

CRYSTAL AND MOLECULAR STRUCTURES
OF SOME TRANSITION METAL
PHOSPHINE COMPLEXES, AND THEIR
RELEVANCE TO HOMOGENEOUS CATALYSIS

A Thesis presented for the
degree of Doctor of Philosophy
in the Faculty of Science
at the University of Leicester

February 1971

Ursula Anne Gregory

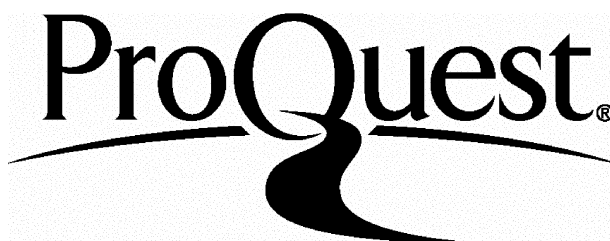
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The experimental work described in this thesis was carried out during the period of registration. It has not been presented, and is not being currently presented, for any other degree.



Ursula A. Gregory
February 1971

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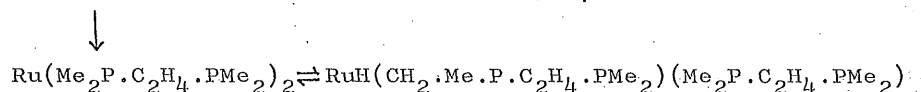
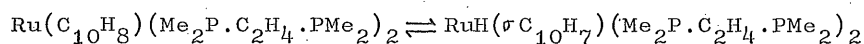
SUMMARY

Homogeneous catalysis of organic reactions by transition metal complexes, is thought to involve some or all of the following:-

- 1) Formation of M-H bonds
- 2) Formation of M-C sigma bonds (M-C-)
- 3) Formation of M-C "olefinic" bonds ($M-\text{II}$)
- 4) $C(\sigma) \leftrightarrow C(\pi)$ equilibria, and hydrogen transfers
- 5) Coordination of small molecules.

Structural information relevant to these processes has been obtained by study of the crystal structures of some appropriate model compounds.

In the system



$RuH(C_{10}H_7)(Me_2P.C_2H_4.PMe_2)_2$ is octahedrally coordinated, with cis hydride and $(\sigma C_{10}H_7)$. Ru-C is 2.16\AA and Ru-P (average) 2.30\AA ; the phosphine ligands are disordered.

The Ru-H observed distance of 1.7\AA agrees with other reported Ru-H bond lengths. The isostructural

$OsH(C_{10}H_7)(Me_2P.C_2H_4.PMe_2)_2$ has Os-C 2.13\AA . The structure analysis of $Ru(Me_2P.C_2H_4.PMe_2)_2$ was unsuccessful.

The structure of a dihydride complex, $FeH_2(Ph_2P.C_2H_2.PPh_2)_2$, could not be solved.

A spectral reinvestigation of the solvated complex $\text{OsHCl}(\text{Ph}_2\text{P.C}_2\text{H}_4.\text{PPh}_2)_2.\text{C}_6\text{H}_6$, has shown that the reported interaction between the hydridic hydrogen and the benzene molecule, does not occur.

The structure of $[\text{IrH}(\text{COOMe})(\text{Me}_2\text{P.C}_2\text{H}_4.\text{PMe}_2)_2]\text{BPh}_4$, formed by addition of MeOH across $\text{IrCO}(\text{Me}_2\text{P.C}_2\text{H}_4.\text{PMe}_2)_2^+$, shows the cation to have a trans octahedral configuration with Ir-C 2.10\AA , Ir-P (average) 2.31\AA . Ir-H was not measured.

The structures, at -70°C , of the isomorphous $\text{NiHCl}(\text{PPr}^i_3)_2$ and $\text{PdHCl}(\text{PPr}^i_3)_2$, are trans-planar, and exhibit the typical distortions found in transition metal complex hydrides. Ni-P is 2.19\AA ; Ni-Cl 2.21\AA ; Pd-P 2.30\AA ; Pd-Cl 2.39\AA . These results are discussed in terms of cis and trans effects. The observed Ni-H distance, 1.4\AA , is short compared to reported M-H bonds.

The structures of $\text{MoCl}_2(\text{Ph}_2\text{P.C}_2\text{H}_4.\text{PPh}_2)_2$ and $[\text{MoOCl}(\text{Ph}_2\text{P.C}_2\text{H}_4.\text{PPh}_2)_2][\text{ZnCl}_3.\text{acetone}]$ were studied at -70°C . $\text{MoCl}_2(\text{Ph}_2\text{P.C}_2\text{H}_4.\text{PPh}_2)_2$ is the product of N_2 loss from the dinitrogenyl complex $\text{Mo}(\text{N}_2)\text{Cl}_2(\text{Ph}_2\text{P.C}_2\text{H}_4.\text{PPh}_2)_2$, while $[\text{MoOCl}(\text{Ph}_2\text{P.C}_2\text{H}_4.\text{PPh}_2)_2][\text{ZnCl}_3.\text{acetone}]$ is an intermediate in the formation of $\text{Mo}(\text{N}_2)\text{Cl}_2(\text{Ph}_2\text{P.C}_2\text{H}_4.\text{PPh}_2)_2$. The cation is trans octahedrally coordinated, with Mo=O 1.69\AA , Mo-Cl 2.46\AA , Mo-P (average) 2.57\AA . The tetrahedral anion has Zn-Cl (average) 2.23\AA , Zn-O 2.12\AA . The complex is solvated with one molecule of acetone.

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CHAPTER 1.1

INTRODUCTION

The research for this thesis has been carried out in Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, largely in conjunction with other studies on homogeneous catalysis. Chemists seeking new routes to industrially important compounds are concerned with understanding the factors affecting catalytic activity. The stereochemistry of a catalytically active transition metal complex probably plays an important part in helping to position an incoming substrate molecule for reaction. Structural information may also help in understanding the distribution of electron density likely to favour reaction and, similarly, structural knowledge about intermediate species is desirable. Although these intermediates are usually too unstable to be isolated, certain general features have emerged as being important; one is that the intermediates very often contain M-H or M-C bonds. The work described in this thesis was undertaken to provide background structural information on transition metal complexes containing these types of bonds. While the actual complexes described are not catalytic intermediates, it is hoped that the results obtained may be related to general principles of catalytic behaviour.

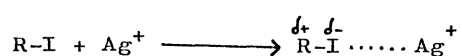
Homogeneous Catalysis by Transition Metal Complexes

The function of metal ions in organic reactions has for some time been the subject of kinetic, mechanistic and structural studies. The metal may act either stoichiometrically or catalytically; only the latter will be discussed in this thesis.

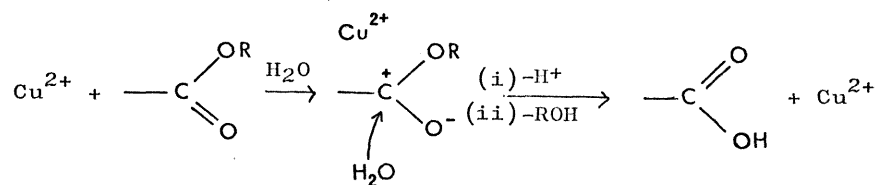
A metal may act catalytically by providing an electronic surface as the reaction site (heterogeneous catalysis). Very often, however, it is more convenient to perform a reaction in solution, in which case the catalyst is introduced in the form of complexed ions, (homogeneous catalysis).

The studies of hetero- and homogeneous catalysis have to a great extent been separate until quite recently, when it has become apparent that many of the ideas developed in the one field, for example the relation between chemisorption and metal (0) complexes, have relevance to the other. However, in this thesis I shall be considering only those aspects of homogeneous catalysis which can be related to structural results. It is a very broad generalisation to state that a catalyst acts by perturbing the electronic state of an organic substrate. Acids, and 'bare' metal ions in high oxidation states, do this by electrostatic polarisation of the molecule:-

E.g. activation of alkyl halides to nucleophilic attack



E.g. catalysis of the hydrolysis of amino acid esters²



This is a short-term inductive effect, and is also shown by small molecules such as the Lewis acids AlCl_3 and BF_3 . These are the so-called 'hard' acids,³ acting as hard catalysts. A characteristic of transition metals is that, although they do form ions of high formal oxidation state and polarising ability, they also, in their lower oxidation states, have the ability to interact much more profoundly with a substrate. In these lower oxidation states, the ion is much more diffuse and the d orbitals usually contain several non-bonding 'd' electrons. In this case, the interaction with ligands, e.g. substrates, is much more than just an electrostatic perturbation, and will be helped by the presence of other ligands which can also alter the electronic distribution about the substrate, by acting as regulators of the electron density at the metal. Evidence that transition metals affect the organic ligands bound to them, is provided by the stabilisation of otherwise highly unstable or non-existent

species, as metal complexes:-

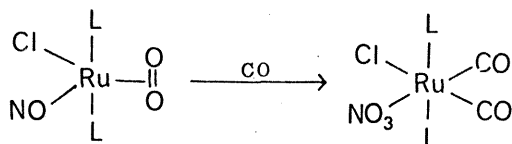
E.g. $\text{Fe}(\text{CO})_3(\text{cyclobutadiene})$ ⁴

E.g. $\text{Fe}(\text{CO})_3 \left[\text{C}(\text{CH})_2(\text{CHPh}) \right]$ ⁵

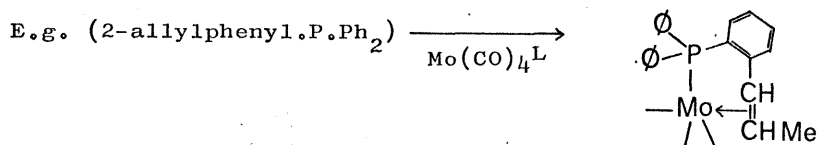
Also, coordination to a transition metal makes many interesting reactions possible:-

E.g. the hundreds of reactions of $\text{Fe}(\text{Cp})_2$

E.g. in situ oxidations:-⁶

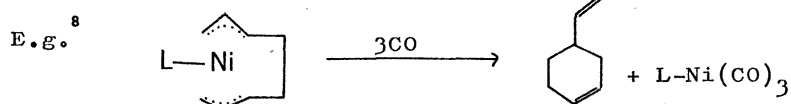


Coordination very often leads to internal isomerisations and rearrangements which may be useful synthetically:-

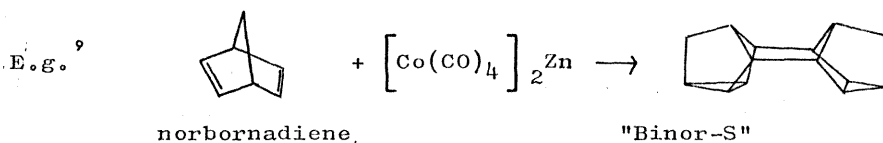


L is norbornadiene

The phosphine has rearranged to the (2-propenyl.P.Ph₂) form.⁷



Many exotic coupling reactions are known:-



In all these examples, the central metal is 'soft' and tends to be complexed to soft ligands, e.g. CO, phosphines, which contain diffuse, highly polarisable atoms.

