT

The crystal structure of μ-chloro-bis(μ-diphenylphosphido)-tris(triethylphosphine)-tri-palladium fluoroborate has been determined by the single crystal x-ray diffraction method. The data was collected automatically at room temperature on a Picker 4-circle diffractometer using MoK radiation. The structure was solved by the heavy atom method, and refined by the full matrix least squares method using only reflections where the net count was greater than 3σ (σ is the estimated standard deviation of the net count).

Crystals of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ are monoclinic with $a = 1614(1)$, $b = 1951.2(8)$, $c = 1691.2(6)$ pm, $\beta = 97.66^{o}(6)$, and space group P_{2_1}/c (no. 14). The measured and the calculated densities are 1.49 and 1.47 g cm^{-3} respectively. Over 4,000 ($2\theta_{max} = 40^{o}$) counter intensities were measured of which 2866 independent reflections were used to refine the structure to an R value of .105. The palladium atoms are arranged approximately in an equilateral triangle, with diphenylphosphido ligands bridging two of the sides and a chloro bridge on the other side. One triethylphosphine ligand is co-ordinated terminally to each palladium atom. Some of the important dimensions of the structure are given. The distance between the palladiums, which are bridged by the chlorine atom, is 289(2) pm whilst the average of the other two Pd-Pd distances is 293(2) pm. The angles

in the palladium triangle are close to 60^{o}, and the average $Pd-PEt_3$ distance is 230(1) pm with the $Pd-Pd-PEt_3$ angle close to 150^{o}. The average Pd-Cl distance is 241(1) pm and the Pd-Cl-Pd angle is $73.8^{o}(8)$. The average $Pd-PPh_2$ distance from the palladiums with the chloro bridge is 222(2) pm as opposed to the average $Pd-PPh_2$ distance from the unique palladium, 227(2) pm, and the average $Pd-PPh_2-Pd$ angle is $81.4^{o}(6)$. The presence of metal-metal bonding in this complex is discussed in some detail and it is concluded that $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ is a metal cluster.

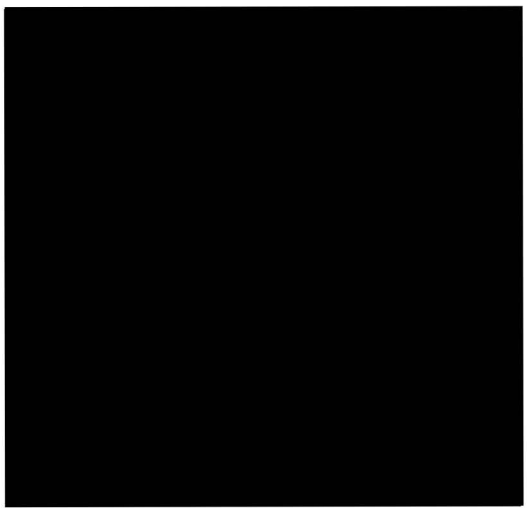


TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGMENTS

I would like to thank my joint supervisors, Dr. G. W. Bushnell and Dr. K. R. Dixon, for their encouragement, guidance and patience throughout this work, and the University of Victoria for its financial support. Acknowledgments are also due to Julie, my friends and members of the chemistry department who made my stay in Victoria both a worthwhile and an enjoyable one. Thanks are also due to my parents for their constant interest and encouragement, and finally to Mrs. Karen Hayes for typing the thesis.

"GO RABH MATH AGAIBH"

CHAPTER 1

INTRODUCTION

1.1 Metal Clusters: General

Metal clusters are compounds with at least one metal ring or polyhedron, where there is a network of metal atoms held together by metal-metal bonds, with at least two metal-metal bonds to each metal atom. They are most commonly found in transition metal compounds with low oxidation states, where the bonds are due to direct overlap of the transition metal d or sp^xd^y hybrid orbitals. Transition metal clusters may be regarded as species intermediate between simple monometallic covalently bonded compounds and the crystalline metals. They exhibit neither metallic conductivity nor metallic optical properties, but transition metal clusters often have colours more intense than those of comparable transition metal derivatives without any metal-metal bonding.

The presence of these metal-metal bonds may be inferred from diagnostic techniques such as mass spectrometry and chemical reactions none of which is conclusive by itself. Spiro (1, p. 1) has found that force constants associated with M-M stretching correlate quantitatively with bond strength, but perhaps the most direct evidence can be obtained by revealing the presence of very short metal-metal distances by x-ray crystallography.

1.2 Metal-Metal Bonding

Compounds involving metal-metal bonds have been divided into two classes (2, p. 120). The first class includes all metals, the simple binary compounds of approximate stoichiometry MX (where M is a metal from the left of the transition metal block and X can be I, Br, O, S etc. i.e. a highly polarizable ligand of low ligand field strength) and the metal-metal bonding found in some classical molecular complexes such as square planar complexes of platinum and palladium. These may crystallise in columns so that the M-M distances are considerably shorter than the normal non-bonding distances (3). The best known examples of columnar packing are to be found in the nickel, palladium and platinum derivatives of dimethylglyoxime which have metal-metal distances of the order of 3.25 $\mathring{A}$ (4). The second class of compound is the large number of molecular complexes which have metal-metal bonds. Some of these contain only two metal atoms and a single two center bond, and others contain three or more metal atoms forming polygons or polyhedra. Our compound belongs to this class and this is the class which will be discussed in most detail. However, before compounds of class I are dispensed with entirely, it is necessary to discuss more rigorously some generalities about both classes.

The most important single condition for the formation of metal-metal bonds is a low formal oxidation state. The position of the metal atoms in the periodic table also plays a significant role in determining the nature and importance of the exchange

interactions. Metal-metal bonds in binary halides, oxides and sulphides are more common in metals to the right of the first row transition series. Effective nuclear charge increases across a period and down a group and for this reason metal-metal bonds are much more common in the chemistry of the second and third row elements, reaching a peak in the middle of the transition block, and the strength of metal-metal bonds increases upon descending a column. Thus, for the bonding d orbitals of the metal, the strength of the metal-metal bond is in the following sequence; 5d > 4d > 3d (5, p. 297).

An example of this is shown by the fact that the iron triangle of $Fe_3(CO)_{12}$ is broken much more readily than the Ru triangle of $Ru_3(CO)_{12}$ upon reaction with reagents such as tertiary phosphines and cyclo-octatetraene.

1.3 Role of the Ligand

The nature of the ligand co-ordinated to a metal, which forms a stable metal-metal bonded complex, plays an equally important though less well-understood role than the metal. In the first class of compound the ligands appear to promote cation-cation interactions. The structures of the MX compounds consist of MX_6 octahedra sharing edges or faces and joined by bridging X groups; the exchange interactions occur through the common octahedral edges of faces. Compounds of metals to the right of the first row of the transition metal block and in the second and third rows usually involve chloride anions and/or

π acid ligands of high field strength such as carbon monoxide and phosphines. These ligands tend to stabilize metal metal bonds in a large number of complexes containing MX_5 tetragonal pyramids with similar entities interacting at the vacant octahedral positions to form dimeric or cluster compounds (2nd class). This class of compound may be taken to include the many bimetallic complexes which contain trigonal, bi-pyramidal, square planar and linear arrangements of ligands about the metal atoms. Substitution by ligands of lower field strength generally leads to weakening of metal-metal bonds.

The trends in the formation of metal-metal bonds can be discussed quantitatively, by concepts developed by Morin, Goodenough and Lewis and Nyholm (2, p. 122) based on a consideration of their molecular orbitals. In compounds of type I, whose structures consist of MX_6 octahedra the extent of metal-metal interactions is determined by the overlap of the t_{2g} orbitals on neighbouring cations and the factors which will favour M-M bonds will be those which favour an increase in the energy of these orbitals relative to the σ bonding orbitals of the MX_6 octahedra. Thus the t_{2g} orbitals must project as far as possible and highly polarizable π electron donors such as oxide or iodide tend to raise the energy of the t_{2g} orbitals in transition metal complexes, facilitating orbital overlap in complexes of this type. Another factor which appears to favour complexes of this

kind are low oxidation states — the d orbitals in cations of high oxidation state are too small to permit sufficient cation-cation interactions. The same effect shows up in the gradual decrease in importance of M-M bonding in non-organometallic compounds in the passage from left to right across the first transition series.

Other factors, such as coulombic forces, are of undoubted importance, whilst it has also been shown (2) that elements which tend to form cluster compounds are those with high enthalpies of sublimation in the metallic state. Sheldon (2) has suggested that metal atoms possess 'preferred valence states', which are strongly determined by the availability of the d-orbitals for bonding. When metals of high preferred valence states are constrained to low formal oxidation states, metal-metal bonding will occur so that the metal atoms attain the preferred higher valence states.

The mode of bonding in cluster compounds is more obscure but comparison with the better known organometallic chemistry is of great value as it is evident that the 'raison d'être' of many organometallic and bimetallic compounds of the transition metals is , by and large, the same. The chemistry of bimetallic compounds bears a strong resemblance to that of organometallic compounds. For instance the metathetical reactions of $NaMn(CO)_5$ with methyl iodide and triphenyltin chloride to produce $MeMn(CO)_5$ and

$Ph_3SnMn(CO)_5$ respectively, have an obvious similarity. The same type of compound is commonly found in organometallic and bimetallic systems such as $Et_3SiCo(CO)_4$ which can be obtained from its silicon organometallic analogue, Et_3SiH (6).

Based on the fact that there are strong parallels between metal-carbon and metal-metal bonding and the fact that the synthesis of many organometallic compounds has been made possible by the presence of good π electron accepting ligands which would increase the energy difference between the highest energy orbital which contains electrons and the lowest energy orbital which is vacant, the stabilities of many organobimetallic complexes have been rationalized.

1.4 Triangular Metal Clusters

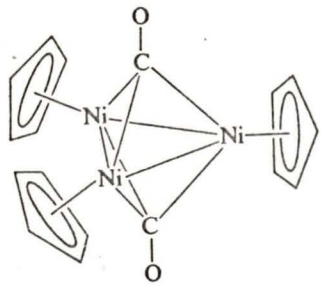
A metal cluster can be represented as a polyhedron with the vertices corresponding to metal atoms, the edges corresponding to metal-metal bonds, and the faces real polygons with at least three sides (edges). The following two factors make the metal triangle the most favourable building block for transition metal clusters: (i) A closed triangle possesses at least two more bonding electrons than the equivalent line (or chain) segment. (ii) Minimizing the maximum metal to metal distance in a basic building block for a metal cluster will maximize the bond delocalization within this building block. The smallest maximum metal to

metal distances are found for the most compact clusters
This distance increases monotonically as the dimensions of the cluster change in the order; 3D → 2D → 1D.

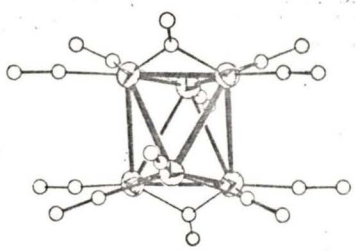
The electronic configurations of transition metal atoms in metal cluster derivatives are most conveniently determined if all metal atoms and surrounding ligands are considered as neutral species, and each metal-metal bond is treated as a covalent bond. Many of the "early triangular clusters" were found to have the favoured 18-outer-electron rare gas configuration (7), however, the more recent ones do not enhance this trend (8).

1.5 Triangular Clusters of Ni, Pd and Pt

It is only within the last ten years that most of the structures of the group VIII triad of Ni, Pd and Pt, which have triangular arrangements of metal atoms, have been elucidated. There are many examples in the literature (5, p. 380) of Ni-Ni bonds in organometallic complexes and considerably more nickel than palladium or platinum clusters have been reported. An early example, which is formed by the reduction of the complex $(\eta^5\text{-}C_5H_5)Ni(CO)_2$ by sodium amalgam, is the triangular cluster $(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$ and is reported (9) to have the structure;



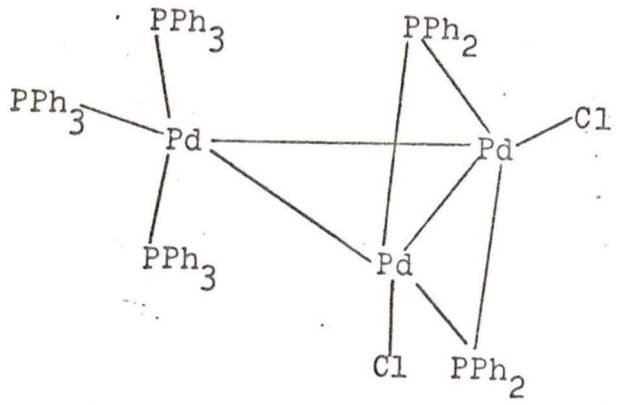
An interesting nickel triangular arrangement is found in the structure of the complex $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$ (10),



This represented the first unambiguous example of a hexanuclear metal carbonyl cluster system with twelve ligands. It is prepared by the reduction of nickel tetracarbonyl with sodium metal in THF ($60^{o}C$, 20 hrs.) or with KOH in methanol ($55^{o}C$, 5 hrs.).

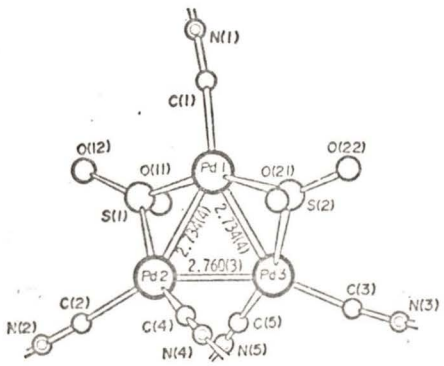
Cluster complexes of platinum and palladium, especially those containing tertiary phosphines have proved notoriously difficult to characterize (11). Clusters with the palladium triangle are the least well characterized.

One of the first palladium clusters was characterized on the basis of ^{31}P N.M.R. work by Coulson et al (15) and thought to have the triangular shape.

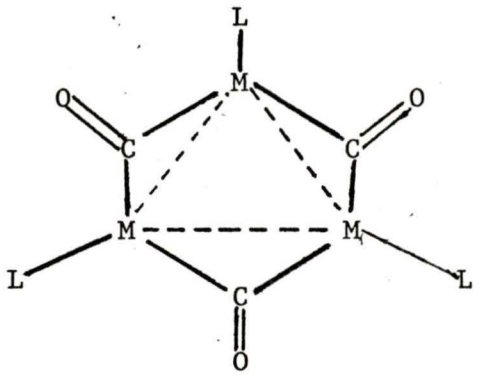


Due to poor resolution of the N.M.R. there was some doubt as to the position of the terminal groups but based on I.R., molecular weight measurement, and N.M.R. evidence and its apparent stability towards triphenyl-phosphine, it seemed likely that it existed as a cluster formation.

The only complex containing a palladium triangle with metal-metal bonding and whose structure has been resolved by x-ray diffraction methods, is the complex di-μ-SO_2 pentakis (t-butyl isocyanide)-triangulo-tripalladium-dibenzene (16).



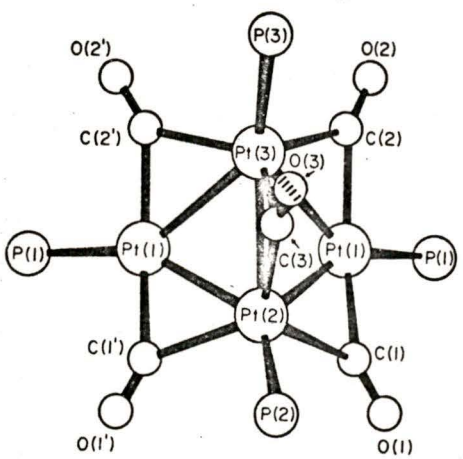
The palladium-palladium distance was found to be ca. 2.75 Å and the oxidation number of the palladium is zero. A similar Pd(0) cluster with three SO_2 bridges has been reported but no structure done (17). Some other Pd(0) and Pt(0) carbonyl complexes have recently been prepared by T. Yoshida et al (18) who were studying the reactivity of ML_2 compounds (M = Pd(0), Pt(0), and L was a variety of phosphine ligands). They found on bubbling CO into a solution of ML_2 in n-hexane, yellow crystals formed and on the basis of I.R. and ^1H N.M.R. evidence they postulated the structure shown,



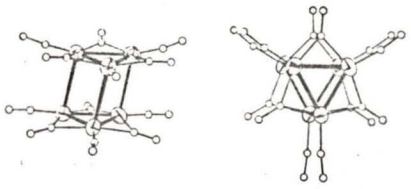
Workers in our lab. have prepared a series of $[Pd_3X(PR_3)_3(PPh_2)_2][Y]$ complexes; (X = Cl, R = Et, Ph, Y = BF_4), (X = Br, I, SCF_3, R = Ph, Y = BF_4) (19) which ON the basis of ^1H N.M.R., ^{31}P N.M.R. and their chemical reactivity are thought to involve a triangular arrangement of palladiums.

The number of fully characterized complexes with platinum triangles is larger than the number of known compounds with palladium

triangles. Some of these are similar to nickel and palladium compounds already mentioned. One of the first palladium complexes to be characterized completely is the tetranuclear metal cluster system $[Pt_4\{PPhMe_2\}_4(CO)_5]$ which consists of two platinum triangles with one equivalent side. The Pt-Pt bond length is 2.79 Å between the unique platinums, Pt(2) and Pt(3), and 2.75 Å between Pt(1) and Pt(2), and Pt(1) and Pt(3). (20).



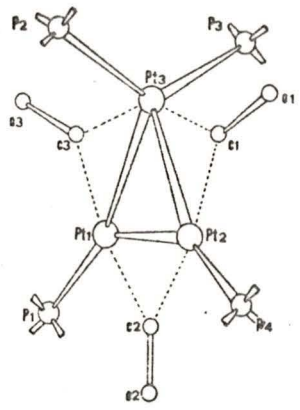
The individual intratriangular distances in the dianion $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$ (22) are all within .01 Å of the average value of 2.66 Å and within the expected range for Pt-Pt single bonds. $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$ is an analogue of the previously mentioned nickel dianion (10) and has numerous oligomers of the type $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ where n is a small integer.



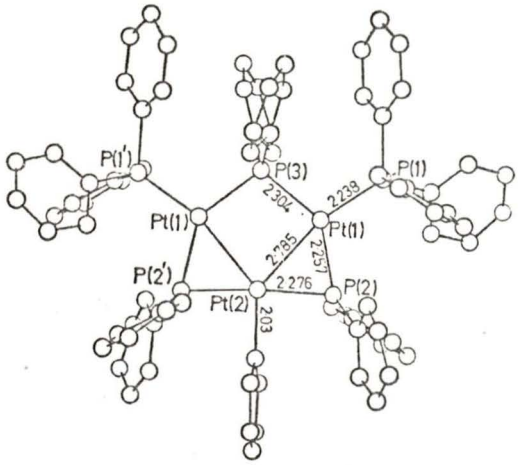
However, there is one marked difference in the structure of these oligomers compared to the nickel analogue, where the metal arrangement is trigonal anti-prismatic, whilst the structure of $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ is trigonal prismatic. These complexes represented the first known examples showing that metal-metal interactions involving first row transition metals can be sufficiently different from those involving third row transition metals to produce two different metal architectures which are conformers of each other.