The discussion of catalytic reactions may be further divided into several categories; two such categories are considered here:-

- (i) Those which involve reactions of organic molecules, e.g. olefines, acetylenes, aldehydes; these have been widely applied in the petrochemical industry for the production, from natural petroleum feed-stocks, of larger organic molecules of high molecular weight;
- (ii) Those which are thought to be simple analogues of the biological processes whereby very simple molecules e.g. O_2 , N_2 , are taken up by metal ions, and are utilised by the enzymes in a biochemical system.

The first part of this thesis will be concerned mainly with type (i); the second part will be concerned with one particular aspect of type (ii).

Factors affecting Catalytic Activity

The following, brief review of some of the factors thought to affect catalytic activity in transition metal ions, is divided into electronic, and other, factors.

Electronic Factors

1. Electron density on the metal atom

The electron density at the metal is very sensitive to the number of d electrons round the metal; by Pauling's Electroneutrality Principle, the charge on the metal will be dispersed into ligand orbitals until very little excess charge remains on the metal. Towards the end of each transition series this is often achieved by coordination with ligands with empty antibonding orbitals, which can accept electron density from the metal. This concept of 'back donation', first formulated by Chatt & Duncanson, and independently by Dewar,¹⁰ is generally accepted as fundamental to an explanation of the stability of metal ions in very low oxidation states, which would otherwise have improbably high electron densities at the central metal atom. The ability of pi-bonding ligands to control this electron density, is almost certainly relevant to the phenomenon of transition metal catalysis.

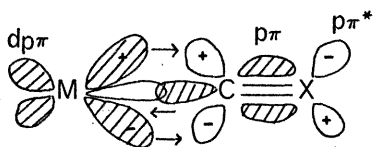
2. Availability of d orbitals

The geometries observed in transition metal complexes are generally associated with regular 4- or 6-coordination.

6-coordinate complexes are usually octahedral, while in 4-coordinate complexes both square-planar and (less often) tetrahedral arrangements occur. 5-coordination, associated with trigonal bipyramidal or square pyramidal arrangements, is less common, but is, however, of extreme importance as an activated configuration in catalytic intermediates. In a simple ligand field model, an octahedral or square-planar arrangement of ligands splits the initially equivalent 'd' orbitals into three nonbonding t_{2g} (d_{xy}, d_{yz}, d_{xz}) and two antibonding e_g^* ($d_{x^2-y^2}$ and d_{z^2}) orbitals. The d electrons will therefore go first into t_{2g} , and only reluctantly into e_g^* orbitals. (In square-planar complexes the d_{z^2} is probably also nonbonding, only the $d_{x^2-y^2}$ being antibonding if the z axis is taken as that perpendicular to the plane of the molecule.)

In a molecular orbital description, combination orbitals are formed from the metal ns, np, and (n-1)d, and the ligand sigma orbitals, and electrons from the sigma M-L bonds go into the bonding combinations. For square-planar complexes, the lowest empty orbital is the $d_{x^2-y^2}$ combination, and the splitting between d_{xy} , the highest nonbonding, and $d_{x^2-y^2}$, the lowest antibonding orbital will be increased for good sigma donors like phosphines, which possess lone pairs of electrons. Good pi-acceptors can also interact with the d_{xy}, d_{yz}, d_{xz} orbitals, thus lowering their energies, increasing ΔE , and stabilising the complex.

The stereochemistry of the available d orbitals may also affect the electronic properties of the complex, e.g. an M-C bond is generally stabilised when the organic part is aryl, acyl, or alkynyl, rather than alkyl, since pi-bonding is possible; with empty $p\pi^*$ ligand and filled $d\pi$ orbitals.

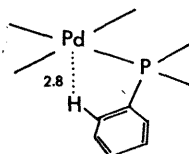
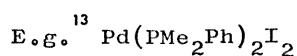
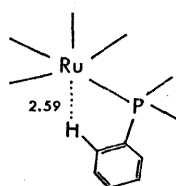
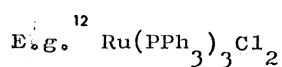


The so-called β -effect whereby metal 'd' orbitals can interact with an orbital on a β -atom, may also affect the stability, as it may provide a low energy path for dissociation of the complex to metal hydride and free olefine."



In some cases, a hydrogen atom several atoms removed from the coordinated atom, may approach quite close to the metal, and if the stereochemistry of the metal 'd'

orbitals is favourable, some interaction may occur.



3. Electronic properties of the other ligands

A very important factor is the resultant electronic effect of the other ligands. Catalytically important complexes usually contain good pi-bonding ligands, e.g. CO, CN^- , phosphines, which will absorb some excess electron density into their antibonding (CO) or d (phosphines) orbitals. They thus stabilise the organometallic complexes that will be seen to be important reaction intermediates.

Cis and trans effects will affect the reactivity of a particular complex, in the sense that a strongly trans-weakening ligand will labilise the bond trans to it.

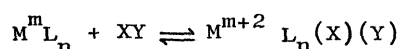
Other Factors

1. Coordinative unsaturation and ease of alteration of coordination number, CN

A very important concept is that of coordinative unsaturation.¹⁴ The preferred coordination number

decreases with increasing number of d electrons, i.e. across a transition series or with decreasing formal oxidation state of a given metal ion. This is a consequence of the fact that, with increasing numbers of nonbonding d electrons, then the higher the coordination number, the larger the number of d electrons which will be forced into antibonding orbitals, e.g. for d^7 to d^{10} configurations some will have to go into the strongly antibonding $d_{x^2-y^2}$ (in square-planar and octahedral) or d_{z^2} (octahedral) orbitals. A common coordination number for d^8 and d^{10} complexes is therefore square-planar CN_4 or even linear CN_2 . However, d^8 complexes (e.g. $Ir(I)$, $Fe(0)$, $Ru(0)$) and d^{10} complexes (e.g. $Pt(0)$), also readily and reversibly add further ligands, increasing their coordination number by one or two, and their oxidation state by two.

In general:-



where $X = H, R, \text{ aryl}$

$Y = H, \text{ halogen, acetylide etc.}$

Obviously this property is of great value in providing sites for attachment of a substrate, and thus, by bringing reacting species into close proximity, increasing their chances of reaction.

2. Ligands and solvent effects

The stereochemistry of the surrounding ligands, also the presence of solvent molecules completing an otherwise incomplete coordination sphere, probably affects the ease of substrate attack. For example, $\text{RhCl}(\text{PPh}_3)_3$ catalyses double bond hydrogenation, but with rhodium complexes containing smaller phosphines, the first step of dissociation, is not sterically so favourable, and these complexes are not effective as catalysts.

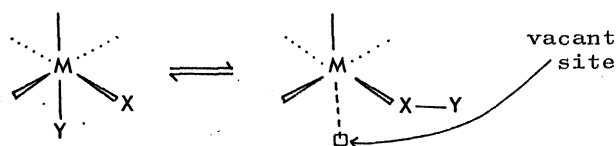
There may be weak electronic interactions between high energy ligand orbitals and those of incoming substrate, which could in turn provide a lower energy path for the reaction.

Metal complexes therefore act by their:-

- (i) ability to add and give up electrons, thus changing their coordination number and oxidation state;
- (ii) ability to reduce the activation energy of reaction, thus providing a low energy reaction path;
- (iii) ability to organise reactants by forming coordination bonds which are at the same time not so strong that they prevent further dissociation and reaction. This leads to a description of a generalised catalytic scheme.

General Steps Observed in Homogeneous Catalysis

1. Generation of a coordinatively unsaturated complex by heat, dissociation of ligands, if necessary;
2. Metal activation by formation of reactive bonds, generally M-H or M-(σ)C, often by reaction with a co-catalyst,
e.g. reduction with AlR_3 , NaBH_4
oxidative addition
hydrogen abstraction;
3. Activation of substrate by coordination, to form a metastable complex susceptible to further reaction;
4. Reaction of substrate with H or C from the activated M-H or M-(σ)C bond. This is often referred to as the 'cis insertion' reaction;
(X is the substrate):-



This stage, as well as actually forming the product, has the function of generating further vacant sites;

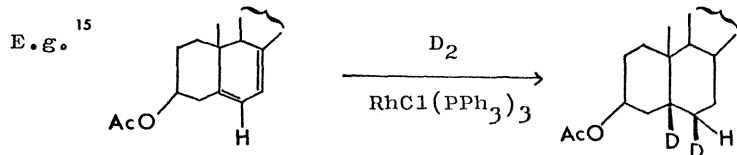
5. Dissociation of the product from the metal complex, which is left ready for further cycles.

Some examples of proposed mechanisms of various reactions will illustrate these general observations:-

- (a) hydrogenation catalysed by Rh complexes;
- (b) olefine isomerisation;
- (c) olefine dimerisation catalysed by Ni complexes.

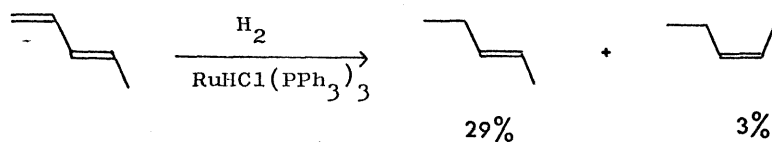
Hydrogenation of Olefines

This takes place at room temperature and pressure, and, depending on the catalyst, is often very stereospecific, usually giving a cis product:-



This type of reduction is invaluable in steroid chemistry.

$\text{RuHCl(PPh}_3)_3$ is the most active and specific catalyst found so far, but does not reduce isolated double bonds:- ¹⁶



$\text{PtCl}_2(\text{R}_3\text{P})_2/\text{SnCl}_2$ similarly reduces dienes to monoenes. ¹⁷

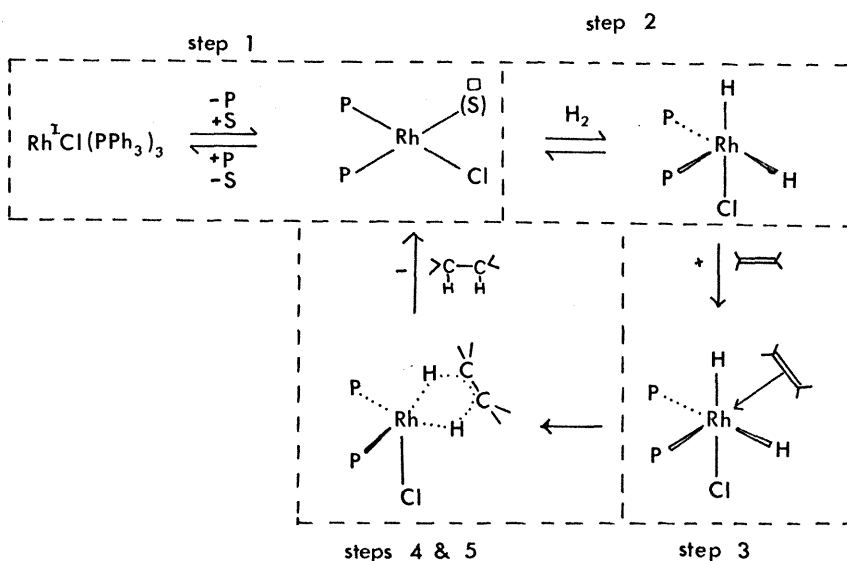
The most studied catalyst system is that using 'Wilkinson's'

catalyst $\text{RhCl}(\text{PPh}_3)_3$.¹⁸ The effectiveness is similar to that of Adam's catalyst, which acts heterogeneously.

The related complex $\text{RhCl}(\text{AsPh}_3)_3$ is 50x less effective as a catalyst for hydrogenation, illustrating the specificity of ligand requirements for catalytic activity.

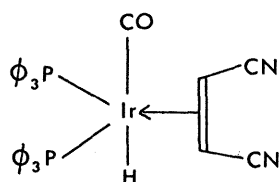
$\text{RuHCl}(\text{PPh}_3)_3$ ¹⁶ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ ¹⁹ selectively hydrogenate terminal double bonds, while $\text{IrH}_3(\text{PPh}_3)_3$ selectively hydrogenates allyl bromides to alkyl bromides.²⁰

The steps involved in the proposed mechanism:-



correspond to the general reaction scheme just outlined.

However, there is no direct evidence that complexation of the olefine is necessary for its activation; this is assumed in the above mechanistic scheme. The crystal structure of a complex containing both hydride and the stabilised olefine fumaronitrile ($(\text{CN})\text{CH}=\text{CH}(\text{CN})$)



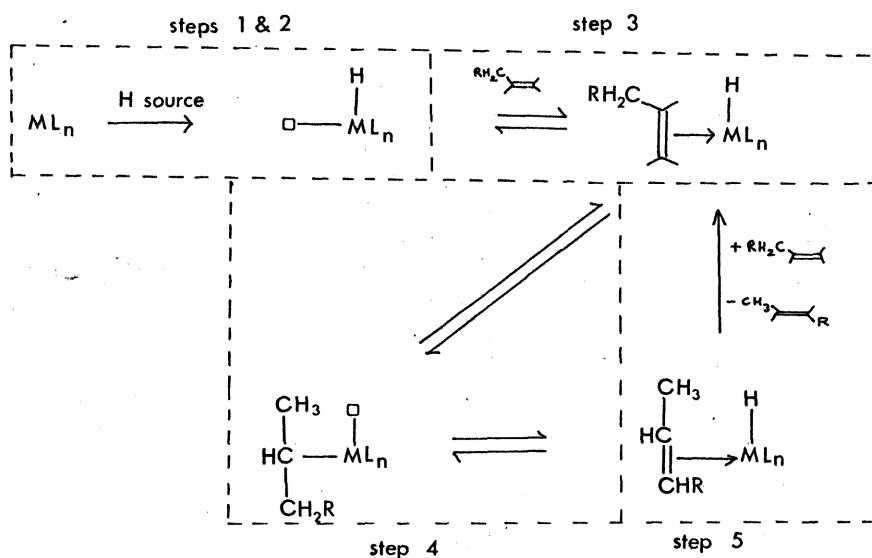
showed that they occupy cis positions,²¹ which suggests that complexation does in fact take place in the actual hydrogenation.

Isomerisation of Olefines

In most catalytic reactions involving unsaturated hydrocarbons, isomerisation from terminal to internal C=C occurs as an undesirable side reaction. As this occurs before the main reaction step, and hence leads to branched-chain products, much research effort has been devoted to understanding the mechanism of isomerisation, and hence to preventing its occurrence.

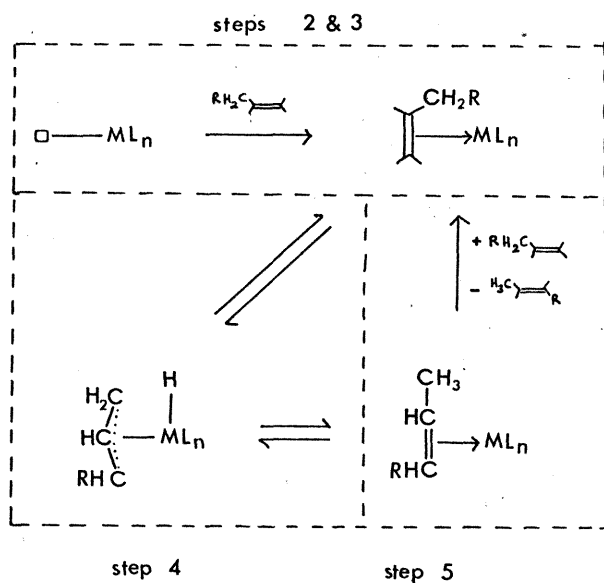
Virtually all transition metal complexes catalyse isomerisations, and although this spans a wide range of electronic situations, it is thought that a common mechanism is involved. Two distinct mechanisms have been proposed, however, to account for the fact that

in some systems a co-catalyst, containing hydrogen (as H^+ , H^- , or H_2), is necessary, while other catalysts which have no obvious source of hydrogen, are equally effective without a co-catalyst. The mechanism suggested²² for co-catalysed isomerisations, grouped into the steps outlined previously, is as follows:-



This probably corresponds to those cases where a metal such as $Rh(I)$ ²² is used, which readily adds hydrogen to form an $Rh(III)$ complex; also in isomerisations accompanying hydroformylation with $HCo(CO)_4$ as catalyst.²³

An allylic mechanism is postulated for those isomerisations in which there is no hydrogen source, e.g. with $\text{Fe}(\text{CO})_5$ ²⁴; in this case, it is thought that the hydrogen comes, either from the olefine itself, or, if there is no allylic hydrogen available, from another ligand. Hydrogen abstraction from a neighbouring ligand is well-known, and is considered in more detail in Chapter 2.2.



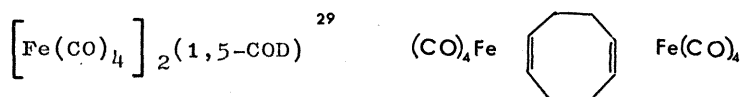
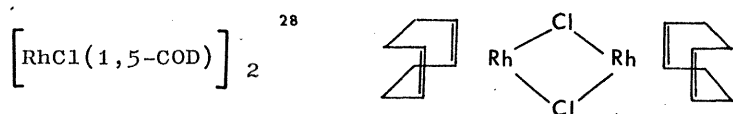
There is little direct evidence for either theory, because of the inherent instability of the intermediates. No metal-alkyl or allyl complexes have been isolated from these reactions, although metal allyl complexes are stable enough to be characterised, and

many have been studied crystallographically,

e.g. $\left[\text{RhCl}(\text{allyl})_2 \right]_2$ ²⁵ $\left[\text{PdCl}(\text{bismethallyl}) \right]_2$ ²⁶

Several complexes of rearranged olefines have been isolated and their crystal structures studied:-

E.g. ²⁷ 1,3-cyclo-octadiene (COD) \longrightarrow 1,5-COD

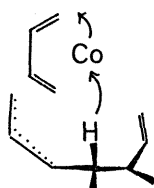


Similarly, although many metal-hydride complexes are known and characterised, there is little direct evidence for their formation as transient intermediates in isomerisations.

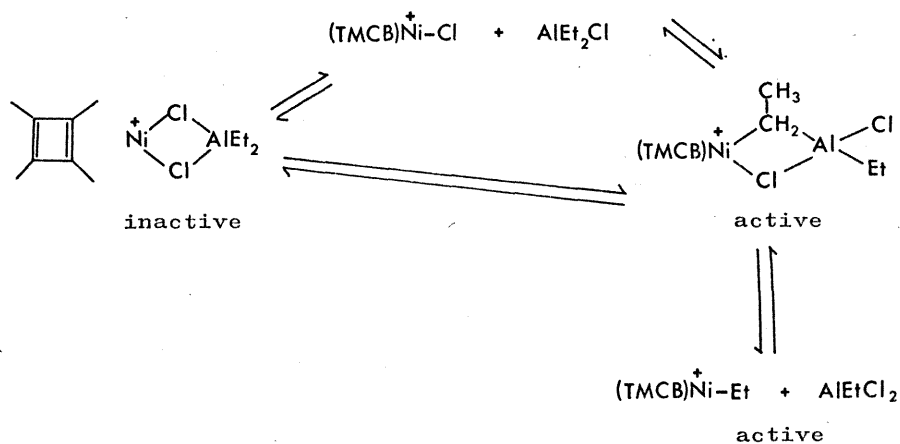
Olefine Dimerisation, Co-dimerisation, and Dienylation

Dimerisations and polymerisations of olefines are catalysed by different metals, the end product being determined by the stability of the intermediates. Ziegler Natta polymerisation involves titanium chloride/aluminium