A triangular Pt(0) compound has been characterized by diffraction methods (23) and its structure is probably similar to

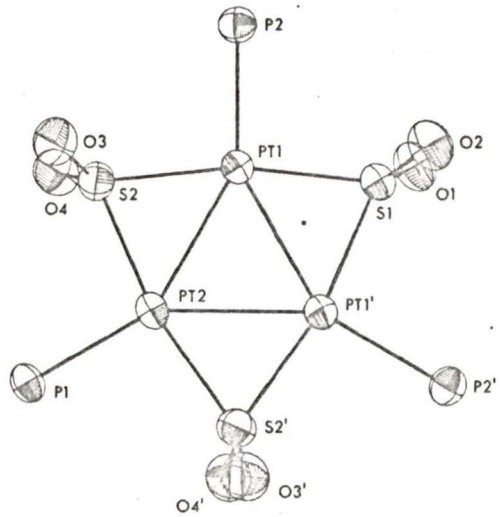
that of other Pd(0) and Pt(0) analogues (18,24). The structure of the complex $Pt_3[P(C_6H_{11})_3]_4(CO)_3$ is shown, and the Pt-Pt bond lengths are ca. 2.7 Å.



An interesting compound, which has been fully characterized by Carty (25), is the complex $[Pt_3(PPh_3)_2(PPh_2)_2Ph]C_6H_6$. The platinum skeleton is basically a triangle but there appears to be no metallic bonding between two of the platinums where the distance between them is 3.63 Å, whilst the other Pt-Pt distances (ca. 2.78 Å) agree with previously cited examples of metal-metal bonding in platinum complexes.



A very symmetrical Pt(0) triangular complex (26) corresponding to the palladium complex (17) has had its structure elucidated recently by x-ray techniques. The structure of $[Pt_3(SO_2)_3(PPh_3)_3]$ is shown and the Pt-Pt distances of 2.695 and 2.712 Å are consistent with those expected for single Pt-Pt bonds.



CHAPTER 2

THE CRYSTAL STRUCTURE OF $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$

2.1 Introduction

Until now, the only crystal structure reported for a palladium triangular metal cluster was one by Sei Otsuba and co-workers (16). Some interesting palladium metal clusters (19) of the type $[Pd_3X(PPh_2)_2(PR_3)_3][Y]$, where X = Cl, R = Et, Ph or R_3 = Me_2Ph; X = Br, I, SCF_3, R = Ph, Y = BF_4, were characterized on the basis of I.R. and ^{31}P N.M.R. and these were considered to have palladium atoms in a triangular arrangement. A preliminary x-ray study was carried out on the $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ complex (27) which suggested a triangular cluster of palladium atoms, with bridging diphenylphosphido and chloride ligands. Due to the high value of the R factor (R = 0.42) obtained, these results could not be relied upon. The high value of the R factor was the result of a phasing problem due to the position of the 'heavy atoms' which contribute very little to half of the reflections. It was felt that this "phasing problem" could be overcome if the size of the unit cell were changed sufficiently to unequivocally alter the positions of the heavy atoms. The obvious method of achieving this was by substitution of some/or all of the co-ordinating ligands, in the belief that the crystal structure would be thus changed.

2.2 Experimental

$[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ is one of several products obtained by pyrolysis of $[PdCl(PPh_3)_3][BF_4]$ in THF in a Carius tube, at 130°C, for several days. $[PdCl(PPh_3)_3][BF_4]$ was prepared by methods outlined in (28,29). The substitution reactions as shown in Fig. 1 were carried out on $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$.

From early recrystallisation attempts it appeared that the most favourable crystals for diffraction studies could be obtained from the tris triethylphosphine substituted cluster. A sample of $[Pd_3Cl(PEt_3)_3(PPh_2)_2][BF_4]$ was recrystallised from hot ethanol under N_2 in the apparatus shown in Fig. 2. Flat rectangular plate shaped crystals formed on cooling the solution slowly inside a polystyrene box, in a refrigerator. The solvent was removed by the addition and subsequent removal of ether/heptane and the crystals were dried under N_2. All samples were characterized by routine methods, including ^{31}P N.M.R.. It was found that the atmosphere caused rapid deterioration — probably oxidation. The crystals went from a translucent orange-red to an opaque dark-brown colour when exposed to the air for more than 90 minutes. The crystals were examined under a microscope and those which appeared single and had approximate dimensions of (.2 mm x .4 mm x .4 mm) were gently dropped into Lindemann capillary tubes of the appropriate diameter. They were fixed in the tube with silicone grease, and the open end of the tubes was sealed by use of a hot nichrome wire.

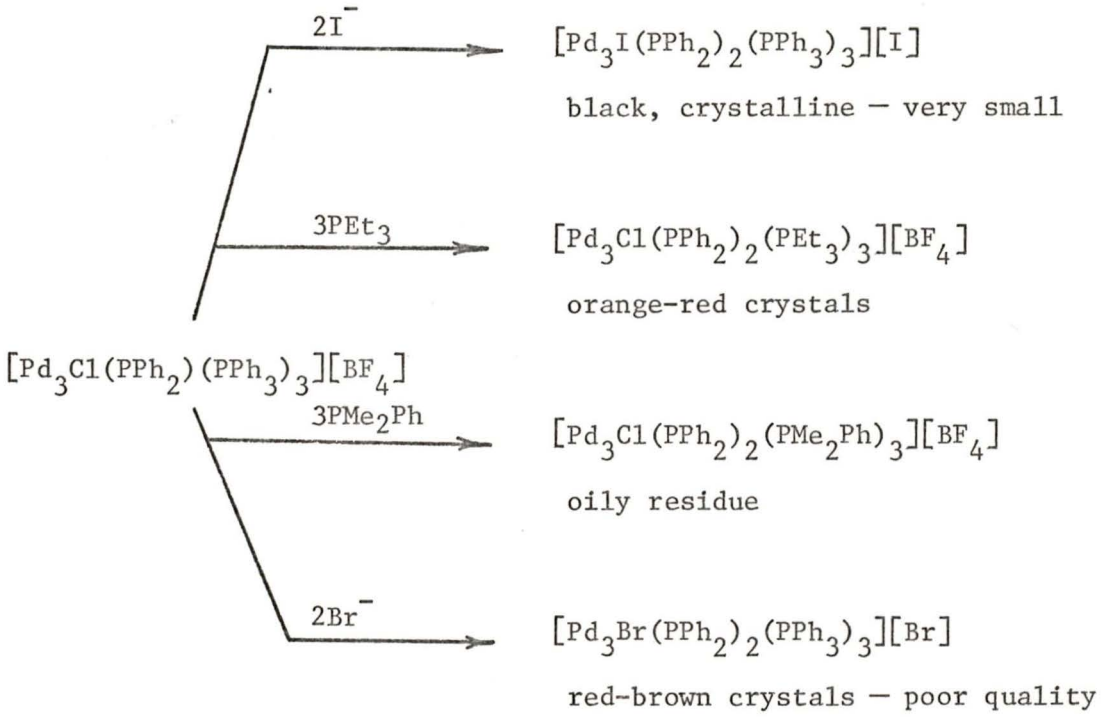


FIG. 1. Some Reactions of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ — Resultant Crystallisation Attempts

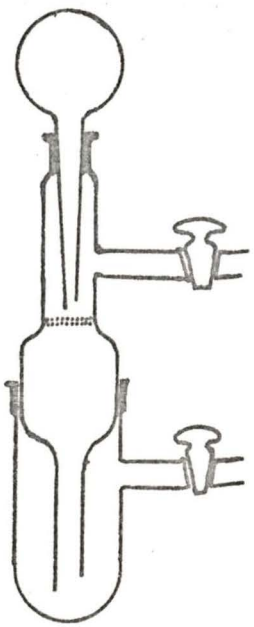


FIG. 2 Apparatus for Crystallisation

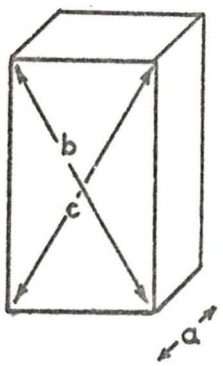


FIG. 3 Cell Axes

The main practical difficulty involved positioning the crystal in the tube so as to have its axes in a co venient position. The b and c axes were generally found to run diagonally across the flat plate of the crystal, as shown in Fig. 3.

Numerous crystals were mounted in Lindemann tubes, but many of these were found to be twinned, from photographic observations. A further difficulty arose when the crystals were also found to be susceptible to MoK radiation. The net count of the standards dropped rapidly after four to five days of constant irradiation with MoK x-rays.

2.3 Crystallographic Measurements

A series of Weissenberg and precession camera photographs were obtained with CuK radiation. The space group $P2_1/c$ was established unequivocally from the systematic absences. Cell parameters were measured from these photographs but, due to mounting problems, the β angle was never recorded on photographs of a single crystal. The unit cell was found to be monoclinic, i.e., $a \neq b \neq c$ and $\alpha = \gamma = 90^{\circ} \neq \beta$. Accurate cell dimensions were determined by mounting a crystal on the diffractometer and measuring the angles at which diffraction maxima occurred for 36 reflections. The cell dimensions were then refined by the method of least squares using $\lambda = 71.07$ pm. The density was measured by floating the crystals in a solution of carbon tetrachloride and n-heptane. Crystal data are given in Table 1.

TABLE I. CRYSTAL DATA FOR
μ-CHLOROBIS(μ-DIPHENYLPHOSPHIDO)TRIS(TRIETHYLPHOSPHINE)-
TRIPALLADIUM FLUOROBORATE

System	Monoclinic
Space Group	$P2_1/c$ (No. 14)
Molecular Formula	$C_{42}H_{65}BClF_4P_5Pd_3$
Molecular Weight	1166.3
Cell Dimensions	a = 1.6141 (11) nm b = 1.9512 (8) nm c = 1.6912 (6) nm β = 97.66 (6) deg
Cell Volume	5.2788 (46) nm^3
Density (Calculated)	1.47 g cm^{-3}
Density (Measured)	1.49 g cm^{-3}
No. of Molecules per unit cell	4
Absorption Coefficient (MoK)	12.5 cm^{-1}

TABLE 1(A). ADDITIONAL DATA

1.	Cell refinement 2θ Range of reflections used	 24-40°
	No. of reflections	36
2.	Structure refinement No. Variables (NV)	 370
	No. Observations (NO)	2866
	NO/NV	7.7
	Weighting Polynomial Coefficients	A = 88.8927 B = -0.18845 C = 0.008997 D = -0.000008

2.4 Diffractometry

The crystal habit of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ is a rectangular tablet showing the 100, 011, and $01\bar{1}$ faces. It was most convenient to mount the crystals in the Lindemann tubes with the 0,1,1 (or $0,1,\bar{1}$) planes approximately parallel to the tube axis. The tube was mounted on the diffractometer with its axis approximately co-linear with the ϕ axis.

Intensity measurements were made automatically at room temperature on a Picker 4-circle diffractometer using MoK radiation and a Zr filter. Reflections were scanned in the $\theta/2\theta$ mode for one minute at a rate of 2.4^{o} per minute. The instrument was operated in the bisecting position with $\omega = 0$. Background counts were measured for 30s at the end of each scan. Three reflections of high intensity were used as standards and their intensity measured for every batch of fifty reflections.

A total of 2872 independent reflections ($2\theta < 40^{o}$), which had the status of observed, where the criterion is that the net count must be $> 3\sigma$, where σ is the standard deviation of the net count, were measured. Due to the effects of MoK radiation the data set was collected in three stages. Three crystals were used, which had the dimensions (.19 mm x .56 mm x .31 mm), (.18 mm x .63 mm x .53 mm) and (.24 mm x .94 mm x .51 mm) and in cases where a reflection was measured more than once the structure factor values were averaged, after a scale factor had been applied. Data collection was terminated

at $2\theta = 40^{o}$ owing to the reason that only a few reflections were above the background.

The intensities were corrected for the Lorentz and polarization effects. An absorption correction was applied independently to the data from each of the crystals.

The effect of absorption may be calculated by evaluation of the following integral:

$$A_{hkl} = \frac{1}{V} \int \exp\left[-\mu_{\lambda}(r_i + r_d)\right] dV \qquad (1)$$

A_{hkl} is the transmission factor, r_i and r_d are the pathlengths along the incident and diffracted beams, and V is the volume of the crystal (cm^3). μ_{λ} is the linear absorption coefficient of a compound for radiation of a specified wavelength λ, and is given by the expression;

$$\mu_{\lambda} = \frac{n}{V_c} \sum_{i} (\mu_a)_i \qquad (2)$$

i = no. of atoms in the asymmetric unit
μ_a = atomic absorption coefficient
n = no. of asymmetric units per unit cell
V_c = volume of unit cell

The intensities of the diffracted rays from a given crystal are proportional to its volume but because of absorption there is an optimum thickness which is a function of the linear absorption coefficient, i.e.

$$t_{optimum} = \frac{2}{\mu_{\lambda}} \qquad (3)$$

From the absorption factor calculation (1) which depends on the pathlength of the incident and diffracted rays, it can be seen that different reflections may suffer to a varying extent from absorption and a systematic error will be introduced into the intensities even for crystals of less than optimum size. The worst case is that of a flat plate for which the paths of rays passing through the longest and shortest dimensions may differ by a factor of 10 or more.

Although μ_{MoK} for $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ is only 12.5 cm^{-1}, and the ideal optimum thickness (.15 cm) is large, the crystals formed as flat rectangular plates which is the worst case for absorption. It was considered imperative that an absorption correction be applied and this factor was evaluated numerically by Gaussian integration using a program supplied by Penfold (32) and modified by Bushnell (33).

The absorption correction was applied after the Lorentz and polarization corrections were applied in the data reduction. Some basis for evaluation of its utility may be ascertained from the following. A preliminary investigation of the structure of this compound was carried out on a data set consisting of 2273 independent reflections from one crystal. The structure was essentially solved from this data set, but due to the non-reliability of the cell dimensions and the fact that the net count of one of the standards dropped by 90% during data collection, indicating a possible equivalent deterioration in the crystal, the complete data

set was collected again in the manner stated. The original data set refined to an R-value of .138 but on application of the absorption correction to the intensity measurements, refinement halted at an R-value of .130.

2.5 Structure Determination

The structure was solved by the usual heavy atom method. The atomic scattering factor curves for Pd, Cl, B, F, P and C were obtained from the work of Cromer and Waber (30). All atoms were assumed to be uncharged and a correction for the anomalous dispersion of palladium (31) made in the final stages of refinement. The calculations were done using a set of programs supplied by Penfold (32) and Bushnell (33). A list of these programs is given in Appendix 1.

The co-ordinates of the three palladium atoms were obtained from a three dimensional Patterson function. A subsequent Fourier synthesis phased with the palladium atoms showed the position of the five phosphorus atoms and the chlorine. The co-ordinates of these nine atoms and the scale factor were refined by minimization of the function $W(|F_o|-|F_c|)^2$ using full matrix least squares. Unit weight was given to all reflections at this stage. One cycle of refinement for the 9 atom model, using anisotropic temperature factors gave an R-value of .231. The remaining light atoms were located using

Fourier and difference Fourier synthesis. When all the atoms were located it was necessary to process the refinement in two stages, having a fixed atom file of either the 24 carbons in the phenyl rings, or the 18 carbons in the ethyl groups and the BF_4 moiety, and refining the positions of the nine heavy atoms along with those atoms which were not in the 'fixed atom file'. Two complete cycles of refinement gave an R value of .117 (R_W = .131) and the structure appeared fully refined at this position.

87 reflections of varying intensity, but whose structure factors had poor agreement with calculated structure factor values, were remeasured on a 'fresh' crystal (.32 x .93 x .55 mm). Lorentz and polarization corrections, an absorption factor and a scale factor were applied to these values, which were then substituted for their respective values in the data set. The reflections (0,1,1), (0,2,0), (1,1,1) and ($\bar{1}$,1,1) were removed from the data set as it was felt, that due to their low 2θ angle (<4.3°) intensity measurements were interfered with by the backstop on the diffractometer. The reflections (2,0,0) and (2,2,0) were also removed as the counter overflowed whilst they were being measured. The palladium atoms were treated as anomalous scatterers and refinement continued using new weights (W) derived by using the weighting scheme proposed by Cruickshank (42)[a]. The final R-value was .105 and, defining the

---

[a] $W = \text{scale} \times [(A + B\,|F_o| + C\,|F_o|^2 + D\,|F_o|^3)]^{-1}$, the coefficients A, B, C and D were obtained by the error analysis of the data.

weighted R-value as $(\Sigma W\Delta^2/\Sigma WF_o^2)^{\frac{1}{2}}$, the corresponding weighted R value was .135. Shifts of the final cycle were less than 3% of the standard deviation for the heavy atoms and less than 15% of the standard deviation for the remaining atoms.

The data was analysed for any systematic errors and revealed that the agreement between $|F_o|$ and $|F_c|$ was poorest for reflections with low $|F_o|$. This variation can be related to the greater degree of uncertainty in the experimental collection of weaker intensity reflections. The accuracy of the data might have been improved for the low intensity reflections by counting each reflection over a longer time period but this would have proved extremely difficult due to crystal deterioration. The function $\Sigma W(|F_o| - |F_c|)^2$ was not significantly dependent on either $|F_o|$ or (sine θ/λ). The average value of the function E, ($E = [\Sigma W(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}$), for different sections with respect to $|F_o|$ and (sine θ/λ) were approximately equal indicating a satisfactory weighting scheme. The average value of E using the weighting scheme was .956.

Due to the high number of parameters in the calculation (see Table 1(a)) no attempt was made to locate the hydrogen atoms. A final difference map gave no indication of any misplaced atoms and showed no peak higher than 1.83 electrons Å^{-3}. The most prominent features are near the palladium and phosphorus atoms and the lowest negative peak (-1.29 electrons Å^{3}) is quite far from any of the

heavy atoms (>300 pm). The ten most prominent positive peaks are scattered irregularly round the palladium atoms. The final positional and temperature factor parameters are listed in Tables 2 and 3. The structure factor table is given in Appendix 2.