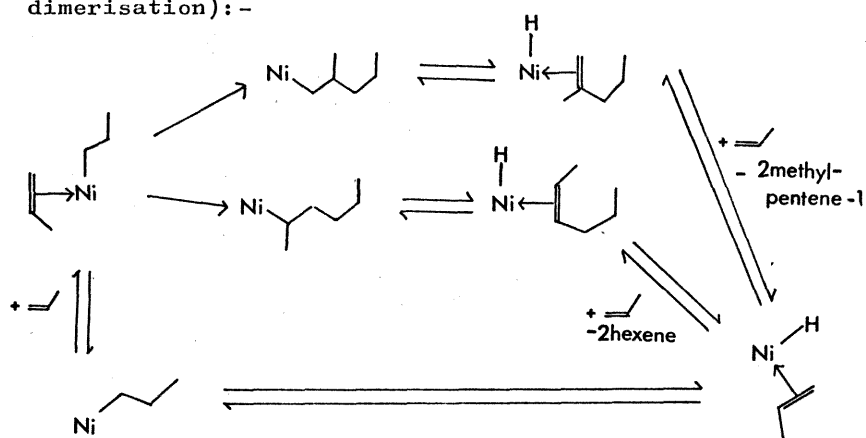
alkyl catalysts, ³⁰ while dimerisation is catalysed by complexes of Group VIII metals, e.g. RhCl_3 , ³¹ PdCl_4^{2-} , ³² CoCl_2 . ³³ The active catalyst in the dimerisation of butadiene to 3-methylhepta-1,4,6-triene has been isolated and shown to contain a methylheptadienyl radical and a butadiene coordinated to cobalt. The structure analysis also supported the postulated mechanism involving hydride shifts. ³⁴



Recently, certain nickel complexes, which can form Ziegler-type systems, have also been found to be effective catalysts, combined with a Lewis acid, and a Lewis base as co-catalyst.³⁵ An effective combination is $\text{AlEtCl}_2/\text{PR}_3/\text{TMCB} \cdot \text{NiCl}_2$ (TMCB is tetramethylcyclobutadiene), and the active catalyst is thought to be a nickel-ethyl:-



The mechanism postulated is (for propylene dimerisation):-



4-methylpentene-2 and 2,3-dimethylbutene-1 are also formed by isomerisation at the first step.

Nickel alkyl complexes would be expected to be even less stable than Pd or Pt alkyl complexes, and no intermediates have been isolated. The role of nickel hydrides and alkyls as possible intermediates is discussed in Chapters 2.8 and 2.9, where their instability is considered.

In all these examples, it can be seen that the important reactions are:-

1. formation M-H bonds;
2. formation M-C(σ) bonds;
3. formation M-C(π) bonds ('sideways on');
4. $\sigma \rightleftharpoons \pi$ equilibria;
5. hydrogen transfers

These may therefore be considered to be the fundamental processes involved in transition metal catalysis, for which structural information is required. The problems studied for this thesis were chosen to illustrate as many as possible of these reactions, and the structural results will be related to this scheme in the appropriate chapters.

CHAPTER 1.2

CRYSTALLOGRAPHIC THEORY AND TECHNIQUES

USED IN THIS RESEARCH

The completed structures described in this thesis were all solved by standard Patterson and Fourier syntheses, and were refined by least squares methods. All the data were collected on a Picker Four circle automatic diffractometer: the general procedure followed for each problem can therefore be collected into one chapter to eliminate unnecessary repetition of experimental details. The mathematical background to structure analysis has been set out in standard texts, e.g.

1. Arndt & Willis "Single Crystal Diffractometry"
2. Buerger "Crystal Structure Analysis"
3. "International Tables for X-Ray Crystallography"
Volumes 1-3,

and will only be explicitly discussed where relevant to the particular programs used in this work.

(A) Crystal Preparation and Photography

The crystals examined were generally of good enough quality for single crystal diffractometry. They were examined under polarized light for any peculiarities in their optical properties, and their densities measured by flotation in cadmium tungstoborate/water mixtures. The crystals were mounted on quartz fibres with araldite; if the complex was likely to react with this adhesive, then Edwards high vacuum silicone grease was used. The quartz fibres were stuck with araldite onto brass pins

made to fit onto the Picker goniometer head. If the crystals were sufficiently stable to air they were then immediately photographed but generally they had to be handled under nitrogen in a dry box and mounted in thin (0.01 mm. walls) Lindemann glass 2 mm. diameter capillary tubes. Where possible, and consistent with absorption factors, large crystals were therefore used, to minimize the loss of intensity due to the capillary tube. Preliminary photographs were taken on Weissenberg (Unicam) and Precession (Supper) cameras, from which the space groups and rough cell dimensions were worked out. The brass pins were then inserted into the special goniometer head made for the I.C.I. Picker, see Fig 1, on which centring and height adjustments are made by warping and raising the central shaft.

(B) Collection of Data

The data were collected on a Picker diffractometer equipped with scintillation counter and pulse height analyser; 0.002" of niobium or zirconium foil were used as filters for MoK α radiation, and aluminium disc attenuators were used when necessary. These reduced the diffracted intensity by factors of:

0.2509, 0.06397, 0.01955, 0.001

Picker Geometry

The Picker is a goniostat with 3 circles (χ , ϕ and ω) for orienting the crystal, and a fourth (two θ)

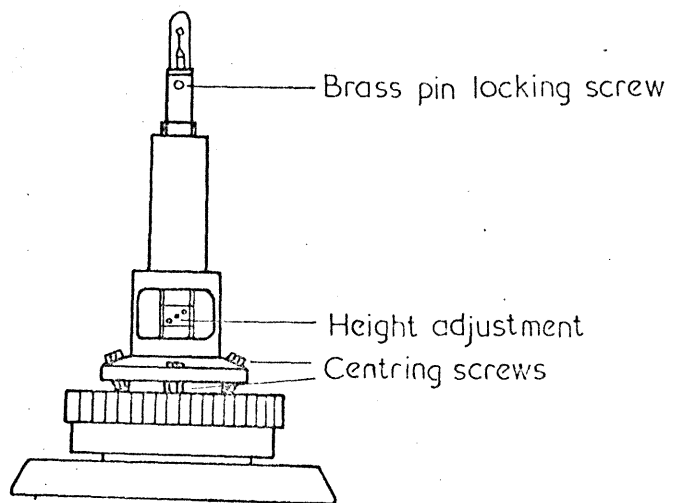


Figure 1.2.1
Goniometer Head

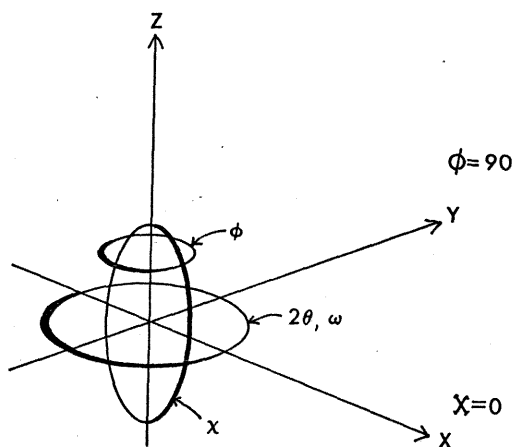


Figure 1.2.2
The Picker Axes

carrying the detector arm. The axes of the instrument (the so-called laboratory axes XYZ), are defined in Fig 2; they remain constant;

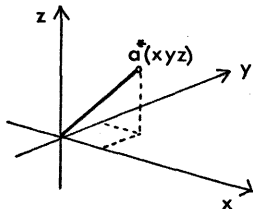
$\chi = 90$ points vertically upwards, and in the direction of the Z axis, the X axis lies in the horizontal plane through the χ circle, and the direction of the Y axis completes a right handed set of axes. A point a^* (hkl in reciprocal space) is represented in laboratory space by xyz.

$$\underline{h} = \begin{bmatrix} h \\ k \\ l \end{bmatrix} \quad \underline{x} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

then $\underline{x}^T = \underline{h}^T S$ where \underline{x}^T is the transpose of \underline{x} , and S is the orientation matrix;

$$S = \begin{pmatrix} x_a^* & y_a^* & z_a^* \\ x_b^* & y_b^* & z_b^* \\ x_c^* & y_c^* & z_c^* \end{pmatrix} \dots\dots\dots (1)$$

This equation therefore relates reciprocal to real space:

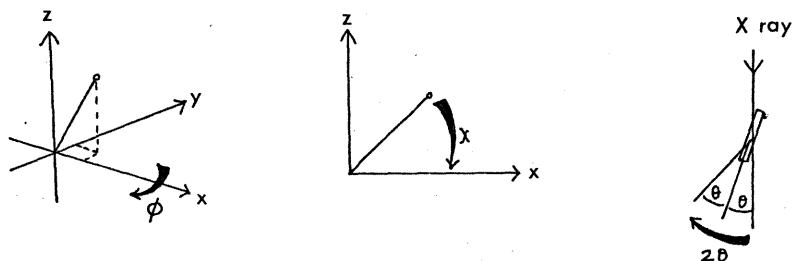


$$a^{*2} = x_a^{*2} + y_a^{*2} + z_a^{*2} \text{ etc.}$$

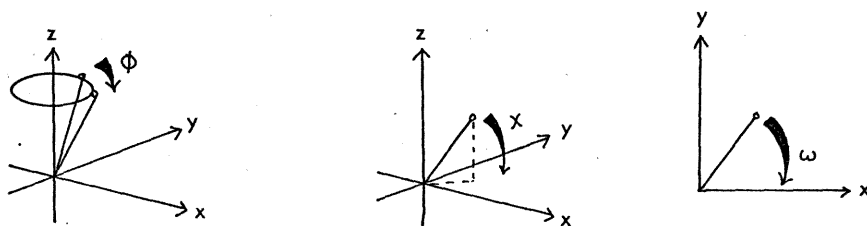
S is required to calculate reflection positions.

Only 2 ($\chi \phi$) of the 3 circles ($\chi \phi \omega$) are necessary to bring a^* into a reflecting position. However, the

extra circle, ω , coaxial with, and in the 2θ plane, is useful for manual setting or when multiple reflections are a problem. In terms of this geometry, the normal to the plane hkl must lie along the χ axis for a^* to be in a reflecting position. This is achieved by 2 rotations, about ϕ , then χ . The θ circle (carrying the detector) must then be moved through 2θ in the horizontal plane. At the same time the reference axial system XYZ is moved through θ .



If the ω circle is being used, then the ϕ rotation orients the crystal about the normal, and this is followed by the χ and ω rotations;



$$[\Phi]_z = \begin{bmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$[\chi]_y = \begin{bmatrix} \cos\chi & 0 & -\sin\chi \\ 0 & 1 & 0 \\ \sin\chi & 0 & \cos\chi \end{bmatrix}$$

$$[\omega]_z = \begin{bmatrix} \cos\omega & -\sin\omega & 0 \\ \sin\omega & \cos\omega & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Having determined the rotations $\chi, \phi, \omega, \theta$; x is given by:

$$\begin{aligned} \tilde{x} &= [\phi]_z [\chi]_y [\omega]_z \begin{bmatrix} 2\sin\theta \\ 0 \\ 0 \end{bmatrix} \\ &= \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos\chi & 0 & -\sin\chi \\ 0 & 1 & 0 \\ \sin\chi & 0 & \cos\chi \end{bmatrix} \begin{bmatrix} \cos\omega & -\sin\omega & 0 \\ \sin\omega & \cos\omega & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 2\sin\theta \\ 0 \\ 0 \end{bmatrix} \\ &= \begin{bmatrix} 2(\cos\omega \cos\chi \cos\phi - \sin\omega \sin\phi) \sin\theta \\ 2(\cos\omega \cos\chi \sin\phi + \sin\omega \cos\phi) \sin\theta \\ 2 \cos\omega \sin\chi \sin\theta \end{bmatrix} \end{aligned}$$

Normally ω is set at 180° , and is not altered during automatic data collection.

Now, $\tilde{x}^T = \tilde{h}^T S$.

Determination of cell dimensions

S may be determined from the angle settings of any 3 non-coplanar vectors. However, the accuracy is improved, by using more than 3 observations and standard deviations

on the cell parameters may be calculated. If there are n observations, a least squares method reduces the summation

$$\sum_{i=1}^n (\tilde{h}_i^T S - \tilde{x}_i^T) (S^T \tilde{h}_i - \tilde{x}_i)$$

to a minimum when

$$S = \left(\sum_{i=1}^n \tilde{h}_i \tilde{h}_i^T \right)^{-1} \left(\sum_{i=1}^n \tilde{h}_i \tilde{x}_i^T \right)$$

The matrix $\sigma^2(S)$ gives the variance in each element of S ;

$$\sigma^2(S) = \left[S \sum_{i=1}^n (S^T \tilde{h}_i - \tilde{x}_i)^2 \right] / (n - 3)$$

$$\text{Since } S = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix}$$

This gives a^* , b^* , c^* , α^* , β^* , γ^* , V^* as functions of S ;

$$\text{e.g. } a^* = S_{11}^2 + S_{12}^2 + S_{13}^2 \quad (\text{from (1)}),$$

$$\cos \alpha^* = S_{21} S_{31} + S_{22} S_{32} + S_{23} S_{33}$$

$$V^* = \text{determinant of } S.$$

Hence a , b , c , α , β , γ , V may be found;

$$\begin{aligned} \text{e.g. } a &= \lambda b^* c^* \sin \alpha^* / V^* \\ V &= \lambda_o^3 / V^* \quad (\lambda_o \text{ is mean peak } \lambda) \end{aligned}$$

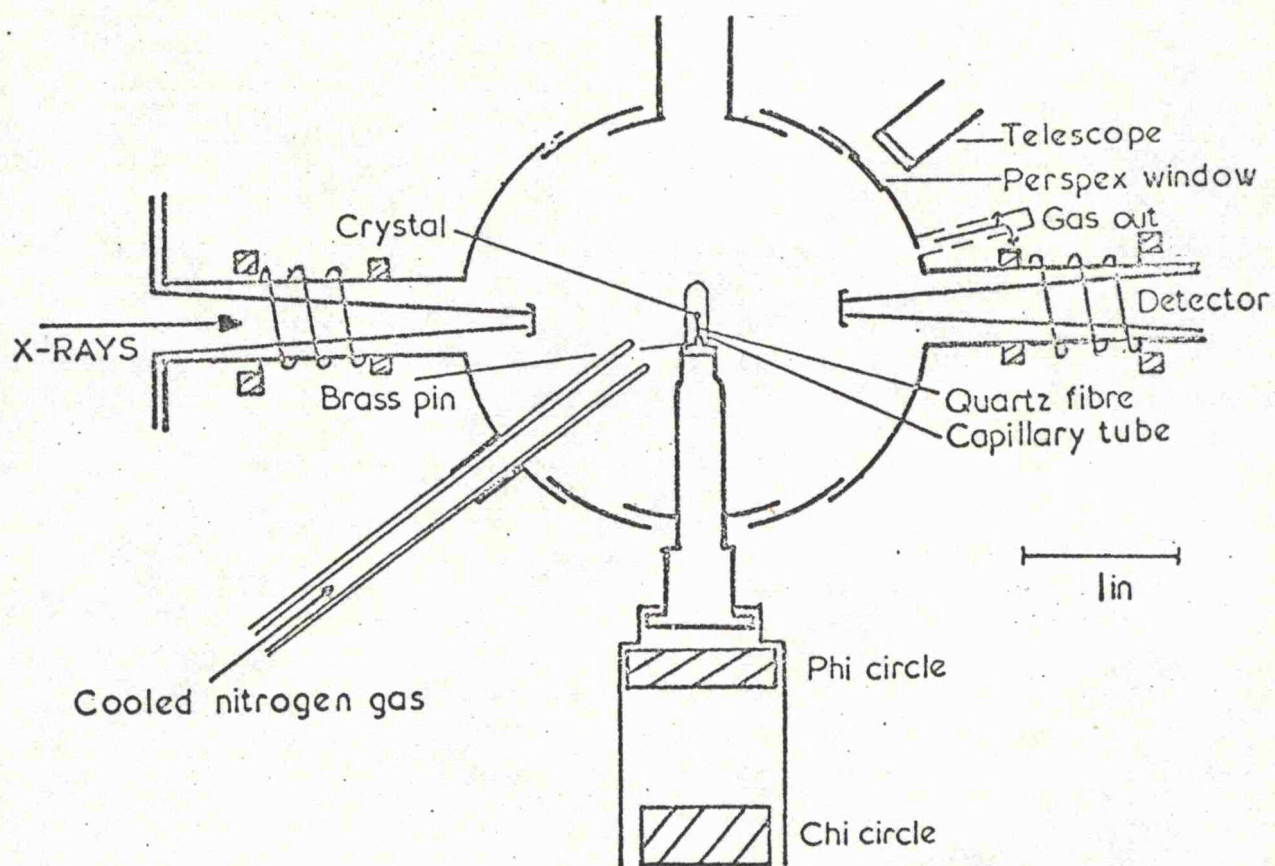
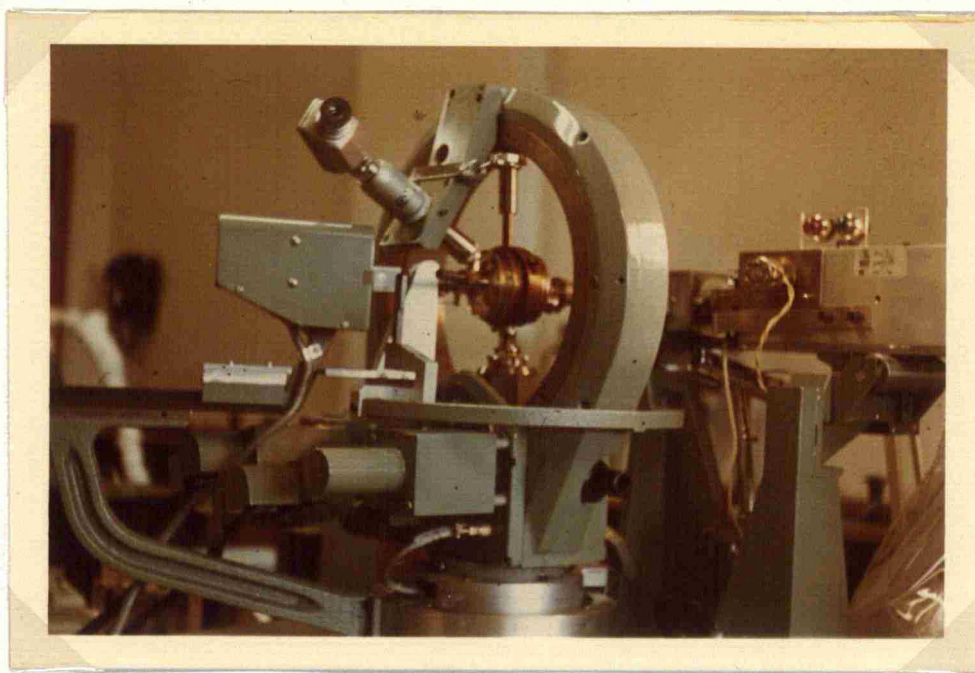


Figure 1.2.3
Section through Cold Sphere ³⁶

The standard deviations in the real and reciprocal cell dimensions (D) are then given by:-

$$\sigma^2_D = \sum_{i=1}^3 \sum_{j=1}^3 \left(\frac{\partial D}{\partial s_{ij}} \right)^2 \sigma^2(s_{ij})$$

where $D = f(s_{11}s_{12}\dots s_{33})$

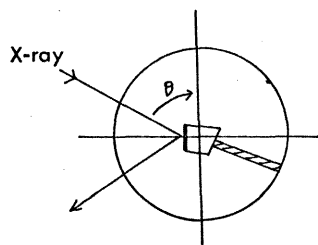
The cold sphere

Data for four structures $\text{NiHCl}(\text{PPr}_3^i)_2$, $\text{PdHCl}(\text{PPr}_3^i)_2$, $(\text{MoOCl}(\text{dppe})_2)(\text{ZnCl}_3\text{acetone})$ and $\text{MoCl}_2(\text{dppe})_2$ were collected at -70°C using a brass sphere specially designed by R H B Mais and made for the I.C.I. Picker. This encloses the goniometer head and has portholes for the X-Ray collimator and the detector arm (see Figure 3). A temperature of -70°C is readily obtainable without any further apparatus, by maintaining a steady flow of nitrogen (cooled by passing through a Dewar of liquid nitrogen) into the sphere. To prevent frosting of the portholes in the sphere, an external stream of air is directed at these windows. If precautions are taken to reduce the humidity of the surrounding air, by enclosing the entire goniostat in a dry box, lower temperatures may be reached. However, manual operations become very hampered and previous experience had shown that a difference of 90°C would make a significant improvement in structural accuracy,³⁶ so this dry box was not used.