Table 2. (A) Positional Parameters for the Heavy Atoms in μ-Chloro-bis(μ-diphenylphosphido)tris(triethylphosphine)-tripalladium fluoroborate[a]

Atom	X	Y	Z
Pd(1)	0.2646(2)	-0.0035(1)	0.3183(1)
Pd(2)	0.2398(2)	0.0111(1)	0.4863(1)
Pd(3)	0.2088(2)	0.1267(1)	0.3792(1)
Cl	0.2011(6)	0.1257(4)	0.5203(5)
P(1)	0.2915(6)	-0.0698(4)	0.2116(5)
P(2)	0.2356(6)	-0.0330(5)	0.6118(5)
P(3)	0.1660(6)	0.2386(5)	0.3651(6)
P(4)	0.2775(5)	-0.0796(4)	0.4209(5)
P(5)	0.2306(6)	0.0980(4)	0.2562(5)

[a]Estimated standard deviations in parentheses.

(B) Anisotropic temperature parameters for the heavy atoms[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	72(2)	27(1)	48(1)	.6(12)	- .8(12)	1.2(12)
Pd(2)	78(2)	27(1)	48(1)	5.5(12)	.8(12)	4.5(12)
Pd(3)	84(2)	26(1)	52(1)	3.8(12)	-5.2(12)	3.3(12)
Cl	144(9)	42(5)	59(5)	18(5)	21(5)	-5(4)
P(1)	92(8)	47(5)	66(6)	11(5)	-5(5)	-8(5)
P(2)	98(8)	52(5)	62(6)	11(5)	7(5)	15(5)
P(3)	99(8)	47(5)	71(6)	6(5)	-7(5)	3(5)
P(4)	67(7)	32(4)	57(5)	5(4)	6(4)	3(4)
P(5)	79(7)	34(4)	56(5)	2(4)	-9(4)	1(4)

[a]$T = \exp - 2\Pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hka^*c^* + 2U_{23}klb^*c^*)$. Tabulated values should be multiplied by 10 to obtain mean square amplitudes in pm^2.

Table 3. (A) Positional and isotropic temperature parameters for C(1A)-C(3F), B and F(1)-F(4) atoms in μ-chloro-bis(μ-diphenylphosphido)tris(triethylphosphine)-tri-palladium fluoroborate[a]

Atom	X	Y	Z	U x 10^{-1} $(pm)^2$
C(1A)	0.1938(28)	-0.0851(23)	0.1470(26)	111(14)
C(1B)	0.1248(28)	-0.1152(24)	0.1815(26)	115(15)
C(1C)	0.3652(21)	-0.0345(17)	0.1484(19)	72(9)
C(1D)	0.4563(30)	-0.0266(26)	0.1825(28)	129(16)
C(1E)	0.3292(23)	-0.1532(20)	0.2398(22)	90(12)
C(1F)	0.3503(28)	-0.2033(24)	0.1650(27)	118(15)
C(2A)	0.3361(28)	-0.0067(24)	0.6756(36)	112(14)
C(2B)	0.3364(43)	0.0681(39)	0.6967(39)	205(27)
C(2C)	0.2249(22)	-0.1242(19)	0.6154(21)	82(10)
C(2D)	0.2109(31)	-0.1488(26)	0.7049(29)	133(17)
C(2E)	0.1536(23)	-0.0051(19)	0.6592(21)	86(11)
C(2F)	0.0682(27)	-0.0088(22)	0.6139(25)	114(14)
C(3A)	0.2442(27)	0.2968(23)	0.4164(25)	112(14)
C(3B)	0.3213(29)	0.3019(25)	0.3722(28)	129(16)
C(3C)	0.1398(25)	0.2725(22)	0.2585(24)	103(13)
C(3D)	0.0990(29)	0.3447(25)	0.2579(27)	128(16)
C(3E)	0.0730(27)	0.2564(24)	0.4179(25)	113(14)
C(3F)	-0.0047(31)	0.2103(27)	0.3844(30)	139(18)
B	0.2569(90)	0.5043(79)	0.4113(83)	318(53)
F(1)	0.2775(31)	0.4598(26)	0.4735(30)	259(20)
F(2)	0.1882(31)	0.4668(26)	0.3702(28)	294(19)
F(3)	0.2284(29)	0.5596(28)	0.4293(28)	301(20)
F(4)	0.3195(31)	0.4904(24)	0.3805(30)	350(20)

[a]Estimated standard deviations in parentheses.

Table 3. (B) Positional and isotropic temperature parameters for C(4A)-C(5L) atoms in μ-chloro-bis(μ-diphenylphosphido)-tris(triethylphosphine)-tri-palladium fluoroborate[a]

Atom	X	Y	Z	U x 10^{-1} $(pm)^2$
C(4A)	0.3818(19)	-0.1109(16)	0.4590(17)	60(9)
C(4B)	0.4458(22)	-0.0732(18)	0.4379(20)	75(10)
C(4C)	0.5309(25)	-0.0867(21)	0.4716(23)	96(12)
C(4D)	0.5458(23)	-0.1441(19)	0.5155(21)	82(11)
C(4E)	0.4815(23)	-0.1858(19)	0.5366(22)	83(11)
C(4F)	0.3974(21)	-0.1718(17)	0.5051(19)	68(9)
C(4G)	0.2048(20)	-0.1501(16)	0.4122(18)	64(9)
C(4H)	0.1166(22)	-0.1292(19)	0.4287(20)	81(10)
C(4I)	0.0523(23)	-0.1802(20)	0.4202(21)	84(11)
C(4J)	0.0800(27)	-0.2476(22)	0.4048(24)	102(13)
C(4K)	0.1555(25)	-0.2661(21)	0.3977(22)	91(12)
C(4L)	0.2225(23)	-0.2212(19)	0.4069(21)	82(11)
C(5A)	0.3075(19)	0.1508(16)	0.2172(18)	59(9)
C(5B)	0.3893(24)	0.1417(20)	0.2559(21)	88(12)
C(5C)	0.4536(31)	0.1839(27)	0.2339(30)	131(17)
C(5D)	0.4348(30)	0.2342(25)	0.1719(27)	118(15)
C(5E)	0.3545(27)	0.2387(21)	0.1387(24)	97(12)
C(5F)	0.2908(20)	0.1992(17)	0.1549(19)	68(9)
C(5G)	0.1391(18)	0.0941(14)	0.1848(16)	51(8)
C(5H)	0.0633(19)	0.0875(15)	0.2158(17)	57(8)
C(5I)	-0.0161(25)	0.0742(22)	0.1547(24)	101(13)
C(5J)	-0.0059(22)	0.0700(18)	0.0778(21)	78(10)
C(5K)	0.0712(23)	0.0780(19)	0.0507(20)	79(11)
C(5L)	0.1457(20)	0.0911(16)	0.1010(18)	65(9)

[a]Estimated standard deviations in parentheses.

CHAPTER 3

3.1 Results

The crystal structure $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ consists of well separated $[Pd_3Cl(PPh_2)_2(PEt_3)_3]^+$ cations and $[BF_4]^-$ anions. The interatomic distances, bond angles and least squares planes are given in Tables 4, 5 and 6. The contents of the unit cell are shown in Figure 4. The roman numeral subscripts on the Pd and B atoms refer to the ions with the following co-ordinates:

I	x, y, z	III	x, ½ - y, ½ + z
II	$\bar{x}$, $\bar{y}$, $\bar{z}$	IV	$\bar{x}$, ½ + y, ½ - z

A perspective view of the $[Pd_3Cl(PPh_2)_2(PEt_3)_3]^+$ cation is given in Figure 5 which also gives the atomic labelling scheme.

Table 4(A) lists the bond distances concerning the heavy atoms. The distances between Pd(1) and Pd(2), and Pd(1) and Pd(3) are equal and slightly larger than the Pd(2) - Pd(3) bond distances. This can be attributed to the difference in the bridging ligands as the chlorine atom bridges the shorter bond length. All Pd-Pd distances are larger than the Pd-Pd distances found in $[Pd_3(SO_2)_2(Bu^tNC)_5]$ (276 pm) (16) and shorter than the non-bonding Pd-Pd distance found in the Cl-bridged complex $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (347.5 pm) (34) but comparable to the metal-metal bonding distance found in $[Pd_2Ac_2(\eta^3\text{-}C_3H_5)_2]$ (294 pm) (19).

The distances between the palladium atoms and their respective terminal phosphorus atoms (P(1), P(2), P(3)) are equal and are consistent with Pd-P values reported for $PdCl(dtt)(PPh_3)_2$ [a] (232 pm) (35) and trans $[(PPh_3)_2PdCl(-C_6H_4N{=}NC_6H_5)]$ (231 pm) (36). The bridging phosphorus atoms (P(4), P(5)) are farther from Pd(1) than Pd(2) or Pd(3). All the palladium to bridging phosphorus distances are shorter than the palladium to terminal phosphorus atom distance and longer than the Pd-P distance found in di-μ-chloro-bis (μ-diphenylphosphidotetracarbonyl iron palladium) (215 pm) (37), but comparable with metal to phosphorus distances found in bridging diphenylphosphido complexes of ruthenium (228.6 pm) (38) and iridium (229.8 pm) (38A). The Pd-Cl distance is longer than reported Pd-terminal chlorine distances (233) (35) but consistent with the Pd-Cl distances found in the chloride bridged complexes, $Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2$ (241 pm) (34) and di- μ-chloro-bis(μ-diphenylphosphidotetracarbonyl iron palladium) (242 pm) (37).

Table 5(A) gives the bond angles round the heavy atoms. The three palladiums are almost an equilateral triangle with the smallest angle opposite the chlorine bridge as expected. The terminal phosphorus atoms are symmetrically placed round the triangle but the bridging phosphorus atoms appear to be drawn closer to the palladium atoms, which the chlorine atom bridges.

Table 6 gives the least squares plane concerning the palladium co-ordination. The heavy atom skeleton is approximately planar, deviations from the least squares plane being P(1), 11; P(2), 10; Cl, -10 pm.

---

[a] dtt = p-tolylNNNtolyl-p.

The bond lengths and bond angles of the triethylphosphine ligands are listed in Tables 4(B) and 5(B) respectively. These values are relatively inexact owing to the high thermal motion of the carbon atoms, more especially the terminal ones. The average P-C distance found in the triethylphosphine ligands is 184 pm as compared to distances found in $[PtCl(PEt_3)_2(phen)][BF_4]$ (186 pm) (39) and $[PtCl_3(PEt_3)]^-$ (184 pm) (39A). The average C-C distance is 155 pm and indicates a single bond. This is consistent with distances found in (39) (154 pm) and in (39A) (155 pm).

The values of the bond angles, given in Table 5(B) are in general close to 109^o and show an approximate tetrahedral arrangement round the phosphorus and carbon atoms. The Pd-P-C angle is generally greater than the tetrahedral angle 109^o and the C-P-C angle less than 109^o and this is consistent with values reported in (39) and (39A).

Tables 4(C) and 5(C) give the bond lengths and angles respectively for the diphenylphosphido ligands. The average P-C length is 180 pm. Diphenylphosphido bridges are present in the structure elucidated by Carty (25) but no P-C bond lengths are given. The P-C distances in our complex, however, are consistent with values reported for trans-di-iodobis(dimethylphenylphosphine)palladium(II) (182 pm) (40). The carbon to carbon distances in the four phenyl rings average 140 pm, 142 pm, 139 pm and 142 pm respectively. These compare favourably with cited examples, e.g. (139 pm) (41). The

bond angles in the phenyl rings are close to 120^{o} and the bond angles round the phosphorus atoms close to tetrahedral.

Tables 4(D) and 5(D) contain the values for the bond lengths and angles respectively of the tetrafluoroborate ion. The error of these values is usually high owing to a very high thermal motion of the fluorine atoms (a trend which is consistent with other crystal structures containing the BF_4^- ion). The average value of B-F bond distances in our complex is 132 pm and the angles round the boron atom are close to tetrahedral. These values are in accord with data reported for $[PtCl(PEt_3)_2(Phen)][BF_4]$ (39) and $[Ni(FB(ONCHC_5H_3\text{-}N)_3P][BF_4]$ (43).

No standard deviations for the bond lengths and angles of the BF_4^- ion are given in these tables. The positions of these atoms were picked from the second last difference map and were only included in one cycle of refinement. When the final cycle of refinement was carried out which produces the input file for ORFFE (Appendix 1), the positional and temperature parameters of the BF_4 moiety (especially the boron) moved by unreasonable amounts and the standard deviations given by the ORFFE output were extremely large. It was felt that the atomic positions before this cycle of refinement were more accurate, because of the values of the bond lengths and angles, and these are given in Tables 4(D) and 5(D).

Table 4. Inter-Atomic Distances in μ-chloro bis (μ-diphenylphosphido)tris(triethylphosphine)-tri-palladium fluoroborate[a]

(A) The heavy atom co-ordination

Bond	Length (pm)	Bond	Length (pm)
Pd(1)-Pd(2)	293(2)	Pd(1)-P(4)	227(1)
Pd(1)-Pd(3)	293(2)	Pd(2)-P(4)	222(2)
Pd(2)-Pd(3)	289(2)	Pd(1)-P(5)	228(2)
Pd(1)-P(1)	231(2)	Pd(3)-P(5)	223(2)
Pd(2)-P(2)	230(1)	Pd(2)-Cl	241(1)
Pd(3)-P(3)	229(1)	Pd(3)-Cl	241(1)

(B) The triethylphosphine ligands

Bond	Length (pm)	Bond	Length (pm)
P(1)-C(1A)	182(7)	C(1A)-C(1B)	145(6)
P(1)-C(1C)	184(5)	C(1C)-C(1D)	151(6)
P(1)-C(1E)	178(4)	C(1E)-C(1F)	167(6)
P(2)-C(2A)	189(7)	C(2A)-C(2B)	150(7)
P(2)-C(2C)	179(4)	C(2C)-C(2D)	163(6)
P(2)-C(2E)	180(5)	C(2E)-C(2F)	157(6)
P(3)-C(3A)	183(6)	C(3A)-C(3B)	154(7)
P(3)-C(3C)	192(5)	C(3C)-C(3D)	155(6)
P(3)-C(3E)	188(6)	C(3E)-C(3F)	159(7)

(C) The di-phenylphosphido ligands

Bond	Length (pm)	Bond	Length (pm)
P(4)-C(4A)	183(5)	P(4)-C(4G)	180(3)
C(4A)-C(4B)	135(4)	C(4G)-C(4H)	154(5)
C(4A)-C(4F)	142(4)	C(4G)-C(4L)	142(5)
C(4B)-C(4C)	144(6)	C(4H)-C(4I)	143(5)
C(4C)-C(4D)	135(5)	C(4I)-C(4J)	142(5)
C(4D)-C(4E)	140(5)	C(4J)-C(4K)	129(5)
C(4E)-C(4F)	142(5)	C(4K)-C(4L)	138(5)
P(5)-C(5A)	180(4)	P(5)-C(5G)	178(6)
C(5A)-C(5B)	140(6)	C(5G)-C(5H)	140(5)
C(5A)-C(5F)	141(4)	C(5G)-C(5L)	144(4)
C(5B)-C(5C)	141(6)	C(5H)-C(5I)	156(7)
C(5C)-C(5D)	144(6)	C(5I)-C(5J)	133(5)
C(5D)-C(5E)	134(5)	C(5J)-C(5K)	139(5)
C(5E)-C(5F)	134(5)	C(5K)-C(5L)	140(6)

(D) The BF_4^- ion

Atoms	Length (pm)	Atoms	Length (pm)
B-F(1)	137	F(1)-F(2)	211
B-F(2)	143	F(1)-F(3)	219
B-F(3)	123	F(1)-F(4)	189
B-F(4)	123	F(2)-F(3)	213
F(3)-F(4)	223	F(2)-F(4)	215

[a]Estimated standard deviations in parentheses in tenths of a pm.

Table 5. Bond Angles in μ-chloro-bis (μ-diphenylphosphido)tris(triethylphosphine)-tri-palladium fluoroborate[a]

(A) The heavy atom co-ordination

Bonds	Angle (deg)	Bonds	Angle (deg)
Pd(2)-Pd(1)-Pd(3)	59.1(8)	Pd(3)-Pd(2)-P(4)	110.3(4)
Pd(1)-Pd(2)-Pd(3)	60.3(4)	Pd(3)-Pd(2)-Cl	53.0(4)
Pd(1)-Pd(3)-Pd(2)	60.5(5)	P(2)-Pd(2)-P(4)	101.8(8)
Pd(2)-Pd(1)-P(1)	151.1(4)	P(2)-Pd(2)-Cl	95.0(9)
Pd(2)-Pd(1)-P(4)	48.3(2)	P(4)-Pd(2)-Cl	163.2(3)
Pd(2)-Pd(1)-P(5)	107.8(6)	Pd(1)-Pd(3)-P(3)	153.2(3)
Pd(3)-Pd(1)-P(1)	149.3(6)	Pd(1)-Pd(3)-P(5)	50.2(9)
Pd(3)-Pd(1)-P(4)	107.4(8)	Pd(1)-Pd(3)-Cl	113.6(9)
Pd(3)-Pd(1)-P(5)	48.7(3)	Pd(2)-Pd(3)-P(3)	146.3(6)
P(1)-Pd(1)-P(4)	102.9(4)	Pd(2)-Pd(3)-P(5)	110.7(3)
P(1)-Pd(1)-P(5)	100.7(4)	Pd(2)-Pd(3)-Cl	53.2(5)
P(4)-Pd(1)-P(5)	156.0(6)	P(3)-Pd(3)-P(5)	103.0(9)
Pd(1)-Pd(2)-P(2)	151.8(3)	P(3)-Pd(3)-Cl	93.2(10)
Pd(1)-Pd(2)-P(4)	50.0(7)	P(5)-Pd(3)-Cl	163.7(3)
Pd(1)-Pd(2)-Cl	113.2(8)	Pd(1)-P(4)-Pd(2)	81.7(6)
Pd(3)-Pd(2)-P(2)	147.8(5)	Pd(1)-P(5)-Pd(3)	81.1(6)
		Pd(2)-Cl-Pd(3)	73.8(8)