Procedure followed for data collection

(1) Initial reflections

Initial reflections were obtained whenever possible by diffraction from a principal face of the crystal, brought into the reflecting position manually by moving the χ and ϕ circles, and then scanning up a row in 2θ . The position for reflection is:-



3 non-collinear reflections having been chosen, these have to be correlated for consistency of sign. This is best illustrated by an example. Given 3 reflections,

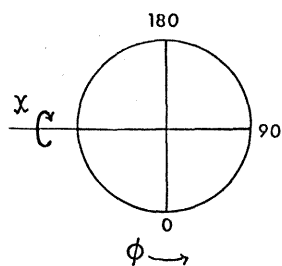
	χ	ϕ
$\pm h \ 0 \ 0$	110	10
$0 \ 0 \ \pm 1$	155	197
$0 \ \pm k \ \pm 1$	190	79

The Picker axes have been shown in Fig 2, and hence the directions of the $\pm h \ 0 \ 0$, $0 \ 0 \ \pm 1$, and $0 \ \pm k \ \pm 1$ vectors are defined as in Fig 4. (For simplicity these are represented in 2 dimensional space.) To complete a rhs., $0 \ k \ 0$ must lie at $\sim \chi = + 0$ in the fourth quadrant, and therefore $0 \ \pm k \ \pm 1$ is $0 \ +k \ -1$.

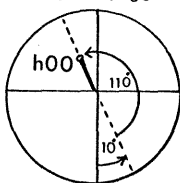
An initial orientation matrix is now generated, from which the positions of additional strong reflections are calculated. These are then measured accurately,

Figure 1.2.4

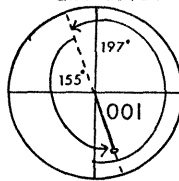
Assignment of Sign to Initial Measurements
(2-dimensional illustration - see text)



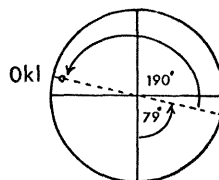
define $+h00$:



and $00+1$:

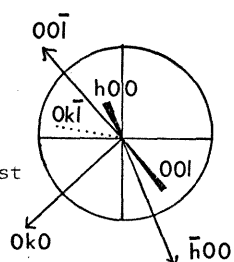


0^*k+1 remains
unsigned:



$h00$ and $00\bar{1}$ define a
right handed set of
axes; $0k0$ lies in
fourth quadrant, almost
in plane of ϕ circle.

$\therefore 0^*k+1$ is $0k\bar{1}$



their χ , ϕ , ω and 2θ values noted, and the most convenient segment of reciprocal space is chosen for collecting data. Because of the mechanical limitations of the Picker, hkl and $hk-l$ are collected separately to minimize large jumps in χ or ϕ . To obtain the best orientation matrix for generating reflection positions, initial measurements are made in the relevant quadrants of reciprocal space. For accurate cell dimensions and best esds., on the other hand, 3 or 4 general reflections are each measured in all 4 quadrants. This is advisable because the computer program is quite general and assumes a triclinic cell. Hence any symmetry-enforced 90° or 120° angles are calculated and refined. This artificial refinement reduces the accuracy of the other derived parameters, but this method minimizes the error introduced.

(2) Card generation

The program Gonioset (see Appendix 1) is used to generate the control cards for each reflection within a specified shell of reciprocal space. The method used is to scan from $(2\theta - \Delta 2\theta_1)$ to $(2\theta + \Delta 2\theta_2)$; the limiting 2θ values are given by:-

$$\begin{aligned} 2\theta_1 &= 2\sin^{-1} \left(\sin\theta_o \cdot \frac{\lambda_1}{\lambda_o} \right) + \Delta 2\theta_1 \\ 2\theta_2 &= 2\sin^{-1} \left(\sin\theta_o \cdot \frac{\lambda_2}{\lambda_o} \right) + \Delta 2\theta_2 \end{aligned}$$

λ_1 and λ_2 are 0.7093 and 0.7135 for molybdenum radiation; θ_o is the peak position. The space group absences for

particular symmetries are input as subroutines, which allow absent reflections to be omitted from the input listing.

(3) Measurement of data

The goniometer is card controlled and each reflection corresponds to a control card punched with $hkl \times \phi \omega 2\theta_1 2\theta_2$ followed by a data card which records $hkl \times \phi \omega 2\theta_1 2\theta_2$ (net count)(bg_1)(bg_2). The detector scans up 2θ , measures the upper background for a fixed time, and then the lower background for the same time. Two standard reflections, of similar 2θ value and intensity, are measured every 2 hours as an indicator of crystal movement and/or decomposition. The data was generally collected in shells or half shells, of increasing 2θ , and each batch of intensities was checked using the program Data Check (See Appendix 1). This is a data reduction routine and enables any anomalous background counts, or bad measurements, to be spotted and repeated if necessary.

(4) Measurement of crystal

A special micrometer eyepiece fitted to a microscope was used to measure the crystals accurately for absorption corrections. A K-code programme MK1196 (See Appendix 1) was used to calculate the surface equations of the crystal (and also the χ and ϕ values of each face, from which the faces could be identified).

Except where stated, all further calculations were done using the K-code Cosmos master program of R H B Mais, in which most crystal structure calculations are standard routines.

(C) Initial Treatment of Data

The L_p factor is given by:-

$$L_p^{-1} = 2 \sin 2\theta / (1 + \cos^2 2\theta)$$

also, if N = peak count

n_1 = upper background

n_2 = lower background

A = attenuation factor

t = fixed time

T = time spent on peak

then the intensity (I) and its deviation are given by:-

$$I = (N/A) - (n_1 + n_2)T/2tA$$

$$\sigma^2(I) = (N/A^2) + (n_1 + n_2)T^2/4t^2A^2$$

The amplitude (F) and its deviations are given by:-

$$|F| = (L_p^{-1} \cdot I)^{\frac{1}{2}}$$

$$\sigma^2(F) = (L_p^{-1}/4I)\sigma^2(I)$$

If the backgrounds are high or uneven then the measurement is rejected, the test being:-

$$\text{reject if } t_1 (n_1 - n_2)T/2tA \geq I$$

where t_1 is a constant.

To eliminate statistically insignificant reflections, one of two tests is applied:- (t_n are constants)

$$a. \text{ reject if } I \leq t_2 + t_3 \sigma(I)$$

$$b. \text{ if } I \leq t_4 + t_5 \sigma(I)$$

$$\text{then set } I = t_6 + t_7 \sigma(I).$$

Test (a) was used for all data collected for this thesis; usually all positive amplitudes were accepted ($t_2 = t_3 = 0$), but when a large amount of good data was collected, t_3 was set to 2 or 3. The scale factor was initially set to unity, and refined during analysis.

No corrections were made for extinction, as no computer programs were available.

Absorption

The intensity I_0 of a beam is reduced by an amount $dI = \mu I_0 dt$ on passing through a crystal of thickness dt , and linear absorption coefficient μ , ie $I = I_0 e^{-\mu t}$

With $\text{MoK}\alpha$ radiation, the reduction in intensity is less serious than with $\text{CuK}\alpha$, but is still sufficient to make a correction desirable, if any dimension of the crystal is more than the optimum thickness $t = 2/\mu$.

A Gaussian correction was used based on that of Busing and Levy,³⁷ modified by R H B Mais³⁸ to give a more even distribution of sample points.

Collate and sort routine

The common reflections were averaged according to the symmetry of each crystal, and the signs inverted where appropriate to obtain (hkl) in positive quadrants if possible. (This is a valid operation provided one does not intend utilising anomalous dispersion effects, or correcting for $4f''$.)

(D) Structure Analysis(1) Patterson syntheses

The unsharpened Patterson function

$$P_{xyz} = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi \underline{hx}$$

was calculated for each problem. The heights of peaks are proportional to the products of the atomic numbers of the 2 atoms concerned, and in most cases it was possible to deduce the heavy atom position from the Harker vectors between symmetry related pairs of these heavy atoms. Usually, no attempt was made to find any light atom positions from the Patterson maps.

(2) Electron density and difference syntheses

The functions

$$\rho_{xyz} = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| \cos [2\pi \underline{hx} - \alpha(hkl)]$$

(acentric)

$$\rho_{xyz} = \frac{2}{V} \sum_h \sum_k \sum_l |F_{hkl}| \cos 2\pi \underline{hx}$$

(centric)

$$\rho_o - \rho_c = \frac{1}{V} \sum_h \sum_k \sum_l (F_o - F_c) \cos 2\pi \underline{hx}$$

were calculated, generally at $\frac{1}{3}$ or $\frac{1}{4}$ Å resolution.

A fourier analysis routine was used to obtain peak positions, by taking the 19 grid points round each map point in turn, testing if this represented a peak, and calculating its position and height.³⁹

(3) Structure factor calculations and refinement

The structure factor

This is expressed by the equation:-

$$F = A + iB = \sum f \exp 2\pi i (\underline{hx})$$

where $A = \sum_{i=1}^n f_i \cos 2\pi \underline{hx}$

$$B = \sum_{i=1}^n f_i \sin 2\pi \underline{hx} (= 0 \text{ for centric space groups})$$

Planes lists

The F_o values used in refinement were selected by a "minimum amplitude" or "minimum amplitude to deviation ratio" test on the observed amplitudes (scale unity). The actual threshold values were therefore only determined after refinement of the scale factor. The minimum amplitude to deviation ratio was preset as 3.0 unless a directive was put in.

Planes lists could be edited by the program MK 1533, which enabled modifications to be made to the existing list.

Formfactors

These were used in the form:-⁴⁰

$$f(S_x) = \sum_{i=1}^n a_i \exp(-b_i S_x^2) + c \quad \text{for } n = 4$$

where a_i , b_i and c are constants particular to each atom.

Approximate corrections for $\Delta f'$, the real part of the anomalous scattering, were made for the heavier atoms in each structure, by altering the constant c .⁴¹

Thermal Parameters

The expression $F_h = \sum f_o \exp 2\pi i(hx)$ takes no account of the fact that atoms vibrate, and hence the diffracted intensity is reduced by the amount of out of phase vibration:-

$$f = f_o e^{-M}$$

$$\text{where } M = 8\pi^2 \overline{u^2} \sin^2 \theta / \lambda^2 = B \sin^2 \theta / \lambda^2$$

($B = 8\pi^2 \overline{u^2}$ assuming a Debye-Waller type of isotropic vibration, and $\overline{u^2}$ is the mean square amplitude of vibration of the atom in \AA^2 .)

The corresponding expression for anisotropic vibration is that the mean square amplitude in the direction

$$\underline{l} = (l_1, l_2, l_3)$$

$$\text{is } \overline{u^2} = \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} R_i l_j$$

where \underline{U} is a symmetrical tensor. \underline{U} and \underline{l} are defined with respect to $a^* b^* c^*$ so that the component of \underline{U} in the (100) direction, i.e. parallel to the a^* axis, is

$$\overline{u^2} = U_{11}$$

The full expression for the scattering factor then becomes:-

$$f = f_o \exp -2\pi^2 \left[U_{11} h^2 a^{*2} + 2U_{12} hka^* b^* + U_{22} k^2 b^{*2} + 2U_{23} klb^* c^* + U_{33} l^2 c^{*2} + 2U_{31} hla^* c^* \right]$$

These are related to b values by the equations:-

$$b_{11} = 2\pi^2 a^{*2} U_{11} \quad \text{etc.}$$

$$b_{23} = 4\pi^2 b^{*c*} U_{23} \quad \text{etc.}$$

The Cosmos routine calculates U_{ij} values; their dimensions are \AA^2 . Isotropic U s were initially set to 0.04 unless otherwise stated, and the initial U_{ii} s were set at the refined U values, while initial U_{ij} s were set zero.

The normal equations of least squares refinement

The function to be minimised is:-

$$(R^1) = \sum_h w_h \Delta^2 = \sum_h w_h (|F_o|_h - |F_c|_h)^2$$

where $\Delta = |F_o| - |F_c|$

are the observational equations and w_h is a weighting term. If p_j ($j = 1, 2, \dots, n$) are the parameters in $|F_c|$ to be adjusted (i.e. a trial set of parameters) then:-

$$F_c = f(p_1 p_2 \dots p_n)$$

and R' is a minimum when $\frac{\partial R'}{\partial p_j} = 0$ ($j = 1 \dots n$)

i.e. when

$$\sum_h w_h \Delta_h \frac{\partial |F_c|_h}{\partial p_j} = 0$$

If the values of p_j are nearly correct, then Taylor's series may be used to find the effect on Δ_h of a small change ξ in the parameter p :-

$$\Delta_h(p + \xi) = \Delta_h(p) - \sum_{i=1}^n \xi_i \frac{\partial |F_c|}{\partial p_i} h$$

Now, if ξ is very small, the changes will tend to make $\Delta_h(p + \xi) = 0$

$$\therefore \Delta_h(p) = \sum_{i=1}^n \xi_i \frac{\partial |F_c|}{\partial p_i} h$$

Substituting in (1):-

$$\sum_h w_h \Delta_h \frac{\partial |F_c|}{\partial p_j} h = \sum_h w_h \sum_{i=1}^n \xi_i \frac{\partial |F_c|}{\partial p_i} h \cdot \frac{\partial |F_c|}{\partial p_j} h$$

These are the normal equations, and there are n of them; expressed in matrix form these are:-

$$\sum_i a_{ij} \xi_i = b_j$$

$$\text{where } a_{ij} = \sum_h w_h \frac{\partial |F_c|}{\partial p_i} h \cdot \frac{\partial |F_c|}{\partial p_j} h$$

$$\text{and } b_j = \sum_h w_h \frac{\partial |F_c|}{\partial p_j} h$$

The conventional "R factor" is defined as:-

$$\frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$$

and the "Convergence factor" as:-

$$\frac{\sum w \Delta_{n-1}^2 - \sum w \Delta_n^2}{\sum w \Delta_{n-1}^2}$$

Weighting scheme and standard deviations

The weighting schemes used⁴² were of the form:-

$$1/W = 1 + \left(\frac{F_o - c_2}{c_1} \right)^2$$

where c_1 and c_2 are constants determined from plots of $W\Delta^2$ against $|F_o|$ for ranges of $|F_o|$, the best function chosen as that in which average values of $W\Delta^2$ remained constant when $W\Delta^2$ was analysed over sine theta or $|F_o|$ ranges. The standard deviation, using this type of weighting scheme, is given by:-

$$\sigma^2(p_i) = (a^{-1})_{ii} (\sum W\Delta^2) / (m - n)$$

where $(a^{-1})_{ii}$ is the inverse of the matrix a_{ii} in the normal equations, m is the number of observations, and n is the number of parameters determined, i.e. we assume that:-

$$\sigma |F| \propto |F_o| - |F_c|$$

This will only represent true esds. when the correct weighting scheme has been applied.

Approximations made in computing

Because of the high costs involved in computing, approximations were necessary. In the initial stages of each analysis full matrixes were used, but as more atoms were added, these matrixes were subdivided into smaller blocks each containing those groups of atoms that were expected to be correlated, i.e. chemical groupings such as P-C-C-P systems, and naphthyl groups.

These were further split into positional and thermal blocks, whenever anisotropic refinements were attempted. Occasionally the block diagonal approximation was used, i.e. only recognising correlations between parameters in the same atom, all off-diagonal terms in the a_{ij} matrix being ignored. Hydrogen atom parameters were not refined, being included as constant contributions in structure factor calculations. Occupancies were always unity except in the calculation on the disordered structure.

A rigid body program became operational in time to be used for the 2 structures with dppe groups; the phenyl rings were constrained to their known geometry, and refined as rigid bodies;⁴³ this reduced the number of parameters from 24 (6 x 4 for isotropic U_s) to 7 (3 to define the position and orientation, and 1 for a group U) for each ring. Any 3 atoms may be used to define the plane of the ring (using Moleg - See Appendix 1), which is described in an orthogonal system of axes; and fixed with respect to the cell axes by an orientation matrix. For the calculation of structure factors, the x, y and z parameters of all atoms are necessary, but for refinement, all the separate derivatives are combined, so that only the 7 rigid body parameters are refined and hence a great saving in computer time is achieved, together with a more realistic description of the geometry of phenyl rings.

For each structure analysis, the calculations are tabulated

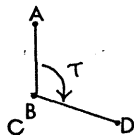
with details of R factors, type of matrix used, weighting, and number of terms. It is hoped this will avoid unnecessary repetition of refinement procedure. Tables of structure factors and agreement analyses, also final positional and vibrational parameters, are listed in Appendix 2.

Molecular geometries and standard deviations

- (I) Cosmos. Bond distances and angles were normally calculated within Cosmos; their esds are given by:-

$$\sigma^2(l_{12}) = \sigma^2(x_1) + \sigma^2(x_2)$$

where x_1 and x_2 are the atomic coordinates measured in the direction of the bond, and the atoms are independent. The torsion angle (τ) about the bond B-C is defined by four atoms A-B-C-D, and is the angle between the directions B-A and C-D projected onto the plane perpendicular to the bond B-C.⁴⁴ A clockwise rotation is defined as positive.



- (II) Moleg was used to calculate best planes and dihedral angles.
- (III) Hcoord was used to calculate the theoretical positions of hydrogen atoms bonded to sp^3 and

sp^2 carbon atoms, as in the methyl groups of dmpe, and for aromatic hydrogens. It was also used to calculate terminal methyl positions in disordered dmpe (see Chapter 2.2), by assuming tetrahedral phosphorus coordination.

Drawings of structures

The Calcomp plot program Ortep was used for drawing molecules and projections of the intermolecular packing.⁴⁵

Direct Methods

The symbolic addition method was used for 1 analysis and will be described in the relevant chapter.⁴⁶

Crystal Geometries

The surface equations for those crystals whose surfaces were accurately measured, are of the form:-

$$lx + my + nz = p$$

where p is the perpendicular distance (in microns) from the centroid of the crystal to each face.

CHAPTER 2.1

TRANSITION METAL COMPLEX HYDRIDES

The key intermediates in the catalytic reactions described in Chapter 1.1 are probably complexes which contain M-H and M-C bonds, and the factors affecting their stability have been briefly considered. Up till c.1960, very few of these complexes were known, and it was believed that the reason was the low covalent energy of these bonds. It is perhaps because of their relative instability, that this type of complex is involved in catalytic reactions, but the corollary of this is that it is difficult to obtain direct information about such intermediates, since isolation is necessary for their study, eg when attempting an X-ray analysis. Generally speaking, the more stable analogues of catalytic intermediates are examined, in the expectation that the results may be extrapolated to the actual intermediates, and in some cases a likely intermediate has been synthesised, rather than isolated. For example, $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ is a hydrogenation catalyst for fumaronitrile, and therefore $\text{IrH}(\text{CO})(\text{PPh}_3)_2(\text{CN}:\text{CH}:\text{CH}:\text{CN})$ is probably an intermediate. This is a rare example of hydride and olefin simultaneously complexed to the same metal, and the X-ray analysis showed ²¹ that they occupy cis positions.

Bridging hydrides are thought to be involved in hydrogenation reactions, and so studies on complexes such as $(\text{CO})_5\text{Cr}-\text{H}-\text{Cr}(\text{CO})_5$ ⁴⁷ may be helpful.

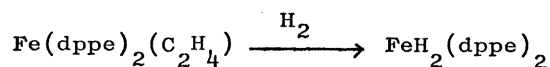
Transition Metal Hydrides

48

Complex hydrides are now known for all transition metals except niobium and hafnium. At the top left of the d block, they are generally stabilised by CO or π Cp, at the bottom right by tertiary phosphines and arsines: the complexes usually conform to the 18e rule (or 16e in Pt(II) complexes).

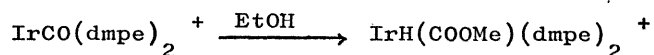
They may be prepared from almost any source of H, and the complexes studied in this thesis represent examples of all the main preparative routes:-

1. From H_2



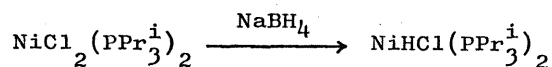
Chapter 2.5

2. From H^+



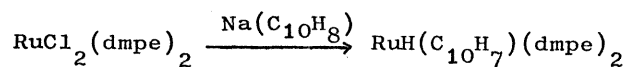
Chapter 2.7

3. From " H^- "



Chapter 2.8

4. From C-H bonds



Chapter 2.2

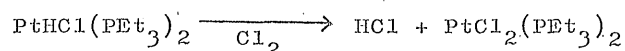
Hydride formation competes in many cases with reduction, and several presumed M^0 complexes are now correctly formulated as hydrides.