(B) The triethylphosphine ligands

Bonds	Angle (deg)	Bonds	Angle (deg)
Pd(1)-P(1)-C(1A)	108.8(21)	Pd(2)-P(2)-C(2A)	107.2(26)
Pd(1)-P(1)-C(1C)	116.2(18)	Pd(2)-P(2)-C(2C)	114.8(13)
Pd(1)-P(1)-C(1E)	113.3(15)	Pd(2)-P(2)-C(2E)	111.7(23)
C(1A)-P(1)-C(1C)	106.9(18)	C(2A)-P(2)-C(2C)	109.3(19)
C(1A)-P(1)-C(1E)	104.4(21)	C(2A)-P(2)-C(2E)	105.0(19)
C(1C)-P(1)-C(1E)	106.5(17)	C(2C)-P(2)-C(2E)	108.4(18)
P(1)-C(1A)-C(1B)	118.5(33)	P(2)-C(2A)-C(2B)	112.0(38)
P(1)-C(1C)-C(1D)	118.9(29)	P(2)-C(2C)-C(2D)	110.6(27)
P(1)-C(1E)-C(1F)	115.4(27)	P(2)-C(2E)-C(2F)	112.1(27)
Pd(3)-P(3)-C(3A)	111.3(19)	C(3C)-P(3)-C(3E)	107.1(28)
Pd(3)-P(3)-C(3C)	116.9(15)	P(3)-C(3A)-C(3B)	111.3(32)
Pd(3)-P(3)-C(3E)	112.1(15)	P(3)-C(3C)-C(3D)	111.1(31)
C(3A)-P(3)-C(3C)	106.4(28)	P(3)-C(3E)-C(3F)	111.6(31)
C(3A)-P(3)-C(3E)	101.8(20)		

(C) The di-phenylphosphido ligands

Bonds	Angle (deg)	Bonds	Angle (deg)
Pd(1)-P(4)-C(4A)	118.3(23)	Pd(1)-P(4)-C(4G)	116.4(23)
Pd(2)-P(4)-C(4A)	113.2(18)	Pd(2)-P(4)-C(4G)	115.6(16)
C(4A)-P(4)-C(4G)	109.5(16)	P(4)-C(4G)-C(4H)	113.0(24)
P(4)-C(4A)-C(4B)	115.2(25)	P(4)-C(4G)-C(4L)	128.0(26)
P(4)-C(4A)-C(4F)	124.0(28)	C(4G)-C(4H)-C(4I)	118.2(32)
C(4A)-C(4B)-C(4C)	121.2(33)	C(4H)-C(4I)-C(4J)	114.8(35)
C(4B)-C(4C)-C(4D)	117.5(39)	C(4I)-C(4J)-C(4K)	126.7(42)
C(4C)-C(4D)-C(4E)	122.6(39)	C(4J)-C(4K)-C(4L)	123.0(41)
C(4D)-C(4E)-C(4F)	119.8(34)	C(4K)-C(4L)-C(4G)	117.7(34)
C(4E)-C(4F)-C(4A)	117.2(33)	C(4L)-C(4G)-C(4H)	117.9(30)
C(4F)-C(4A)-C(4B)	120.7(32)		
Pd(1)-P(5)-C(5A)	122.0(12)	Pd(1)-P(5)-C(5G)	113.7(14)
Pd(3)-P(5)-C(5A)	113.6(22)	Pd(3)-P(5)-C(5G)	115.1(20)
C(5A)-P(5)-C(5G)	109.1(14)	P(5)-C(5G)-C(5H)	116.0(22)
P(5)-C(5A)-C(5B)	114.1(25)	P(5)-C(5G)-C(5L)	120.4(30)
P(5)-C(5A)-C(5F)	125.6(29)	C(5G)-C(5H)-C(5I)	116.8(28)
C(5A)-C(5B)-C(5C)	118.8(38)	C(5H)-C(5I)-C(5J)	117.3(34)
C(5B)-C(5C)-C(5D)	119.9(48)	C(5I)-C(5J)-C(5K)	123.1(44)
C(5C)-C(5D)-C(5E)	116.6(48)	C(5J)-C(5K)-C(5L)	123.6(36)
C(5D)-C(5E)-C(5F)	126.8(42)	C(5K)-C(5L)-C(5G)	115.8(36)
C(5E)-C(5F)-C(5A)	117.4(38)	C(5L)-C(5G)-C(5H)	123.3(37)
C(5F)-C(5A)-C(5B)	120.3(36)		

(D) The BF_4^- ion

Bonds	Angle (deg)	Bonds	Angle (deg)
F(1)-B-F(2)	98	F(2)-B-F(3)	106
F(1)-B-F(3)	115	F(2)-B-F(4)	108
F(1)-B-F(4)	93	F(3)-B-F(4)	131

[a]Estimated standard deviations are given in parentheses in tenths of a degree.

Table 6

Least squares plane ($k_1x + k_2y + k_3z = k_4$) of heavy atom co-ordination in μ-chloro bis (μ-diphenylphosphido)-tris-(triethylphosphine)-tri-palladium fluoroborate

Plane	k_1	k_2	k_3	k_4	χ^2
Pd(1), Pd(2), Pd(3), P(1)-P(5), Cl	0.9334	0.2813	0.2228	446.49	476.91
Max. dev. (pm)	P(1) = 11.0(9)[a]				
	P(2) = 9.8(9)				
	Cl = -10.4(9)				

[a]Estimated standard deviation in parentheses.

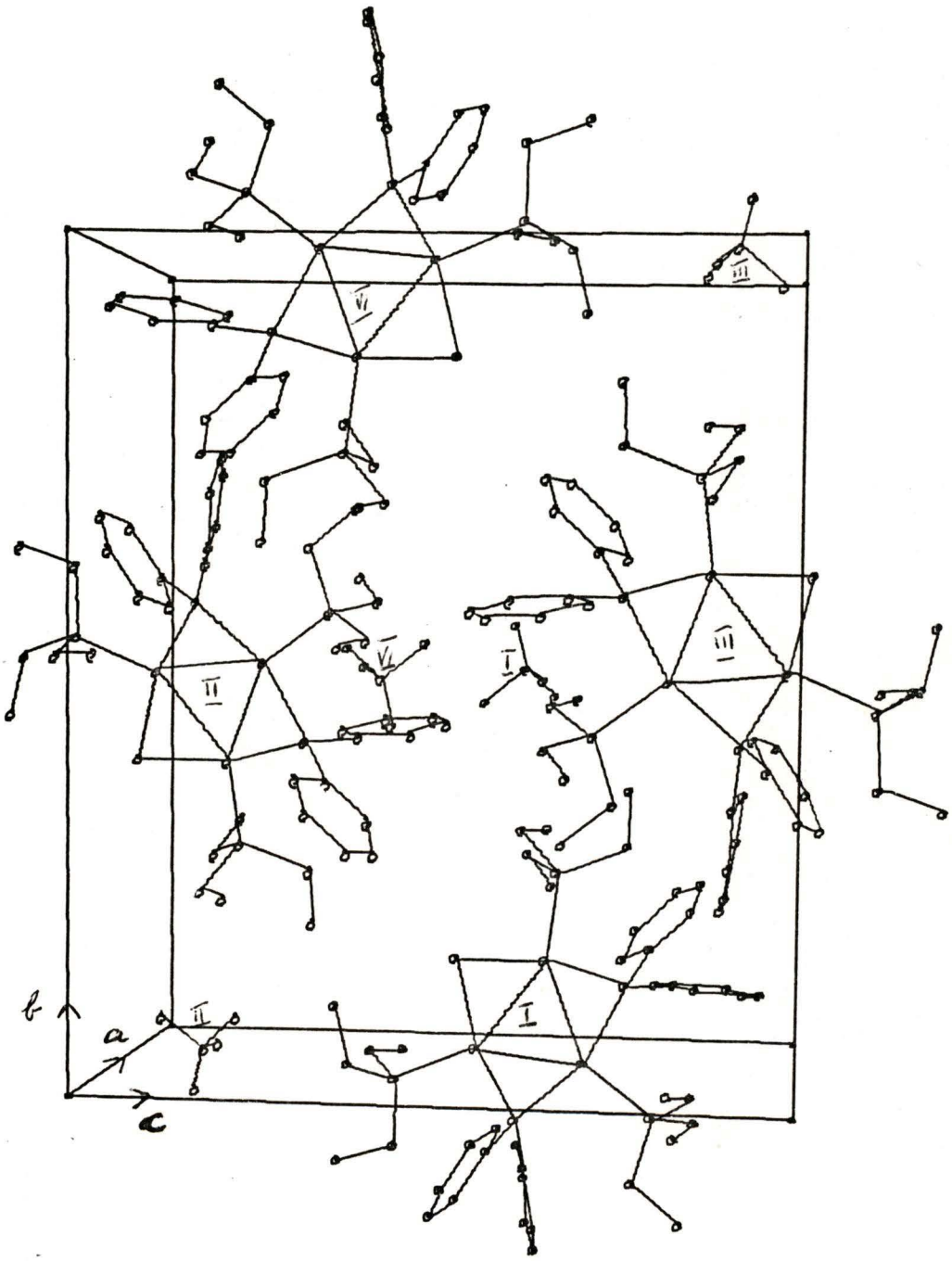


Figure 4. The Unit Cell Contents of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$.

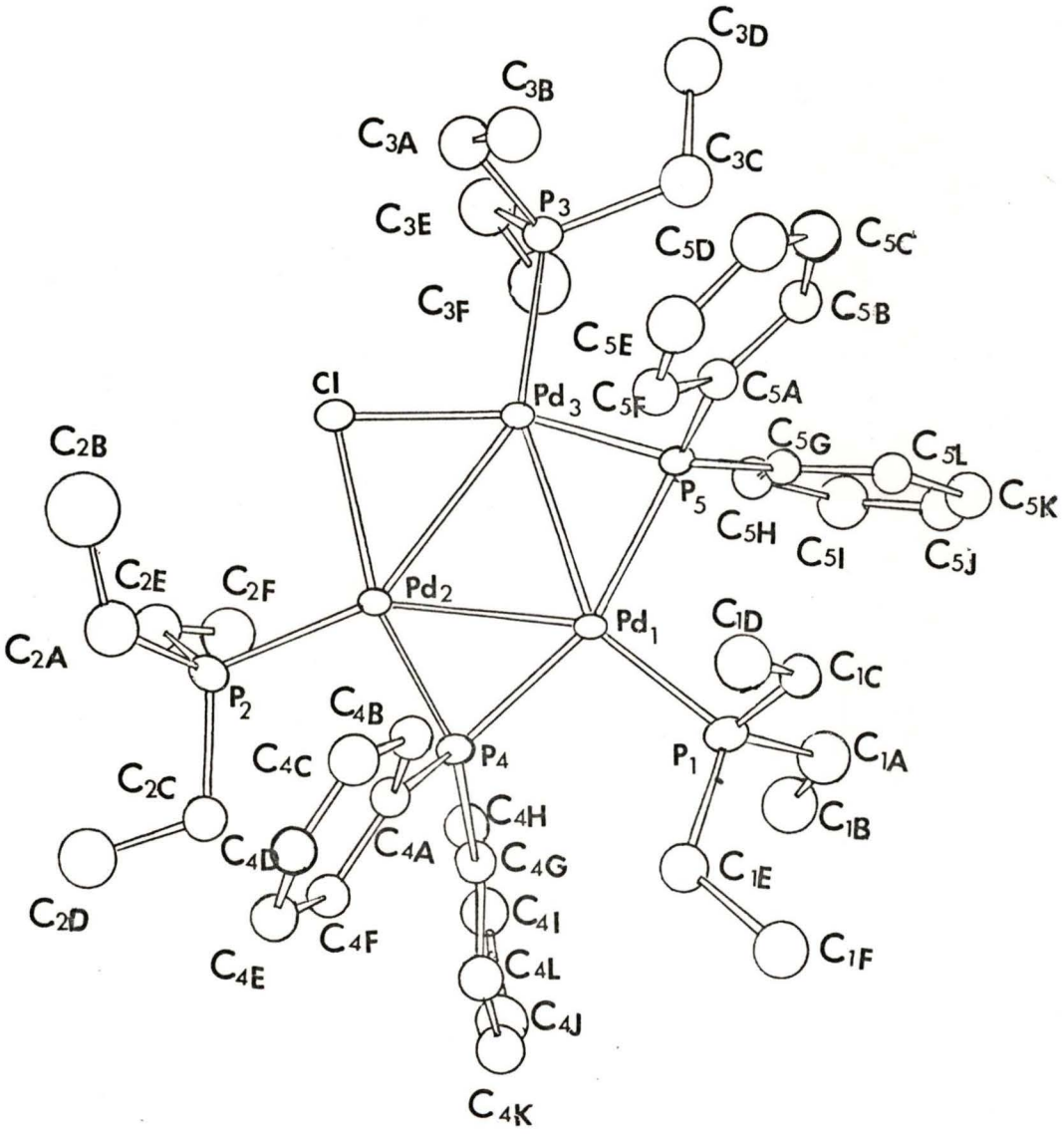


Figure 5. The Crystal Structure of the $[Pd_3Cl(PPh_2)_2(PEt_3)_3]^+$ Cation

3.2 Discussion

Although not entirely conclusive, the most useful criterion for detecting the presence of metal-metal bonds in a compound is the revelation of short metal-metal distances by x-ray crystallography. Metal-metal bond lengths are often a good indication of the bond strength. Bond lengths of strong metal-metal bonds are usually of the same order of magnitude as the interatomic distances in the metals but a continuous range of progressively weaker interactions can occur up to the non-bonding situation represented by van der Waals contacts (350-400 pm). Bonding interactions are, however, not usually considered significant between metals more than about 320 pm apart.

The range of distances over which metal-metal bonds may be found necessitates the assistance of other criteria in detecting their presence. Vibrational spectroscopy can give an insight into the nature of chemical bonds, since the measured frequencies can be used to calculate valence force constants. Spiro (1) has attempted to establish a scale of force constants associated with the stretching of metal-metal bonds in the hope that such a scale will reflect relative metal-metal bond strengths. Metal-metal vibrational frequencies show up at the low end of the spectrum, usually below 250 cm^{-1}, and infrared and Raman spectra have been used for the identification of these frequencies (44). There are difficulties inherent in identifying these metal-metal frequencies. Not only are clusters often symmetrical molecules in which the metal-metal

stretching frequencies are infrared inactive but the interpretation of the spectra is complicated by the many low-frequency molecular motions that can contribute. In the case of Raman spectroscopy, data are few but may become more common with the introduction of laser Raman spectroscopy.

The magnetic susceptibility of a compound may also be used as evidence for the presence of metal-metal bonds. The outer sphere electrons on metals involved in metal-metal bonding should be paired, and as anticipated, most known clusters are diamagnetic.

The intense colours of cluster compounds should allow their ultraviolet and visible absorption spectra to be useful techniques for detecting the presence of metal-metal interactions. However, very few investigations of the electronic spectra of clusters have been carried out because of the theoretical difficulties. Even satisfactory assignments of the spectra of simple binuclear metal-metal bonded carbonyls have yet to be made.

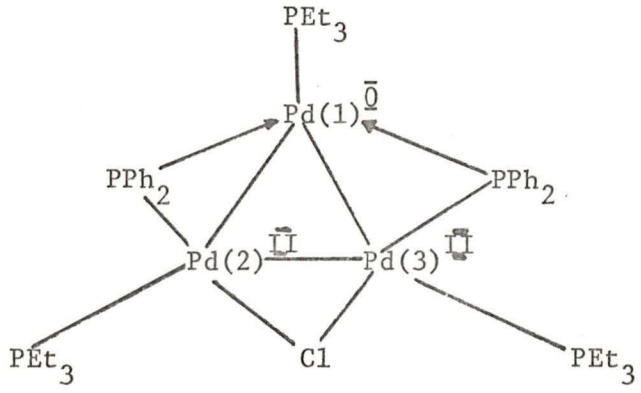
All these physical methods of detecting metal-metal bonds have certain limitations, and these difficulties are enhanced, especially in the case of x-ray crystallography and magnetic measurement, when bridging ligands are present, as is the case in our complex. No clear judgement can be made from internuclear distances and as to the magnetic criterion, significant depression of paramagnetism can occur through spin exchange via bridging ligands. These difficulties are by no means insurmountable and in the

discussion to follow, sufficient evidence will be produced to show there is a significant amount of metal-metal onding in $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$.

Metal-metal bonding is most common when the metals involved have zero or low oxidation states. The oxidation number of palladium is zero in $Pd_3(SO_2)_2(Bu^tNC)_5$, $2(C_6H_6)$ (16), the only other palladium cluster fully characterized. Platinum has a zero oxidation state in the complexes $Pt_3[P(C_6H_{11})_3]_4(CO)_3$ (23), $Pt_4[P(C_6H_5)(CH_3)_2]_4(CO)_5$ (20) and $Pt_3(SO_2)_3(PPh_3)_3$ (26). The oxidation state, as defined by Lewis and Nyholm (45), is the "formal charge left on an atom when all the ligands are removed in their closed shell configurations and any element-element bonds are broken homolytically so as to leave an equal number of electrons on each atom". By this definition the average formal oxidation state of palladium in our complex is 4/3. This is the same as the formal oxidation state of platinum in Carty's complex, $[Pt_3(PPh_3)_2(PPh_2)_3Ph] \cdot C_6H_6$ (25), which is an analogue of our complex. However, the structure of our complex is more similar to the structure of $Pd_3(SO_2)_2(Bu^tNC)_5 \cdot 2(C_6H_6)$ (16), than that of Carty's complex where one of the platinum-platinum distances in the triangle (363 pm), by our earlier definition, is greater than that allowable for metal-metal interactions.

The observed bond lengths in our complex provide some evidence that electron density is not evenly distributed between

the three palladiums. The fact that the shorter Pd-Pd distance is found between the two palladiums with the Cl bridge, and the distances from the respective phosphorus bridging atoms to these palladiums is less than the corresponding Pd(1)-PPh_2 distances, suggests that the dominant canonical form of our structure is:



Two of the palladiums have an oxidation number of 2 and the other zero, which is also an intuitively satisfying electron density distribution.

The average metal-metal distances found in our complex (see Table 4(A)) are approximately 20 pm longer than the interatomic distance in the metal (275 pm), which is of the same order of magnitude as the corresponding average distances in $Pd_3(SO_2)_2(Bu^tNC)_5$, $2C_6H_6$ (274 pm) (16), the only other trimeric palladium cluster to be characterized by x-ray diffraction techniques. Two other trimeric palladium structures have been studied by x-ray diffraction techniques, but their average metal-metal bond lengths, 315 pm in trimeric palladium(II) acetate (14) and 352 pm in [Pd(2,2'-dimercaptodiethyl-sulphide)]$_3$ (46) indicate they have only very weak or zero metal-

metal bonding. This is especially strange in the case of the trimeric palladium(II) acetate as the platinum analogue, platinum(II) acetate, is tetrameric (21) and the very short Pt-Pt distances (249 pm) are indicative of strong metal-metal bonds. The metal-metal distance in our complex is somewhat long for strong metal-metal bonding. However, the dimeric η^3-allyl complex, $([(\eta^3\text{-}C_3H_5)Pd(ac)]_2)$, is considered to have a weak palladium-palladium bond (47) and has a Pd-Pd distance (294 pm) similar to ours. Also the metal-metal distances in our complex are much shorter than those found in chlorine bridged palladium complexes, such as $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (Pd-Pd distance of 347.5 pm) (34) with no metallic bonding. Further support for the hypothesis of metal-metal bonds in our complex is obtained from the platinum analogue. In Carty's complex (25), two of the metal-metal distances are well within the range for metal-metal bonding whilst the other distance is clearly non-bonding. Much larger metal-metal distances should thus be present in our complex if there was no metallic bonding.

As we have discussed earlier, the triangle is an ideal building block for metal clusters. The '18 electron rule' is not always obeyed in the chemistry of cluster compounds. Most of the known platinum and palladium clusters are two electrons short, but without the existence of metal-metal bonds, the number of electrons associated with metal atoms is lower.

The diamagnetism of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ and its red-orange colour both in solution and when crystalline, are only suggestive of metal-metal bonding. More confirmatory evidence is found in the chemical reactivity of the complex. Its stability towards excess triethylphosphine is a good indication of the presence of Pd-Pd bonding. This is based on the fact that although the diphenylphosphido bridge is very strong in dimeric palladium complexes with no metal-metal bonding, such as $[PdCl(PPh_2)(PR_3)]_2$ (48,49) and not readily cleaved by neutral phosphine ligands, halogen bridges in dimeric complexes are generally reactive to this type of ligand, especially PEt_3. Thus a triangular structure involving only two diphenylphosphido and one chloro bridge should not be stable to bridge cleavage by phosphines, unless supported by metal bonds.

Of work done previously outside this laboratory, the most closely related is by Coulson (15). The structure of $[Pd_3(PPh_2)_2(PPh_3)_3Cl_2]$ (see page 9) was formulated, on the basis of analyses, ebullioscopic molecular weight, ^{31}P N.M.R. and stability of the compound to excess triphenylphosphine, as a neutral covalent cluster. $[Pd_3Cl(PPh_2)_2(PPh_3)_3][Cl]$, synthesised from $[Pd_3Cl(PPh_2)(PPh_3)_3][BF_4]$ by anion exchange (19), has an infrared spectrum identical to that of Coulson's complex. The structure proposed by Coulson is incorrect as $[Pd_3(PPh_2)_2(PPh_3)Cl_2]$ evidently contains a similar cationic cluster to ours, but with triphenylphosphine groups substituted for

triethylphosphine. This same skeleton of atoms was proposed by Ch'eng Wan (27) in his structural study of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$, which was not completed because of the previously mentioned phasing problem. It seems reasonable, therefore, to suggest that the molecular structures of all the complexes, $[Pd_3X(PPh_2)_2(PR_3)_3][Y]$, should be similar and ^{31}P N.M.R. studies have supported this hypothesis.

Chemical shifts and coupling constants have provided useful structural information in the ^{31}P N.M.R. studies of these complexes. In fact, based on the findings of Dixon and Rattray (19), ^{31}P N.M.R. may become a more popular tool in detecting M-M bonding in clusters that have bridging phosphido ligands. It seems reasonable to expect a larger coupling constant between two phosphorus nuclei, bonded to different metals which are metal-metal bonded, than between two phosphorus nuclei, bonded to different metals which are joined by bridges. Furthermore, large chemical shift variations for the bridging phosphorus atoms might be expected due to electron delocalisation when M-M bonds are present. Both of these effects have been found in practice for the present complex. The details are as follows: ^{31}P N.M.R. spectra for $[Pd_3Cl(PPh_2)_2(PR_3)_3][BF_4]$, R = Ph or Et, were originally interpreted as belonging to the AB_2X_2 spin system. It is now clear that the actual molecular system is ABB'XX' (A, B and B' are PR_3 groups and X and X' are PPh_2). This appears like an AB_2X_2 system under certain circumstances, notably when $J_{BB'}$ is large and a type of virtual coupling prevails. The

resulting parameters for both complexes are similar, and the data follows for the triphenyl (and the triethyl substituted clusters) respectively: J_{AB} = 83.7 (93) Hz, J_{AX} = -11.0(-13.5) Hz, ∂_A = 128.3 (139), ∂_B = 121.5 (125), ∂_X = -81.4 ppm (-61.8) relative to $P(OMe)_3$, positive values are upfield. Features unique to the cluster system are the large values of J_{AB}, and the large downfield shift of the PPh_2 groups. The other parameters are not uniquely determinable from the spectrum and the assigned spin system agrees with the crystal structure. Comparison of these values with the corresponding parameters in the absence of Pd-Pd bonding ($J_{AA'}$ < 5 Hz, ∂_X = +273 ppm) in $[Pd_2Cl_2(\mu\text{-}PPh_2)_2(PHPh_2)_2]$ (50) emphasizes the dramatic effects of metal-metal bonding. Thus in its absence the coupling constant is quite small and the chemical shift of the bridging phosphorus is very far upfield.

3.3 Conclusion

Not all the techniques for detecting M-M bonds have been used for our complex. Some of these have not been used for practical reasons and others, such as, in the case of infrared spectra, where Pd-Pd vibrational frequencies have yet to be assigned, have only been used for comparison purposes. However, substantial evidence has been given to show that there is significant metal-metal bonding between each palladium in our complex. The primary evidence in our case is obtained from the bond lengths, the differences in structure of the

platinum analogue and the effects of metal-metal bonding on the ^{31}P N.M.R. parameters. Secondary evidence is obta ned from the chemical reactivity of the complex and evidence of lesser importance from the triangular shape of the molecule, its magnetic properties and the colour of the complex.

Based on Johnson's definition of a cluster (51, p. 472), the structure determination of $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$ has completed the characterization of the first palladium cluster with an oxidation number greater than zero. It has also increased the number of known crystal structures of palladium clusters by 100%, and can be considered a significant addition to the field of cluster chemistry.

BIBLIOGRAPHY

1. T. G. Spiro, Progr. Inorg. Chem., 11, 1 (1970).

2. M. C. Baird, Progr. Inorg. Chem., 9, 1 (1968).

3. T. W. Thomas and A. E. Underhill, Chem. Soc. Rev., 1, 99 (1972).

4. D. E. Williams, G. Wohlauer and R. E. Rundle, J. Am. Chem. Soc., 81, 755 (1958).

5. R. B. King, Progr. Inorg. Chem., 15, 287 (1972).

6. J. F. Harrod and A. J. Chalk, J. Am. Chem. Soc., 87, 1133 (1965).

7. C. H. Wei and L. F. Dahl, J. Am. Chem. Soc., 82, 1821 (1966).

8. C. H. Wei and L. F. Dahl, J. Am. Chem. Soc., 90, 3960 (1968).

9. E. O. Fischer and C. Palm, Chem. Ber., 91, 1725 (1958).

10. J. C. Calabrese, A. Cavalieri, P. Chini, L. F. Dahl, G. Longoni and S. Martinego, J. Am. Chem. Soc., 96, 2616 (1974).

11. See for example; R. Ugo, S. Cenini, M. F. Pilbrow, B. Deibl, and G. Schneider, Inorg. Chim. Acta, 18, I13 (1976); and references therein.

12. G. Allegra, G. T. Casagrande, A. Immirzi, L. Porri, and G. Uitulli, J. Am. Chem. Soc., 92, 289 (1970).

13. M. R. Churchill and R. Mason, Nature, 204, 777 (1964).

14. A. C. Skapski and M. L. Smart, Chem. Comm., 658 (1970).

15. D. R. Coulson, Chem. Comm., 1530 (1968).

16. S. Otsuka, Y. Tatouno and M. Miki, Chem. Comm., 445 (1973).

17. K. V. Werner, W. Beck and U. Böhner, Chem. Ber., 107, 2434 (1974).

18. T. Yoshida and S. Otsuka, J. Am. Chem. Soc., 99, 2134 (1977).

19. A. D. Rattray, Ph.D. Thesis, University of Victoria, (1975).

20. R. G. Vranka, L. F. Dahl, P. Chini and J. Chatt, J. Am. Chem. Soc., 91, 1574 (1969).

21. M. A. A. F. De C. T. Carrondo and A. C. Skapski, Chem. Comm., 410 (1976).

22. J. C. Calabrese, P. Chini, L. F. Dahl, G. Longoni and S. Martinego, J. Am. Chem. Soc., 96, 2614 (1974).

23. A. Albinati, G. Carturan and A. Musco, Inorg. Chim. Acta, 16, L3 (1976),

24. J. Chatt and P. Chini, J. Chem. Soc. (A), 1538 (1970).

25. N. J. Taylor, P. C. Chieh and A. J. Carty, Chem. Comm., 448 (1975).

26. D. C. Moody and R. R. Ryan, Inorg. Chem., 16, 1052 (1977).

27. G. Bushnell and C. Wan, Private Communication.

28. K. R. Dixon and D. J. Hawke, Can. J. Chem., 49, 3252 (1971).

29. F. G. Mann and D. Purdie, J. Chem. Soc., 1549 (1935).

30. D. T. Cromer and J. T. Waber, Acta Cryst., 18, 104 (1965).

31. J. A. Ibers, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. IV, Table 2.3.1, 149 (1974).

32. B. R. Penfold, University of Canterbury Crystallographic Programs, Christchurch, New Zealand.

33. G. W. Bushnell, University of Victoria, B. C., Canada.

34. A. F. Smith, Acta Cryst., 18, 331 (1965).

35. L. Toniolo, A. Immirzi, U. Croatto and G. Bombieri, Inorgan. Chim. Acta, 19, 209 (1976).

36. R. W. Siekman and D. L. Weaver, Chem. Comm., 1021 (1968).

37. B. T. Kilbourn and R. H. B. Mais, Chem. Comm., 1507 (1968).

38. R. Eisenberg, A. P. Gaughan Jr., C. G. Pierpoint, J. Reed and A. J. Schultz, J. Am. Chem. Soc., 94, 6240 (1972).

38A. P. L. Bellon, C. Bendicenti, C. Caglio and M. Manessero, Chem. Comm., 946 (1973).

39. G. W. Bushnell, K. R. Dixon and M. A. Khan, Can. J. Chem., 52, 1367 (1974).

39A. G. W. Bushnell, A. Pidcock, and M. R. Smith, J. Chem. Soc. Dalton, 572 (1975).

40. N. A. Bailey and R. Mason, J. Chem. Soc. (A), 2595 (1968).

41. J. A. Ibers, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. III, Table 4.2.2, 276 (1962).

42. J. S. Rollett, "Computing Methods in Crystallography", Pergamon Press, 114 (1965).

43. G. A. Mair, H. M. Powell and L. M. Venanzi, Proc. Chem. Soc., 170 (1961).

44. D. Hartley, P. A. Kilty and M-J. Ware, Chem. Comm., 493 (1968).

45. J. Lewis and R. S. Nyholm, Sci. Progr. (London), 557 (1964).

46. E. M. McPartlin and N. C. Stephenson, Acta Cryst., B25, 1659 (1969).

47. G. E. Coates, M. L. H. Green and K. Wade, Organometallic Cpds., 2, 54 (1968).

48. R. G. Hayter, J. Am. Chem. Soc., 84, 3046 (1962).

49. R. G. Hayter and F. S. Humiec, Inorg. Chem., 2, 306 (1963).

50. K. R. Dixon, University of Victoria, Private Communication.

51. R. D. Johnson, Advances in Inorg. Chem. and Radiochemistry, 13, (1970).

APPENDIX 1

1. AUTOMATIC: A program in BASIC for measuring reflections automatically on the diffractometer, used by a P.D.P. 11 minicomputer, written by G. W. Bushnell and S. Wong.

2. CELGLS: Least squares refinement for the cell parameters, written by Busing and Levy, modified by G. W. Bushnell.

3. CRYSTAL: Data reduction program for use on C.M.S., written by G. W. Bushnell and Y. T. Chen.

4. BICABS: Absorption correction program, written by Coppens, Leiserowitz and Rabinovich. Modified by F. H. Allen and since modified by G. W. Bushnell.

5. FORDAP: Patterson, Fourier and D. Fourier Program written by A. Zalkin.

6. BUCLS: Full matrix least squares refinement for atomic and thermal parameters, written by Busing, Martin and Levy. Modified and supplied by B. R. Penfold.

7. RANGER: Checking for the weighting reflection program, written by P. W. R. Corfield.

8. DANFIG: Bond lengths and bond angle calculation, written by W. H. Baur.

9. ORFEE: Bond lengths and bond angles with their estimated standard deviations calculation, supplied by B. R. Penfold. (Original by Busing, Martin, and Levy.)

10. MEANPLANE: Least squares mean plane calculation, written by Pippy and Ahmed.

11. ORTEP: Plotting of stereo diagrams of the crystal structure, written by C. K. Johnson.

12. FILIST: List of F_o and F_c for publication purposes, supplied by B. R. Penfold.

APPENDIX 2

Chloro bis (μ-diphenylphosphido)tris(triethylp osphine)-tri palladium fluoroborate

Final Values of 10 x F_{obs} and 10 x F_{calc}

K	L	OBS	CALC
**** H = 0****			
0	2	584	534
0	4	1449	1393
0	6	1106	1041
0	8	1676	1510
0	10	1090	1236
0	14	458	452
0	16	558	633
1	2	1065	935
1	3	906	880
1	4	1244	952
1	5	1230	1113
1	6	1530	1487
1	7	1522	1498
1	9	655	823
1	10	914	1174
1	11	1062	1171
1	13	582	490
2	1	1567	1296
2	2	659	635
2	3	494	197
2	4	1248	1201
2	5	1230	1160
2	6	2780	2348
2	7	1670	1698
2	8	592	700
2	9	907	941
2	10	857	1084
2	11	479	640
2	14	479	375
2	15	731	686
3	1	230	211
3	3	1219	833
3	4	1594	1418
3	5	3215	2980
3	6	1745	1394
3	7	259	212
3	9	410	619
3	10	946	1015
3	11	1153	1292
4	0	1272	1392
4	3	400	362
4	4	330	425
4	6	3162	2700
4	7	742	767
4	8	943	1014
4	10	536	635
4	12	613	380
4	13	458	434
5	1	1079	853
5	2	982	759
5	5	3315	2837
5	6	713	703
5	11	1176	1273
5	13	400	93
6	0	1483	1369
6	1	1635	1589
6	2	492	444
6	4	1340	1214
6	5	822	950
6	6	2591	2487
6	7	1087	1204
6	10	840	879
6	13	435	461
6	14	430	457
6	15	560	551
7	1	3370	3586
7	3	1361	1132
7	4	1000	847
7	5	2036	1872
7	6	1022	1071
7	7	1072	1219
7	9	572	654
7	11	604	751
7	12	523	518
7	13	671	546
7	14	470	501
8	0	4198	4026
8	2	813	415
8	3	847	800
8	4	534	570
8	5	538	545
8	6	1709	1906
8	8	1048	1182
8	10	678	679
8	11	616	621
8	14	671	647
9	1	2307	2400
9	2	2035	1863
9	3	661	716
9	4	930	790
9	5	1551	1425
9	6	917	991
9	7	831	873
9	9	378	475
9	10	630	652
9	13	521	390
10	0	1774	1915
10	1	724	1000
10	3	1380	1320
10	4	1046	852
10	5	721	599
10	6	1429	1373
10	7	1058	1138
10	8	461	460
10	9	478	448
10	11	554	782
10	12	577	620
11	2	1319	1170
11	4	972	860
11	5	2160	1903
11	6	649	719
11	9	675	798
11	10	453	429
11	11	713	907
12	0	1332	1194
12	4	1357	1242
12	5	942	893
12	6	761	750
12	8	1183	1109
12	12	743	839
13	1	456	462
13	2	645	650
13	4	378	475
13	5	1160	1052
13	6	492	551
13	8	697	597
13	9	716	746
13	11	833	879
14	0	1601	1447
14	3	432	438
14	5	830	738
14	6	741	720
14	7	800	662
14	8	634	608
14	10	584	506
15	1	1054	1092
15	2	890	771
15	5	485	477
15	6	704	585
15	7	497	430
15	8	525	478
16	0	1508	1565
16	4	335	405
16	6	1119	912
17	1	375	326
17	3	469	557
17	5	595	561
18	3	830	797
18	4	585	368
**** H = 1****			
0	2	3717	3652
0	4	402	211
0	6	1338	1520
0	8	868	803
0	10	407	320
0	12	714	735
1	0	2105	1933
1	2	848	763
1	3	1070	1156
1	4	233	216
1	5	519	433
1	6	1004	959
1	7	1354	1474
1	8	1151	1492
1	9	336	402
1	10	439	542
1	11	422	304
1	13	508	577
2	0	526	289
2	1	205	267
2	2	285	442
2	3	1025	1208
2	4	417	200
2	5	1014	839
2	6	2439	2268
2	7	1711	1447
2	8	1606	1562
2	9	919	1062
2	10	394	557
2	11	702	758
2	12	896	932
2	14	490	454
3	0	573	158
3	1	1039	720
3	2	1163	1052
3	3	624	736
3	5	1345	1232
3	6	458	434
3	7	3373	3117
3	8	1083	1283
3	11	459	348
3	13	876	1046
4	0	450	341
4	1	1255	1168
4	2	1409	1285
4	3	538	328
4	4	454	562
4	6	2161	2149
4	7	246	214
4	8	1318	1491
4	12	1021	1113
4	14	713	797
5	0	1100	1109
5	2	561	434
5	3	1637	1448
5	4	835	768
5	5	447	301
5	6	665	623
5	7	2479	2750
5	8	376	491
5	10	412	379
5	11	422	327
5	13	839	1064
6	0	1371	1076
6	1	1882	1538
6	2	1421	1219
6	3	998	1037
6	4	1310	1228
6	5	1236	1333
6	6	1123	1288
6	7	825	815
6	8	813	765
6	9	456	524
6	11	382	325
6	12	1075	1103
6	13	411	525
7	0	1865	1459
7	1	2080	1774
7	2	1892	1579
7	3	550	492
7	4	1223	1181
7	5	1087	913
7	7	557	578
7	8	423	419
7	9	363	237
7	11	759	691
7	13	570	631
8	0	948	907
8	1	1185	950
8	2	2744	2690
8	3	1308	1358
8	4	1532	1353
8	5	438	531
8	8	820	715
8	10	783	700
8	12	687	644
9	0	1644	1597
9	1	2382	2303
9	2	651	794
9	3	761	517
9	5	963	1008
9	6	856	786
9	7	1230	1036
9	8	1052	980
9	9	443	446
9	11	523	366
10	1	1684	1740
10	2	530	536
10	3	650	542
10	6	1498	1206
10	7	1588	1383
10	9	456	492
10	12	784	729
11	0	1665	1555
11	1	274	290
11	2	857	781
11	4	521	578
11	5	734	777
11	7	1259	1171
11	8	860	903
11	9	267	360
11	10	316	250
12	1	210	261
12	3	1349	1326
12	5	359	402
12	6	1125	1084
12	8	580	568
12	9	249	141
12	10	870	732
12	12	826	716
13	1	643	650
13	2	269	316
13	4	1199	1209
13	7	1017	1001
13	9	288	408
13	11	448	174
14	2	1054	1044
14	3	1039	1085
14	5	541	546
14	6	284	226
14	8	329	350
14	10	570	408
15	0	374	354
15	1	971	1037
15	2	516	691
15	3	405	533
15	4	1021	960
15	5	503	505
15	6	341	248
15	7	316	352
16	2	1394	1460
16	3	754	752
16	4	489	580
16	5	355	424
16	6	404	406
16	7	468	467
16	8	423	359
17	0	574	562
17	1	767	805
17	2	736	641
17	5	705	721
17	6	678	682
18	1	905	943
18	4	450	487
**** H = 2****			
0	2	1580	1480
0	4	504	470
0	6	2493	2356
0	8	1473	1698
0	10	491	644
0	12	378	423
0	14	317	329
1	0	1426	1350
1	1	3080	3357

K	L	OBS	CALC	K	L	OBS	CALC	K	L	OBS	CALC	K	L	OBS	CALC
1	2	1970	1466	7	8	368	306	16	1	484	464	5	2	1647	1733
1	3	1728	1571	7	9	630	672	16	2	366	306	6	3	1710	1592
1	5	1749	1580	7	11	514	519	16	4	348	322	6	4	589	419
1	6	619	762	7	12	672	622	16	5	1179	1293	6	5	640	608
1	7	1171	1449	7	13	479	470	17	0	355	441	6	6	610	648
1	9	396	404	7	14	514	504	17	1	528	560	6	7	1143	1061
1	10	527	569	8	0	3836	3761	17	2	476	469	6	8	627	752
1	11	803	878	8	3	1023	1102	17	3	670	629	6	11	344	371
1	12	316	379	8	4	554	616	17	5	623	704	6	12	921	903
1	13	388	277	8	5	532	454	18	0	328	369	6	13	372	317
1	14	395	408	8	6	2521	2618	18	1	410	388	6	14	506	389
2	1	1213	1390	8	7	245	194	18	3	446	507		1	2118	2007
2	2	2566	2590	8	8	1183	1009						2	1767	1713
2	3	420	577	8	10	309	202					7	3	1005	923
2	4	1476	1429	8	11	784	676	*	*	* H = 3	* * *	7	4	420	446
2	5	1284	1203	9	1	1752	1679					7	5	1617	1451
2	6	1282	1275	9	2	1105	1066	0	0	2377	1577	7	7	1673	1365
2	7	435	437	9	3	543	566	0	2	4690	4308	7	8	457	361
2	8	386	207	9	4	216	232	0	4	1346	1320	7	9	955	722
2	9	793	992	9	5	1808	1752	0	6	267	376	7	10	577	539
2	10	741	898	9	6	762	706	0	8	2132	2376	7	11	559	645
2	11	228	198	9	7	1387	1199	0	12	500	562	7	13	546	440
2	12	581	556	9	8	652	584	1	0	788	536	8	0	2091	1956
2	14	335	429	9	9	333	235	1	1	3049	3206	8	1	538	560
2	15	536	554	9	10	616	458	1	4	291	178	8	2	1990	2131
3	0	1648	1537	9	11	312	317	1	5	679	653	8	3	1175	1066
3	1	1990	1804	10	0	1833	1821	1	6	1055	1106	8	4	2026	2053
3	2	1698	1714	10	1	1817	1787	1	7	1249	1462	8	7	414	336
3	3	1804	1532	10	2	835	818	1	8	530	566	8	8	1628	1344
3	4	429	397	10	3	606	673	1	9	782	1020	8	10	541	458
3	5	1517	1644	10	4	486	573	1	10	398	493	8	11	273	211
3	6	733	764	10	5	235	251	1	13	656	704	8	12	521	469
3	8	282	156	10	6	1023	1003	2	0	729	837	8	13	291	235
3	9	694	861	10	7	456	423	2	1	274	58	9	0	1213	1153
3	10	1089	1221	10	8	374	377	2	2	2863	2365	9	1	1773	1952
3	11	1280	1371	10	9	829	754	2	3	365	350	9	2	303	286
3	14	364	349	10	11	622	478	2	4	400	317	9	3	532	541
3	15	331	308	10	12	610	739	2	5	519	573	9	4	563	582
4	0	1344	1479	10	13	605	494	2	6	1395	1527	9	5	1012	874
4	1	532	579	11	0	256	345	2	7	1277	1261	9	6	1065	974
4	2	407	392	11	1	231	338	2	8	1351	1341	9	7	1290	1178
4	3	853	864	11	2	731	665	2	9	573	559	9	8	791	582
4	4	1646	1368	11	3	558	591	2	10	299	338	9	9	789	606
4	5	390	192	11	4	688	690	2	11	763	682	9	12	393	350
4	6	2243	1924	11	5	1275	1261	2	12	797	959	9	13	691	651
4	7	483	484	11	6	341	336	2	14	436	408	10	1	608	640
4	8	1542	1501	11	7	357	432	2	15	342	457	10	2	1233	1251
4	9	299	353	11	9	717	662	3	0	493	395	10	5	653	607
4	10	529	591	11	10	727	605	3	1	333	158	10	6	758	774
4	12	804	775	11	11	936	805	3	2	853	661	10	7	1209	1205
4	13	526	563	12	0	337	517	3	3	326	358	10	8	333	335
4	14	306	371	12	1	231	232	3	4	270	163	10	12	847	762
5	0	214	243	12	3	392	295	3	5	379	496	11	0	1669	1626
5	1	1813	1778	12	4	965	987	3	6	1053	1082	11	2	579	506
5	2	1026	815	12	5	996	1002	3	7	2089	2189	11	3	338	457
5	4	393	341	12	6	553	511	3	8	1349	1345	11	4	668	658
5	5	2446	2154	12	7	318	211	3	9	401	486	11	5	628	671
5	6	1011	905	12	8	1086	1082	3	13	1133	1237	11	7	853	896
5	9	449	477	12	9	386	376	4	0	1949	1606	11	8	918	818
5	10	223	162	13	1	995	992	4	1	477	108	12	0	946	904
5	11	1014	1061	13	2	488	588	4	2	588	397	12	1	410	486
5	12	423	220	13	4	623	656	4	3	607	508	12	2	408	470
5	14	624	672	13	5	943	935	4	5	439	384	12	3	1031	1025
6	0	2294	2292	13	6	544	635	4	6	2055	1830	12	6	1185	1211
6	1	2110	1984	13	9	969	923	4	8	1349	1222	12	8	471	413
6	2	1343	1120	13	11	897	775	4	9	462	474	12	9	342	304
6	5	932	828	14	0	1336	1294	4	10	789	708	12	10	902	744
6	6	1765	1720	14	1	642	639	4	11	238	301	12	11	314	218
6	7	995	764	14	3	362	379	4	12	949	1072	13	1	659	597
6	8	413	339	14	4	256	253	4	14	995	932	13	2	537	371
6	9	371	261	14	5	845	978	5	0	1599	1265	13	3	296	340
6	10	935	849	14	6	487	664	5	1	273	156	13	4	1176	1275
6	12	332	298	14	7	438	464	5	2	266	325	13	5	354	425
6	13	701	705	14	8	432	460	5	4	1277	1136	13	7	660	678
6	14	431	473	14	10	399	364	5	6	486	306	13	9	361	412
7	0	645	744	15	1	1055	1096	5	7	2663	2625	14	0	510	481
7	1	2547	2722	15	2	662	740	5	8	337	324	14	2	1333	1392
7	2	724	682	15	3	394	509	5	9	552	548	14	3	1013	1080
7	3	1518	1417	15	4	445	402	5	11	376	500	14	5	448	456
7	4	1096	1060	15	5	424	509	5	12	610	579	14	8	395	416
7	5	1716	1803	15	6	415	534	5	13	1072	1103	15	0	393	375
7	6	1028	973	15	7	741	715	6	0	588	465	15	1	1275	1350
7	7	1362	1497	16	0	1248	1291	6	1	473	531	15	2	759	827

K	L	OBS	CALC
15	3	415	542
15	4	712	734
15	5	868	769
15	7	487	533
16	0	261	320
16	1	377	385
16	2	1122	1220
16	3	676	661
16	4	596	666
16	7	398	394
17	0	470	497
17	1	851	965
17	2	281	434
17	5	602	707
18	1	433	495

**** H = 4****

K	L	OBS	CALC
0	0	5056	4541
0	2	465	479
0	4	556	571
0	6	1735	1807
0	8	829	784
0	12	685	611
1	0	1582	1445
1	1	2823	2666
1	2	560	502
1	3	1211	1199
1	5	1449	1614
1	6	329	303
1	7	1744	1808
1	8	595	620
1	10	373	420
1	11	656	762
1	14	329	281
2	0	3551	3970
2	1	2773	2828
2	2	1164	1091
2	4	452	387
2	5	854	857
2	6	900	816
2	8	443	399
2	9	1144	1256
2	10	350	418
2	12	488	513
2	13	251	233
2	14	295	341
3	0	1356	1153
3	1	2133	1963
3	2	860	786
3	3	997	944
3	4	623	533
3	5	910	961
3	6	662	489
3	8	357	458
3	10	1099	1045
3	11	1081	1086
4	0	1726	1419
4	2	1872	1682
4	3	919	948
4	4	1028	964
4	5	298	163
4	6	1474	1232
4	7	368	356
4	8	1501	1464
4	10	912	826
4	12	847	664
4	14	630	717
5	0	424	525
5	1	2173	1837
5	2	1533	1319
5	3	409	346
5	4	222	255
5	5	902	912
5	6	731	701
5	8	626	617
5	11	799	691
5	12	490	468
5	14	570	551
6	0	1986	2027
6	1	1476	1357
6	2	710	912
6	3	188	247
6	4	779	628
6	5	614	550
6	6	2535	2172
6	8	727	542
6	10	919	758
6	11	401	344
6	13	684	537
6	14	567	606
7	0	1292	1234
7	1	1502	1387
7	2	518	493
7	3	1233	1211
7	4	1153	1046
7	5	1336	1389
7	6	370	322
7	7	1854	1486
7	8	464	477
7	9	237	203
7	12	595	490
8	0	1438	1532
8	2	444	482
8	3	1063	1117
8	4	227	225
8	5	436	391
8	6	3097	2799
8	8	664	516
8	11	764	636
9	0	853	913
9	1	864	1004
9	2	1195	1123
9	3	1019	917
9	4	248	231
9	5	1469	1400
9	7	1379	1124
9	8	811	709
9	10	400	297
9	11	352	325
10	0	1851	1838
10	1	1398	1495
10	2	329	387
10	3	343	398
10	4	378	379
10	5	278	189
10	6	701	681
10	9	1033	805
10	11	429	290
10	12	654	528
11	0	630	576
11	1	1219	1277
11	2	880	895
11	3	513	622
11	4	766	751
11	5	731	683
11	8	457	403
11	9	707	597
11	10	680	563
11	11	937	730
12	0	723	785
12	2	711	648
12	4	749	810
12	5	756	803
12	7	261	250
12	8	977	902
12	9	612	553
13	1	1111	1083
13	2	336	380
13	4	590	554
13	5	761	770
13	6	434	420
13	7	252	265
13	9	719	647
14	0	1278	1233
14	1	638	686
14	3	316	308
14	5	981	1071
14	6	577	699
14	8	253	236
15	1	679	854
15	2	313	299
15	3	562	628
15	4	463	485
15	5	643	571
15	7	901	862
16	0	369	919
16	2	342	428
16	3	326	372
16	6	1151	1286
17	0	739	656
17	3	444	585

**** H = 5****

K	L	OBS	CALC
0	0	1352	1298
0	2	3264	3095
0	4	1591	1435
0	6	941	1066
0	8	2367	2700
0	10	475	525
0	12	377	413
0	14	393	293
1	1	2999	2692
1	2	1209	1144
1	3	282	149
1	4	1020	802
1	5	324	253
1	6	1096	1148
1	7	1651	1858
1	8	339	373
1	9	1179	1245
1	10	372	421
1	11	314	313
1	13	326	426
2	0	411	456
2	1	1932	1738
2	2	2238	1948
2	3	232	229
2	4	802	654
2	5	652	616
2	6	826	812
2	7	1577	1726
2	8	1693	1709
2	10	369	344
2	11	343	369
2	12	656	686
2	14	413	359
3	0	283	310
3	2	866	845
3	3	1029	1166
3	6	1152	1093
3	7	1646	1677
3	8	1148	1158
3	9	355	384
3	10	532	542
3	13	954	991
4	0	1916	1702
4	2	621	529
4	4	415	411
4	6	1523	1419
4	8	570	452
4	9	430	415
4	10	578	509
4	12	1008	1003
4	14	840	831
5	0	1177	965
5	1	519	564
5	2	1000	1038
5	3	1001	904
5	4	631	590
5	5	764	606
5	7	1848	1742
5	8	568	553
5	9	423	406
5	10	407	372
5	11	546	565
5	13	1238	1290
6	2	1823	1664
6	3	1238	1207
6	4	559	483
6	6	439	590
6	7	871	780
6	8	1138	1016
6	10	474	532
6	11	272	212
6	12	536	621
7	1	1813	1903
7	2	1274	1236
7	3	989	865
7	4	478	459
7	5	1736	1537
7	7	1974	1760
7	9	1002	765
7	10	421	354
7	11	342	364
7	13	628	566
8	0	1433	1532
8	1	783	692
8	2	1279	1403
8	3	617	665
8	4	1054	1078
8	5	329	371
8	6	529	567
8	8	1966	1610
8	10	309	230
8	12	271	186
9	0	376	398
9	1	1882	1853
9	2	300	241
9	4	714	656
9	5	745	671
9	6	1012	823
9	7	1365	1279
9	8	390	267
9	9	638	524
9	10	307	231
10	0	436	369
10	2	1131	1229
10	3	320	306
10	5	1138	1036
10	7	751	670
10	8	741	711
10	10	426	299
10	11	356	307
11	0	817	785
11	3	651	677
11	4	579	644
11	5	435	527
11	6	499	515
11	7	548	514
11	8	673	618
11	10	360	278
12	0	1334	1334
12	1	758	648
12	2	756	741
12	3	709	681
12	4	384	500
12	6	696	749
12	10	752	700
13	2	608	616
13	3	556	639
13	4	1080	1119
13	5	390	444
13	6	489	513
13	7	526	519
13	9	307	263
14	0	382	453
14	1	376	383
14	2	1173	1235
14	3	1157	1191
14	8	525	546
15	1	868	991
15	2	732	778
15	3	335	442
15	4	469	533
15	6	658	654
15	7	782	813
16	0	323	323
16	1	304	286
16	2	931	1023
16	3	379	385
16	4	521	603
17	1	683	765

**** H = 6****

K	L	OBS	CALC
0	0	2356	2187
0	4	1277	1209

K	L	OBS	CALC
0	6	1034	1108
0	8	243	193
0	10	291	253
0	12	626	586
1	0	573	479
1	1	2643	2534
1	2	273	239
1	3	727	760
1	4	365	293
1	5	861	900
1	7	1305	1316
1	8	276	305
1	9	686	807
1	11	463	594
2	0	2824	2554
2	1	1542	1438
2	2	1355	1137
2	3	1119	1040
2	4	429	377
2	5	681	669
2	6	1058	1041
2	7	433	414
2	9	846	810
2	12	370	225
3	0	1746	1613
3	1	3074	2722
3	3	538	516
3	4	325	253
3	5	271	379
3	6	695	709
3	8	537	504
3	9	251	196
3	10	582	521
3	11	802	802
4	0	1279	1480
4	1	836	741
4	2	2433	2233
4	3	596	567
4	5	388	219
4	6	471	372
4	8	738	694
4	10	1111	1048
4	11	533	529
4	12	528	480
5	0	279	350
5	1	2137	1945
5	2	509	452
5	4	1264	1226
5	5	565	632
5	7	371	235
5	8	783	710
5	9	417	379
5	11	808	705
5	12	556	497
5	13	315	257
6	0	1477	1740
6	1	803	817
6	2	594	627
6	3	853	732
6	4	930	815
6	5	826	767
6	6	1915	1739
6	8	290	173
6	9	785	673
6	10	424	389
6	11	580	501
6	12	539	329
6	13	485	457
7	0	1156	1152
7	1	804	887
7	3	839	853
7	4	886	886
7	5	1439	1278
7	7	1526	1189
7	8	509	519
7	10	357	319
7	12	315	257
8	0	1317	1382
8	2	454	384
8	3	1177	1065
8	5	302	244
8	6	2028	1792
8	12	490	343
9	0	509	628
9	1	308	458
9	2	423	471
9	3	346	310
9	5	749	713
9	6	756	651
9	7	936	863
9	8	694	543
9	9	575	519
9	10	505	386
10	0	1357	1359
10	1	611	642
10	5	561	501
10	6	665	635
10	7	443	474
10	9	930	760
11	0	491	467
11	1	1472	1435
11	2	335	396
11	4	410	366
11	5	286	278
11	8	639	608
11	9	489	435
11	10	561	500
12	0	1009	952
12	2	909	897
12	4	320	363
12	5	572	594
12	8	465	432
12	9	626	537
13	0	255	363
13	1	1138	1225
13	3	291	177
13	4	781	815
13	5	416	397
14	0	722	703
14	1	500	492
14	2	258	227
14	3	835	906
14	6	810	833
14	7	329	297
14	9	345	607
15	3	676	739
15	4	591	500
15	5	769	790
16	0	370	361
16	1	420	369
16	2	284	395
17	0	946	965

**** H = 7****

K	L	OBS	CALC
0	0	1158	990
0	2	1826	1629
0	4	740	815
0	6	1330	1331
0	8	1947	2068
1	0	626	541
1	1	1736	1816
1	2	1108	1164
1	4	469	494
1	6	276	244
1	7	1690	1742
1	9	1180	1223
1	11	254	266
1	13	517	495
2	0	252	286
2	1	1673	1587
2	2	1531	1380
2	3	337	361
2	4	252	248
2	5	271	280
2	6	819	798
2	7	581	606
2	8	1524	1522
2	9	233	249
2	11	339	343
2	12	411	431
2	13	426	402
3	1	510	514
3	2	1703	1694
3	3	1230	1283
3	5	1277	1201
3	7	957	869
3	8	494	487
3	10	280	387
3	11	298	264
3	13	853	824
4	0	1342	1337
4	1	951	789
4	2	1469	1475
4	3	330	326
4	5	356	218
4	6	434	429
4	7	416	399
4	9	288	269
4	12	1100	1073
5	0	271	171
5	1	322	281
5	2	1011	965
5	3	1610	1540
5	4	251	170
5	5	622	570
5	7	820	700
5	10	840	766
5	11	503	504
6	0	445	463
6	1	1248	1229
6	2	1506	1475
6	3	1194	1215
6	4	723	694
6	5	596	562
6	7	439	372
6	8	980	893
6	9	444	424
6	12	491	410
7	0	566	593
7	1	1513	1548
7	2	1066	999
7	3	544	524
7	4	321	305
7	5	1042	938
7	7	1696	1506
7	9	633	562
8	0	1063	1160
8	1	420	427
8	2	1035	1056
8	4	527	505
8	5	705	687
8	6	376	416
8	8	1531	1405
8	11	303	249
9	0	250	276
9	1	1351	1304
9	3	376	361
9	4	975	925
9	6	547	493
9	7	1265	1200
9	9	601	447
9	10	331	357
10	1	371	359
10	2	1174	1070
10	3	295	213
10	4	336	444
10	5	1133	1129
10	6	262	210
10	7	582	543
10	8	932	884
10	9	311	223
11	1	343	344
11	3	736	797
11	4	834	813
11	6	585	535
11	7	623	479
12	0	1068	1165
12	1	358	292
12	2	830	823
12	3	368	424
12	4	503	535
12	5	277	215
13	0	311	321
13	2	439	675
13	3	594	713
13	4	385	372
13	6	446	451
14	0	431	491
14	1	563	556
14	2	1012	1013
14	3	945	957
14	5	299	247
15	0	473	468
15	1	598	571
15	2	465	473
15	4	268	275

**** H = 8****

K	L	OBS	CALC
0	0	869	895
0	2	430	488
0	4	312	354
0	6	1170	1172
0	10	525	562
0	12	710	628
1	0	702	581
1	1	1153	1291
1	3	240	213
1	5	1083	1163
1	6	295	262
1	7	559	624
1	8	326	319
1	9	691	778
2	0	1657	1714
2	1	816	885
2	2	734	839
2	3	316	331
2	6	863	908
2	7	464	467
2	9	404	357
2	10	275	276
2	12	526	540
3	0	1197	1322
3	1	2165	2241
3	2	419	443
3	7	274	207
3	8	513	534
3	11	590	658
4	0	1311	1683
4	1	719	682
4	2	1642	1738
4	4	467	511
4	6	273	243
4	10	661	638
5	0	438	415
5	1	1935	1940
5	4	939	938
5	7	488	460
5	8	504	525
5	9	266	194
5	11	475	457
6	0	1103	1169
6	2	281	389
6	3	1039	1014
6	4	485	513
6	5	423	485
6	6	1276	1324
6	7	479	395
6	8	279	307
6	9	353	419
6	11	589	589
7	0	513	518
7	1	427	483
7	2	521	605
7	3	652	640
7	4	706	648
7	5	711	719
7	7	670	640
7	9	488	515
7	10	376	393
8	0	653	654
8	2	408	341
8	3	444	399
8	5	507	434
8	6	1094	1139
8	7	419	323
8	1	354	378
8	8	369	369
8	6	677	682

K	L	OBS	CALC
9	7	722	668
9	8	353	361
9	9	582	623
9	10	317	263
10	0	1152	1160
10	5	686	645
10	6	722	707
10	7	447	480
10	9	521	477
11	0	324	283
11	1	1226	1263
11	5	342	320
11	7	374	371
11	8	478	551
12	0	851	785
12	2	901	877
12	5	476	473
13	1	1042	1084
13	4	795	812
14	0	372	342
14	3	639	640
15	1	309	292
15	2	272	253

K	L	OBS	CALC
9	8	978	1059
9	0	451	380
9	1	628	692
9	2	308	216
9	3	378	409
9	4	643	617
9	5	318	338
9	7	861	869
10	1	337	268
10	2	636	638
10	5	712	764
10	3	734	733
11	3	603	665
11	4	716	724
12	0	859	909
12	2	870	852
12	3	458	349
12	4	414	475
13	0	486	537
13	2	463	490
13	3	812	887
14	1	648	626
14	2	924	933
15	0	494	486

K	L	OBS	CALC
5	13	768	821
6	1	1157	1153
6	2	635	523
6	3	1243	1122
6	4	1316	1354
6	5	1425	1421
6	6	2021	1387
6	8	809	934
6	9	648	699
6	12	1178	1207
6	13	563	549
7	1	206	125
7	2	404	423
7	4	1257	1136
7	6	472	594
7	7	881	929
7	8	943	965
7	11	879	799
7	12	394	563
7	13	551	643
8	2	2222	2115
8	3	966	931
8	4	1024	969
8	10	510	480
8	12	971	988
9	1	1280	1226
9	2	2029	1817
9	3	431	365
9	5	360	464
9	6	477	310
9	8	781	804
9	11	698	583
9	13	486	568
10	1	1469	1735
10	2	757	811
10	3	1049	957
10	4	1077	943
10	5	746	698
10	6	1269	1097
10	7	775	813
10	9	909	920
10	12	732	683
11	1	1552	1400
11	2	1180	1059
11	3	893	936
11	4	736	722
11	5	1044	762
11	7	1433	1374
11	8	530	633
11	13	827	827
12	3	1105	1001
12	5	516	476
12	6	1417	1170
12	8	575	733
12	12	642	573
13	1	1249	1253
13	4	1361	1280
13	7	943	885
14	2	709	726
14	3	1046	1022
14	5	846	892
14	7	465	474
15	1	795	850
15	4	1236	1220
15	5	388	486
15	6	537	523
15	7	443	265
15	9	520	538
16	2	915	1008
16	3	871	880
16	5	454	594
16	7	571	559
17	2	945	1180
17	5	518	576
18	1	1241	1105
18	4	546	608

K	L	OBS	CALC
0	8	1042	976
0	10	1682	1262
0	14	532	515
0	16	666	678
1	1	2991	2700
1	2	1050	1263
1	3	223	322
1	4	783	839
1	5	1232	1163
1	6	963	1023
1	7	690	784
1	8	939	919
1	9	679	713
1	10	714	777
1	11	1137	1407
1	13	438	396
1	14	384	379
2	1	226	169
2	2	1187	1258
2	3	243	115
2	4	738	1035
2	5	664	563
2	6	2095	2183
2	7	2265	2240
2	9	435	425
2	10	1080	1279
2	11	506	593
2	12	425	612
2	14	413	347
2	15	703	724
3	1	991	1165
3	2	1254	1268
3	3	1340	1074
3	4	332	232
3	5	4103	3981
3	6	252	319
3	7	734	709
3	10	658	741
3	11	1144	1219
4	2	1276	1314
4	4	1370	1455
4	5	558	836
4	6	2690	2967
4	8	418	488
4	9	833	961
4	10	428	551
4	12	676	804
5	1	1036	1071
5	2	277	314
5	3	270	427
5	5	3962	3895
5	6	911	1176
5	8	969	1123
5	11	1063	1196
5	15	426	351
6	1	1319	1031
6	2	367	310
6	3	674	678
6	4	997	964
6	5	470	560
6	6	2370	2717
6	7	1058	1284
6	8	498	410
6	9	381	466
6	10	715	676
6	15	491	506
7	1	2436	2468
7	2	363	359
7	4	583	494
7	5	1362	1553
7	7	434	795
7	9	401	414
7	11	578	726
7	13	800	770
7	14	399	365
8	1	564	457
8	2	1339	1367
8	3	616	512
8	4	477	550
8	5	560	399
8	6	730	698
8	8	456	544
8	10	908	838

****** H = 9******

K	L	OBS	CALC
0	0	470	511
0	2	368	353
0	6	843	947
0	8	1368	1476
1	0	341	379
1	1	613	717
1	2	428	531
1	3	332	253
1	7	1242	1287
1	9	803	835
1	11	379	376
2	1	919	977
2	2	1156	1220
2	5	467	476
2	6	468	538
2	7	277	331
2	8	977	1064
2	9	389	387
3	1	577	620
3	2	654	825
3	3	1208	1313
3	4	410	360
3	6	518	473
3	7	484	503
3	9	321	307
4	0	798	975
4	1	335	403
4	2	1422	1482
4	4	502	553
5	0	559	573
5	1	484	484
5	2	609	547
5	3	1144	1229
5	5	461	461
5	7	555	544
5	8	391	349
5	10	438	428
5	11	353	455
6	1	796	844
6	2	1019	964
6	5	422	423
6	8	779	765
6	9	456	514
7	0	311	216
7	1	947	906
7	2	538	509
7	3	276	369
7	4	277	256
7	5	395	333
7	7	1344	1325
7	9	360	346
7	10	348	296
8	0	399	447
8	2	479	453
8	3	628	647
8	6	447	499

****** H =-1******

K	L	OBS	CALC
0	2	2938	3007
0	4	3898	3737
0	6	530	462
0	12	902	907
1	2	219	125
1	3	232	227
1	4	695	933
1	5	559	558
1	6	181	111
1	7	414	649
1	8	1583	1609
1	9	547	589
1	11	625	525
1	12	460	572
1	13	425	539
2	1	1393	1161
2	3	209	357
2	4	968	974
2	6	1367	1433
2	7	1256	1180
2	8	1464	1192
2	9	687	947
2	11	398	426
2	12	850	896
2	13	601	605
2	14	459	469
3	1	324	660
3	2	176	60
3	3	1865	2264
3	4	1434	1439
3	7	2725	2697
3	8	938	1213
3	11	420	310
3	13	850	965
3	14	432	535
4	1	1693	1560
4	2	385	63
4	3	331	329
4	4	1369	1490
4	5	1942	2067
4	6	3357	3019
4	7	271	304
4	8	781	927
4	12	1036	1033
4	14	546	601
5	1	1803	1744
5	2	313	316
5	3	358	336
5	4	1722	1564
5	5	368	198
5	6	652	845
5	7	2756	2978
5	10	462	426
5	11	551	371
5	12	413	480

****** H =-2******

K	L	OBS	CALC
0	2	1111	1594
0	4	1380	1185
0	6	417	386

K	L	OBS	CALC
8	14	696	731
9	1	2590	2619
9	2	924	879
9	4	1408	1213
9	5	1714	1529
9	6	1724	1557
9	8	530	566
9	9	513	528
9	10	762	701
9	11	442	642
9	12	440	509
9	13	638	517
10	1	317	466
10	2	1092	950
10	3	1708	1517
10	4	1174	1068
10	5	580	336
10	6	1201	1304
10	7	1191	1124
10	11	862	841
10	12	673	718
11	4	1117	892
11	5	2026	2322
11	6	912	855
11	9	463	471
11	10	542	501
11	11	770	787
11	13	439	504
12	2	1002	1017
12	4	1636	1263
12	6	1259	1186
12	8	877	802
12	9	374	336
12	10	384	359
12	12	607	760
13	2	464	431
13	5	1334	987
13	6	636	480
13	8	759	629
13	11	323	837
14	5	917	637
14	6	1035	885
14	7	774	622
14	8	781	658
14	9	680	742
14	10	750	680
15	1	784	816
15	2	414	475
15	3	534	398
15	6	964	680
15	8	994	774
16	2	394	410
16	6	794	619
16	7	508	227
17	1	574	686
17	5	465	385
18	1	412	625
18	3	874	850
18	4	568	464

**** H =-3 ****

0	2	1318	1559
0	4	579	203
0	6	410	510
0	8	500	752
0	12	1354	1353
1	1	242	168
1	2	1973	1951
1	3	1089	1280
1	4	676	782
1	5	362	403
1	7	212	216
1	8	583	776
1	9	760	852
1	10	353	411
1	11	1116	964
1	12	361	414
1	13	732	740
1	14	396	430
2	1	2373	2376
2	2	1302	1251
2	3	539	622
2	4	642	615
2	5	222	272
2	6	1019	1320
2	7	583	603
2	8	519	522
2	9	703	814
2	12	791	782
2	13	479	472
2	14	520	432
2	15	431	276
3	1	1988	1776
3	2	1129	1074
3	3	1755	1846
3	4	331	404
3	6	324	263
3	7	2828	2623
3	8	415	549
3	10	353	404
3	11	422	204
3	13	562	590
3	14	446	309
4	1	357	311
4	2	1035	804
4	3	235	159
4	4	1782	1982
4	5	815	932
4	6	2849	2590
4	8	1465	1693
4	12	711	684
5	1	660	618
5	2	343	201
5	3	654	569
5	4	1303	1345
5	6	489	567
5	7	2023	2289
5	10	511	495
5	11	470	436
5	13	446	536
6	1	1131	1202
6	2	388	386
6	3	780	748
6	4	1341	1366
6	5	1588	1805
6	6	764	974
6	7	491	578
6	8	900	939
6	9	453	382
6	12	1000	1001
6	13	713	637
6	15	574	466
7	1	242	396
7	2	216	204
7	4	1072	1030
7	6	1570	1629
7	7	743	677
7	9	564	630
7	11	842	645
7	12	700	719
7	13	394	565
7	14	718	742
7	15	394	362
8	2	1137	1177
8	3	1034	1246
8	4	662	690
8	7	674	645
8	8	499	490
8	12	1203	1116
8	14	418	334
9	1	962	885
9	2	2061	1849
9	4	438	198
9	8	343	286
9	10	907	1013
9	11	869	644
9	13	496	605
10	1	1215	1335
10	2	1223	1195
10	3	1533	1573
10	4	1543	1385
10	5	1145	1017
10	6	1311	1102
10	7	447	322
10	9	394	859
10	12	817	687
11	1	1555	1773
11	2	772	851
11	3	1246	1100
11	4	486	497
11	7	1426	1331
11	8	412	374
11	10	383	355
11	13	638	561
12	3	1106	1046
12	4	708	658
12	5	733	678
12	6	1322	966
12	8	536	605
12	12	479	452
13	1	1097	1176
13	4	1288	1204
13	5	669	652
13	7	1138	965
13	8	502	486
13	11	470	354
14	3	667	691
14	5	1152	1086
14	7	631	601
15	1	396	542
15	3	385	299
15	4	758	771
15	5	609	613
15	6	1024	860
15	9	614	582
16	3	546	580
16	7	577	529
16	9	422	315
17	2	1262	1357
18	1	1256	1248
18	3	610	761
18	4	506	581

**** H =-4 ****

0	2	2376	2437
0	4	447	330
0	10	2122	2456
0	14	834	725
0	16	442	358
1	1	2843	2651
1	2	605	640
1	3	272	238
1	4	485	657
1	5	484	584
1	6	341	409
1	8	878	1065
1	9	1146	1402
1	10	420	404
1	11	1107	1143
1	12	419	399
1	13	318	370
1	15	297	223
1	16	477	365
2	1	582	520
2	2	243	130
2	3	299	265
2	4	1358	1536
2	5	217	303
2	6	1730	1979
2	7	1163	1408
2	10	983	1141
2	11	368	424
2	12	359	436
2	13	338	161
2	15	365	412
2	16	638	519
3	1	235	315
3	4	254	229
3	5	2917	2882
3	7	1064	1289
3	8	589	737
3	10	408	407
3	11	953	912
3	15	626	567
4	1	303	296
4	2	421	387
4	4	2559	2163
4	5	237	255
4	6	1787	2153
4	9	526	579
4	10	731	878
4	12	646	556
5	1	599	559
5	4	487	473
5	5	2510	2890
5	6	285	314
5	7	622	843
5	8	510	595
5	10	292	289
5	11	923	943
5	15	563	549
6	1	344	332
6	3	343	453
6	4	1133	1078
6	6	1483	1582
7	9	5	759
7	9	834	957
7	10	866	775
7	15	524	345
7	1	2054	1919
7	2	223	166
7	3	290	399
7	5	1795	1725
7	6	484	322
7	8	909	920
7	9	562	510
7	11	836	955
7	13	679	541
8	2	1077	979
8	3	1026	857
8	4	1375	1163
8	5	575	515
8	10	1435	1378
8	11	427	306
8	14	635	621
9	1	1921	2113
9	2	404	236
9	4	1702	1321
9	5	1534	1261
9	6	1364	1066
9	8	713	680
9	9	758	619
9	10	493	396
9	11	883	981
9	12	495	570
9	13	615	456
10	1	342	521
10	2	675	669
10	3	1487	1224
10	4	1252	1119
10	5	815	794
10	7	1092	966
10	9	356	373
10	11	708	690
10	13	430	351
11	2	392	247
11	4	899	822
11	5	1748	1836
11	10	489	419
11	11	612	596
12	2	855	912
12	4	1531	1115
12	6	1509	1361
12	8	679	585
12	9	733	602
12	10	465	384
12	12	505	493
13	3	417	403
13	5	1284	1039
13	6	524	406
13	8	781	577
13	11	659	630
14	3	629	585
14	6	1070	903
14	7	823	556
14	8	712	607
14	9	748	729
14	10	766	716

K	L	OBS	CALC
15	2	355	376
15	5	647	400
15	8	791	559
17	4	428	480
18	1	728	836
18	3	597	555

**** H =-5****

K	L	OBS	CALC
0	2	259	283
0	4	524	681
0	5	810	1051
0	8	1705	1517
0	10	702	713
0	12	1150	1159
0	14	362	620
1	1	338	443
1	2	1082	1134
1	3	962	1027
1	4	490	520
1	6	705	946
1	7	611	847
1	9	1449	1504
1	10	347	312
1	11	617	688
1	13	951	915
1	14	579	439
2	1	2085	1864
2	2	609	563
2	3	797	805
2	4	1242	1368
2	6	864	1324
2	7	793	853
2	8	369	410
2	9	389	407
2	11	323	118
2	12	540	571
2	13	345	362
2	14	427	217
2	15	448	377
3	1	2285	2318
3	2	1025	1011
3	3	2022	2197
3	4	900	1023
3	6	360	534
3	7	2273	2211
3	8	353	563
3	13	356	368
4	1	935	813
4	4	1290	1493
4	5	715	837
4	6	1852	1642
4	8	1094	1417
4	10	315	281
4	12	349	412
5	1	1153	1080
5	3	1078	1226
5	4	1316	1287
5	6	588	782
5	7	1904	1683
5	9	370	400
5	12	274	315
5	14	496	461
5	15	292	49
6	1	1192	1226
6	2	400	180
6	3	464	414
6	4	1457	1496
6	5	1322	1493
6	6	863	1215
6	7	302	1124
6	8	594	727
6	10	408	326
6	12	703	714
6	13	457	481
6	15	642	503
7	1	482	347
7	3	425	321
7	5	337	154
7	6	1234	1272
7	7	642	756
7	8	467	618
7	9	397	501
7	11	563	642
7	12	340	356
7	13	598	577
7	14	678	628
8	1	360	493
8	3	749	733
8	4	722	671
8	6	771	846
8	7	515	475
8	8	616	584
8	11	411	385
8	12	1214	1336
8	13	405	350
9	2	1921	1881
9	3	726	715
9	4	264	150
9	5	574	594
9	6	376	357
9	9	339	352
9	10	800	864
9	11	557	592
9	12	323	317
9	13	706	726
10	1	939	1101
10	2	796	754
10	3	1485	1532
10	4	1401	1386
10	5	496	472
10	6	745	730
10	7	508	452
10	9	600	563
10	10	317	129
10	11	425	402
10	12	551	555
11	1	1741	1861
11	2	1138	1127
11	3	1041	960
11	5	445	365
11	7	784	765
12	2	510	529
12	3	449	518
12	4	948	951
12	5	402	343
12	6	404	427
12	7	431	355
12	8	391	357
12	9	391	302
12	12	336	225
13	1	1174	1210
13	2	273	132
13	3	331	370
13	4	940	917
13	5	345	290
13	6	832	783
13	7	1042	945
13	8	500	537
13	9	350	439
14	3	417	442
14	5	1110	1119
14	7	907	850
15	1	343	377
15	2	235	423
15	4	698	687
15	6	1040	952
15	8	728	703
15	9	584	574
16	1	485	626
16	3	606	635
16	5	343	409
16	7	643	611
17	2	1063	1164
17	4	398	497
18	1	735	842

**** H =-6****

K	L	OBS	CALC
0	2	1476	1608
0	4	1273	1466
0	8	632	575
0	10	1537	1706
0	12	669	566
0	14	454	445
1	1	1513	1416
1	2	540	576
1	4	376	464
1	5	794	961
1	8	448	419
1	8	470	620
1	9	1240	1604
1	11	955	990
1	12	392	497
2	1	1010	860
2	2	372	297
2	4	500	594
2	5	908	972
2	6	1305	1322
2	7	574	710
2	8	370	555
2	9	327	173
2	10	1009	1119
2	12	255	81
2	13	320	244
3	1	489	364
3	2	1018	954
3	3	488	414
3	4	424	257
3	5	1753	1859
3	6	308	162
3	7	1061	1306
3	9	488	607
3	10	329	301
3	11	641	673
3	12	315	258
3	15	723	678
4	2	730	700
4	4	1537	1632
4	5	557	706
4	6	1942	2249
4	7	287	179
4	9	447	571
4	10	571	783
4	12	372	279
4	14	374	324
5	1	381	417
5	3	411	526
5	4	712	578
5	5	2233	2383
5	7	838	990
5	8	633	761
5	11	653	639
5	15	790	680
6	1	487	547
6	2	366	220
6	3	314	512
6	4	1146	1226
6	5	877	918
6	6	1255	1312
6	7	457	342
6	9	816	880
6	10	679	799
6	13	324	329
7	1	1364	1382
7	3	678	674
7	4	408	289
7	5	1312	1322
7	6	534	578
7	8	614	684
7	11	616	642
7	13	416	482
8	2	527	572
8	3	731	718
8	4	1294	1294
8	5	498	508
8	7	429	334
8	8	321	315
8	10	866	966
8	11	394	462
8	12	403	230
8	14	470	461
9	1	1034	1081
9	3	425	336
9	4	1096	1046
9	5	1337	1229
9	6	394	448
9	7	435	532
9	8	359	494
9	9	428	479
9	11	821	839
10	1	686	666
10	2	360	385
10	3	513	519
10	4	826	1010
10	6	616	625
10	7	404	508
10	9	480	405
10	10	526	563
10	12	362	227
10	13	440	438
11	3	528	428
11	4	352	397
11	5	1404	1434
11	6	276	302
11	7	597	597
11	8	472	344
11	11	438	521
12	2	684	700
12	3	360	319
12	4	730	857
12	6	1117	1145
12	10	462	478
13	5	1003	1010
13	8	361	400
13	10	495	431
13	11	455	517
14	3	358	330
14	6	389	417
14	7	359	408
14	8	386	378
14	9	643	672
14	10	544	637
15	7	303	330
15	8	434	487
16	1	496	542
17	2	418	408
17	3	343	359
17	4	338	410
17	5	376	447

**** H =-7****

K	L	OBS	CALC
0	2	898	739
0	4	442	284
0	6	2060	2372
0	8	1097	1214
0	10	400	217
0	12	954	1035
0	14	796	634
1	2	525	487
1	3	420	450
1	4	437	364
1	5	371	330
1	6	804	972
1	7	737	804
1	8	399	378
1	9	1109	1100
1	11	338	382
1	12	300	253
1	13	392	944
2	1	333	299
2	2	311	332
2	3	380	365
2	4	1031	1028
2	6	679	770
2	7	974	1065
2	8	356	390
2	11	295	243
2	12	737	776
2	15	375	342
3	1	1645	1701
3	2	831	827
3	3	1387	1461
3	4	740	689
3	5	494	490
3	6	993	1070
3	7	656	768
4	1	817	784

K	L	OBS	CALC
4	2	353	268
4	3	692	710
4	4	1353	1349
4	5	617	665
4	6	675	740
4	8	770	830
4	10	449	450
4	12	375	387
4	14	385	304
4	15	302	200
5	1	704	744
5	3	1375	1399
5	4	1074	992
5	5	520	444
5	6	813	870
5	7	994	1101
5	8	520	378
5	10	387	357
5	11	468	416
5	14	496	530
6	2	248	114
6	3	250	126
6	4	766	730
6	5	1063	1057
6	6	790	865
6	7	1231	1249
6	8	358	232
6	10	424	342
6	12	619	494
6	14	318	202
7	2	403	485
7	3	825	736
7	5	635	676
7	6	782	755
7	7	530	535
7	8	578	518
7	9	658	672
7	11	407	481
7	13	524	423
7	14	385	342
8	1	546	501
8	2	451	460
8	3	921	912
8	5	413	411
8	6	1268	1211
8	7	448	412
8	8	511	476
8	10	544	480
8	11	376	352
8	12	906	851
8	13	389	308
9	2	803	826
9	3	800	802
9	4	569	436
9	5	710	745
9	7	363	305
9	9	576	561
9	10	580	641
9	11	397	432
9	12	544	406
9	13	567	577
10	1	255	324
10	2	433	448
10	3	1004	940
10	4	841	878
10	6	462	478
10	9	372	360
10	11	503	511
10	12	554	585
11	1	1301	1318
11	2	971	1028
11	3	627	636
11	5	488	460
11	7	412	354
11	8	305	257
11	10	571	527
11	11	353	411
11	12	362	340
12	1	466	510
12	2	417	429
12	3	420	428
12	4	1130	1268
12	5	442	319
12	6	437	244
12	7	369	337
12	9	515	456
13	1	882	932
13	3	412	409
13	4	383	393
13	5	611	516
13	6	742	763
13	7	448	395
13	8	533	531
13	9	331	359
14	4	449	461
14	5	744	790
14	7	728	754
14	8	434	275
15	2	395	447
15	6	566	604
15	8	720	649
16	1	574	640
16	2	326	331
16	3	655	673
16	6	374	381
17	2	938	955
17	3	315	319

**** H =-8****

K	L	OBS	CALC
0	4	1318	1375
0	6	600	599
0	8	505	545
0	10	1033	1021
0	12	747	601
0	14	366	286
1	1	465	392
1	2	471	483
1	3	420	372
1	5	1324	1441
1	6	629	600
1	7	453	422
1	8	326	369
1	9	899	1058
1	11	626	498
1	14	291	234
2	1	997	982
2	4	655	643
2	5	574	583
2	6	960	937
2	7	290	405
2	8	337	233
2	10	1115	1132
2	12	271	165
2	13	339	374
3	1	448	435
3	2	446	327
3	5	1424	1520
3	6	329	318
3	7	957	918
3	9	716	743
3	11	578	605
3	13	302	190
4	2	729	611
4	4	1070	1283
4	5	1578	1704
4	8	583	576
4	10	545	598
4	14	342	397
5	1	480	553
5	2	306	317
5	4	469	395
5	5	1555	1652
5	7	842	859
5	8	559	703
5	9	379	219
5	10	324	224
5	11	701	727
5	13	293	134
5	14	399	226
6	1	829	841
6	2	304	276
6	3	266	167
6	4	1317	1334
6	5	691	707
6	6	631	622
6	9	667	582
6	10	708	715
6	13	520	457
7	1	557	558
7	2	477	485
7	3	814	929
7	5	1066	962
7	6	768	644
7	7	354	336
7	8	330	309
7	11	886	840
8	1	302	213
8	4	1590	1621
8	7	323	297
8	8	547	554
8	10	663	586
8	12	420	251
9	1	483	531
9	2	532	480
9	3	369	385
9	4	319	247
9	5	1085	983
9	7	528	534
9	11	796	670
9	12	516	369
10	1	776	700
10	4	652	692
10	5	353	303
10	10	777	736
11	3	460	444
11	5	1049	1068
11	7	374	358
11	9	652	593
12	2	505	615
12	6	1002	998
12	9	436	274
12	10	561	504
13	4	429	388
13	5	903	920
14	4	331	319
14	5	493	449
15	3	321	388
15	5	302	335
15	7	370	360
16	1	505	511
16	4	487	543

**** H =-9****

K	L	OBS	CALC
0	2	779	759
0	4	409	456
0	6	1529	1633
0	8	692	670
0	12	504	410
0	14	554	475
1	3	980	940
1	4	458	515
1	5	351	320
1	6	400	390
1	7	361	487
1	8	363	302
1	9	841	842
1	11	352	454
1	13	619	555
2	2	330	397
2	3	768	802
2	4	395	468
2	6	742	661
2	7	528	618
2	8	519	420
2	9	355	207
2	12	491	434
2	13	330	260
3	1	716	812
3	2	516	614
3	3	804	852
3	4	544	526
3	5	331	507
3	7	362	225
3	11	517	454
4	1	590	632
4	3	618	651
4	4	1136	1087
4	13	350	230
5	1	570	723
5	2	356	292
5	3	971	938
5	4	369	388
5	6	572	445
5	7	414	305
5	8	398	376
6	1	348	450
6	5	388	269
6	6	611	607
6	7	1044	922
6	12	741	674
7	2	391	523
7	3	770	836
7	5	931	849
7	6	379	230
7	7	498	422
7	8	489	457
7	9	543	423
8	2	605	765
8	3	551	551
8	5	1036	935
8	10	382	304
8	11	494	399
8	12	690	566
9	2	594	583
9	3	784	790
9	4	359	283
9	5	449	551
9	7	442	464
9	9	695	598
9	11	557	309
10	3	510	553
10	4	383	431
10	8	406	324
10	11	586	520
11	1	960	1050
11	2	806	824
11	3	448	470
11	4	340	335
11	5	490	487
11	10	448	286
12	1	387	375
12	2	457	397
12	4	931	1043
12	5	430	428
12	9	452	426
12	10	321	375
13	1	569	521
13	2	340	307
13	3	469	478
13	5	518	541
13	6	672	673
13	8	544	507
14	1	477	519
14	5	330	401
14	7	683	681
15	2	502	495
15	3	319	326

**** H =10****

K	L	OBS	CALC
0	0	509	542
0	2	395	356
0	6	663	730
0	10	402	585
1	1	842	900
1	2	311	319
1	4	260	125
1	5	528	530
1	7	435	424
1	9	643	707
2	0	915	926
2	2	520	535
2	3	404	352
2	5	306	257
2	6	615	689
2	7	371	333
3	0	560	568

K	L	OBS	CALC
3	1	1860	1911
3	2	517	535
3	7	448	425
3	8	331	367
4	0	1805	1845
4	1	448	527
4	2	921	899
4	4	734	751
5	1	1538	1513
5	3	419	492
5	4	614	583
5	6	511	459
5	7	475	430
6	0	714	583
6	3	727	644
6	4	478	470
6	6	819	863
6	7	442	484
7	2	603	598
7	3	342	311
7	5	443	438
7	7	447	460
7	9	358	473
8	0	377	390
8	3	344	286
8	5	309	338
8	6	872	880
9	6	742	778
9	7	557	542
10	0	751	769
10	1	290	282
10	5	524	577
10	6	321	347
11	0	303	354
11	1	836	901
12	0	845	900
12	2	533	609
12	4	420	412
13	1	963	911

**** H =11****

K	L	OBS	CALC
0	6	498	485
0	8	1075	1130
1	7	997	1056
1	9	547	533
2	1	762	784
2	2	527	394
2	3	300	308
2	6	308	429
2	8	779	824
2	9	322	363
3	1	514	526
3	2	384	412
3	3	836	908
3	7	370	375
3	8	316	257
3	9	358	383
4	1	545	586
4	2	1592	1614
4	3	276	131
4	4	334	467
4	8	372	352
5	0	704	708
5	1	781	732
5	3	844	884
5	5	277	217
5	6	282	103
5	7	373	350
5	8	342	402
6	1	577	577
6	2	853	900
6	7	314	232
6	8	558	580
7	1	230	275
7	7	719	744
8	6	362	528
9	0	405	385
9	1	265	186
9	4	415	422
10	2	481	439
10	3	281	254
10	5	550	561
11	3	711	742
12	0	328	367

**** H =12****

K	L	OBS	CALC
0	2	581	584
0	6	491	513
1	1	396	334
1	5	326	285
2	0	421	339
2	2	705	772
3	0	455	535
3	1	1203	1265
3	2	444	448
3	4	377	319
4	0	1284	1316
4	1	430	408
4	4	698	728
4	6	330	316
5	1	1193	1296
5	2	377	433
5	4	325	289
5	7	436	470
5	0	516	428
6	1	332	429
6	3	370	379
6	4	278	207
6	6	351	316
7	1	316	379
8	5	287	188
9	1	319	358
10	0	316	329
10	2	294	286

**** H =13****

K	L	OBS	CALC
0	0	380	270
1	3	300	312
2	1	344	393
2	2	484	475
3	1	336	453
3	3	642	730
4	2	1078	1086
5	0	378	414
5	1	561	631
5	3	502	559
5	5	379	221
6	2	442	456
7	3	344	386

**** H =14****

K	L	OBS	CALC
0	0	293	248
0	2	412	480
1	1	384	433
2	2	438	453
3	1	455	530
4	0	447	467
5	1	456	467
5	2	387	358
6	0	489	483
6	1	376	399

**** H =-10***

K	L	OBS	CALC
0	4	1076	987
0	6	487	534
0	10	924	871
1	2	332	307
1	3	1289	1272
1	6	494	462
1	9	687	676
1	11	622	570
2	1	508	530
2	4	837	774
2	5	643	548
2	6	519	544
2	7	337	295
2	10	935	880
3	1	425	467
3	4	452	431
3	5	962	836
3	7	500	373
3	9	856	784
3	11	352	448
4	2	359	429
4	4	394	335
4	6	888	859
4	8	593	547
4	10	689	543
5	5	946	925
5	6	573	483
5	7	445	442
5	9	458	346
5	11	508	424
6	4	1065	986
6	5	601	627
6	7	385	337
6	9	414	370
6	10	620	471
7	3	723	674
7	5	944	930
7	6	780	732
7	11	777	576
8	4	1183	1103
8	8	498	399
8	10	731	518
9	3	434	410
9	5	882	895
10	4	744	707
10	10	902	761
11	5	579	510
11	9	648	555
12	2	407	394
12	6	455	516
13	5	530	539

**** H =-11 ***

K	L	OBS	CALC
0	2	451	498
0	4	568	650
0	6	1078	1042
0	8	522	435
0	12	425	370
1	3	750	732
1	4	344	288
1	5	421	446
1	8	441	303
1	9	451	423
2	2	493	555
2	3	519	504
2	4	491	523
2	6	487	472
2	7	398	333
2	8	520	443
2	9	340	254
2	12	434	376
3	3	463	399
3	4	658	751
3	8	426	463
3	11	375	335
4	3	466	522
4	12	353	190
5	3	645	570
5	8	395	310
6	2	643	727
6	6	387	551
6	7	799	760
7	1	354	327
7	3	798	873
7	5	444	550
7	7	396	345
7	8	434	333
7	9	521	444
8	2	531	570
8	3	378	362
8	6	658	698
9	2	422	358
9	3	723	766
9	5	355	258
10	4	368	335
10	8	424	240
11	1	437	529
11	3	376	417
11	4	376	358
12	4	588	568
13	1	377	438

**** H = -12 ***

K	L	OBS	CALC
0	4	676	621
0	6	365	240
0	10	568	497
1	5	1239	1216
1	5	349	326
1	9	445	425
1	11	378	402
2	4	593	639
2	5	390	469
2	6	457	437
2	7	404	429
2	10	694	604
3	2	334	315
3	5	528	475
3	6	464	436
3	9	684	587
4	8	462	253
4	10	681	558
5	5	481	404
5	6	512	481
5	9	391	262
6	4	865	867
6	5	463	430
6	6	351	318
6	10	579	349
7	3	507	465
7	5	651	686
7	6	466	523
8	4	855	852
9	5	610	683
10	4	477	517
11	5	392	381

**** H =-13 ***

K	L	OBS	CALC
0	2	391	344
0	4	715	833
0	6	559	593
0	8	335	311
1	3	814	831
2	6	351	291
2	8	395	326
3	4	368	375
3	8	460	310
5	2	346	294
6	1	368	313
6	2	382	490
7	3	549	610
8	2	396	451
8	6	436	435
9	3	466	442

**** H =-14***

K	L	OBS	CALC
0	4	819	812
0	6	440	472
1	5	925	828
2	4	446	392
6	4	509	541
7	3	377	353

**** H =-15 ***

K	L	OBS	CALC
0	2	403	230
1	3	448	495

VITA

Surname: *MORONEY* Given Names: *PEARSE*

Place of Birth: *DUBLIN, IRELAND* Date of Birth: *DECEMBER 8, 1951*

Educational Institutions Attended, with Dates of Entering and Leaving:

TRINITY COLLEGE, DUBLIN, IRELAND	*1970* to	*1974*
UNIVERSITY OF VICTORIA, B.C. Canada	1975 to	1977
	____ to	____

Degrees, Diplomas, Etc., Awarded, with Dates and Names of Institutions:

B.A.MOD.	*1974*	*Dublin University*

Honors and Awards:

University of Victoria Fellowship, 1975/76

University of Victoria Scholarship, 1976/77

Publications:

PARTIAL COPYRIGHT LICENSE

I hereby grant the right to lend my thesis or dissertation (the title of which is shown below) to users of the University of Victoria Library, and to make *single copies only* for such users or in response to a request from the library of any other university, or similar institution, on its behalf or for one of its users. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by me or a member of the University designated by me. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission

Title of Thesis

THE CRYSTAL STRUCTURE OF A COMPOUND WITH A TRIANGULAR PALLADIUM CLUSTER

Author [redacted]

27.7.77.
Date