The stability of transition metal hydrides follows opposite trends to that of covalent main group hydrides, ie it increases down each series (see Chapters 2.2 and 2.8 particularly). Most hydrides are air and moisture sensitive, and decompose on heating.

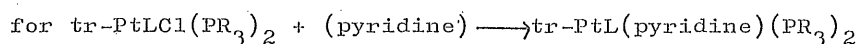
They are generally neutral, but may be acidic or basic; early studies gave conflicting results, eg. $FeH_2(CO)_4$ is acidic,⁴⁹ but $ReH(\eta-Cp)_2$ is basic.⁵⁰

Theoretical calculations are not conclusive,⁵¹ though they suggest a negatively charged hydride. Dipole measurements indicate a net positive charge on H.⁵² Probably a whole range of polarities exists, with the net polarity dependent on the electronegativities of the other ligands. The resultant polarity is undoubtedly important in determining, for example, the direction of addition of M-H across an unsymmetrical olefin, eg. $CoH(CO)_4$ changes in its behaviour towards olefines,⁵³ when CO groups are replaced by phosphines. The electronic properties of H are very similar to (Me) because in the case of hydrogen, the 1s orbital is a good sigma donor. For (Me), also, only sigma bonding is possible. Since H is so small and simple it is an ideal model for studying M-L bonding, but, also because of this, it is not strictly typical of most ligands.

The chemical reactions of H are similar to those of a normal anionic ligand, e.g.:⁵⁴



It appears to have a trans labilising effect, i.e. promotes reaction at the trans position, e.g.:⁵⁵



The order found was $\text{PMe}_3 > \text{PEt}_3 \approx \text{H} > \text{PPr}_3^{\text{n}} > \text{Me} > \text{Ph} > \text{Cl}$

It also adds across double bonds, e.g.:⁵⁴



The most extensive studies of M-H have, however, been on its physical properties, which are readily measured. Also, it is difficult to detect H by chemical analysis or stoichiometry of reaction because of its small percentage in compounds, and its low molecular weight. Accordingly, physical properties are used diagnostically.

All well-defined hydrides are diamagnetic. (One reported paramagnetic hydride $\text{OsHCl}_2(\text{PBu}_2^{\text{n}}\text{Ph})_3$ ⁵⁶, was later shown to be a nitrogen complex.⁵⁷) The M-H stretching vibration mode is a pure vibration which occurs in the IR between 1700 and 2250 cm^{-1} , as a broad but strong band, unless masked by $\nu(\text{C}\equiv\text{O})$ or $\nu(\text{N}\equiv\text{N})$. It can usually be confirmed by the deuteration shift to lower frequency (ratio $\nu_{\text{H}}/\nu_{\text{D}} \sim 1.4$). A previously reported⁵⁸ exception to this is discussed in Chapter 2.6. The bending mode, at

650-850 cm^{-1} , (a weak to medium band) is usually masked by ligand vibrations. Bridging hydrides have a band at 1000-1250 cm^{-1} .

Trans dihydrides, and cis when trans to similar groups, have one broad band, usually at lower frequency than corresponding monohydrides (1615-1750 cm^{-1}).

Cis dihydrides have two bands in the normal range.⁵⁹

$\nu(\text{M-H})$ in some complexes, is sensitive to solvent (lowest in n-hexane, highest in CHCl_3), and also to other groups in the molecule. It increases on descending a series, corresponding to increasing M-H strength, and it has been shown that for Pt-H, decreases with increasing trans effect of the trans ligand. For Ru-H the order differs in detail but not in overall sense.⁶⁰ Incoherent inelastic neutron scattering can be used for studying hydrogen vibrations and complements IR as it, also, gives information about vibrational energy levels.⁶¹ The disadvantage of this technique is that huge samples are required.

d-d transitions in hydride complexes are often obscured in the UV by charge transfer bands, but for $\text{RuHCl}(\text{dmpe})_2$, the large hypsochromic shifts⁶² suggest that H has a strong ligand field, similar to CN^- . However, studies on $\text{RhH}(\text{NH}_3)_5^{2+}$ suggest a rather weak ligand field, similar to H_2O or NH_3 .⁶³

The very large positive NMR shift is the main diagnostic test for M-H (there are no known exceptions) since there is no interference in the range under observation. The shifts are between 10 and 45 τ (solvent dependent), and

the magnitude of δ was used as evidence for the early theory⁶⁴ that hydride was buried in the electron shell of the metal. There is no general relationship between δ and trans effect, though high ν are often partnered by high δ values. The splittings of δ by other nuclei, and $J(P-H)$, the coupling constant between H and P, have been used to elucidate the stereochemistry of complexes, particularly as in the case of Ir hydrides, when there are many isomers (J is 10-20 cps. for H cis to P, 120-160 cps. trans to P.)

The most valuable tool for studying M-H however, is diffraction analysis, since this is the only physical technique which provides information about the whole molecule. Since the effect H has on the rest of the molecule is possibly more important from the catalytic viewpoint than the M-H bond length itself, this is invaluable. Before considering the results obtained, mainly by X-ray studies, it is worth setting out some of the disadvantages of X-ray structure analysis for characterising hydrogen atoms.

Since X-rays are scattered by electrons, hydrogen is the most ineffectual scatterer. In electron diffraction the scattering is caused by the electric potential at an atom, and at small Bragg angles hydrogen is not swamped so much. (The electron density at the centre of a hydrogen in an organic crystal is 0.6-0.7 $e/\text{\AA}^3$, cf. 7-10 $e/\text{\AA}^3$ for carbon. The electric potential at the centre

of hydrogen is 30-35 volts, cf 130 volts for carbon.⁶⁵⁾

The scattering by neutrons is composed of two parts, the potential scattering which $\propto A^{\frac{1}{3}}$ (A is mass number); the resonance scattering which varies randomly in magnitude and sign, and for H is comparable to C. At zero theta, the coherent elastic scattering amplitudes (in 10^{-12} cm.) are:-⁶⁶

	<u>electron</u>	<u>X-ray</u>	<u>neutron</u>
H	5300	0.28	-0.38
C	24500	1.69	0.66

Other factors being equal, therefore, neutron studies would be best, but few nuclear reactors are available, and it is generally difficult to obtain large enough hydride crystals.

X-ray studies are thus more feasible, and, even if the M-H bond cannot be measured, the hydride position can often be deduced.

Because of its small size and its one electron, the scattering factor falls off very rapidly with theta; also, since hydrogens are almost always in terminal positions, they vibrate rapidly and so the scattering falls off even more quickly. Therefore the low angle reflections are most important when studying the M-H bond.

Because of the greater stability of 2nd and 3rd row hydrides, these are most often studied, but because the heavier metal will dominate the scattering, one is even less likely to see the hydrogen than in an organic molecule, or first row complex.

The other factors affecting the problem are:-

1. Errors in the data.
 - (a) Absorption. Mo is better than Cu radiation since it is absorbed less.
 - (b) Extinction. This affects low angle spots most and so could be an important source of error in searching for hydrogens.
 - (c) Choice of radiation. Cu is better than Mo because there is less white radiation streaking to hamper measurements at low angles.
 - (d) Completeness of data.
 - (e) A good crystal.
2. Crystal composition.
 - (a) An even distribution between heavy, medium and light atoms is the most favourable situation.
 - (b) A rigid structure, eg. PPh_3 groups rather than PPr_3^n , since these can help to tie down the hydrogen.
3. Errors in the model.
 - (a) Scattering factor curves. These are strictly

only accurate for the free, spherically symmetrical atoms. Any errors will be particularly important for hydrogen, and lead to errors in U values.

- (b) Anomalous scattering. When the inner shell electrons scatter with frequency comparable to that of the X-rays, then this has to be allowed for.

$$f = f_0 + \Delta f' + i \Delta f''$$

($\Delta f'$ is the real, and $\Delta f''$ the imaginary part of the anomalous scattering.)

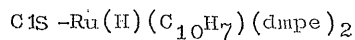
This is most important for polar space groups, and leads to errors in the positional parameters of the anomalous scatterer.⁶⁷

- (c) Anharmonic vibrations. This will introduce errors into the positional parameters.⁶⁸

Structural results are now available for hydrides of most transition metals, with some gaps in the first series. These will be discussed in Chapter 2.10.

CHAPTER 2.2

THE CRYSTAL AND MOLECULAR STRUCTURE OF



Transition metal hydrides are often formed by hydrogen abstraction from an organic molecule, which may be a coordinated ligand. However, a hydride is not always formed; the abstraction may result in:-

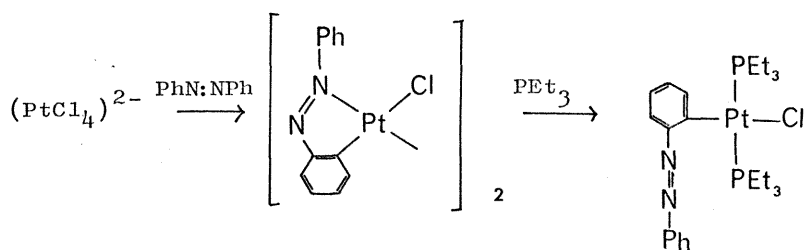
1. loss of hydrogen, and formation of an $\text{M-C}(\sigma)$ bond;
2. irreversible formation of M-H and $\text{M-C}(\sigma)$ bonds;
3. an equilibrium in which a hydridic structure (high coordination number and oxidation state) coexists with a coordinatively unsaturated structure of lower formal oxidation state.
4. in some cases hydrogen abstraction does not occur; in which case we have the borderline situation in which there is a weak interaction between the metal and a ligand hydrogen atom.

It is apparent that hydrogen abstraction and $\text{C}(\sigma)$ bond formation do not occur with saturated hydrocarbons, but only when some stabilising substituent, e.g. phenyl, is also present in the organic molecule. This is

consistent with current ideas on the formation and stability of $M-C(\sigma)$ bonds in general. Activation of CH_4 is a problem of importance since the advent of natural gas as a petroleum feedstock, but abstraction of hydrogen to form $H-M-CH_3$ has not been reported.

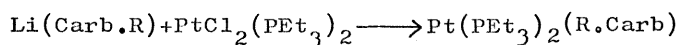
Examples of these types of abstraction reactions are given below:-

1. Pd- and Pt- carbon sigma bonded complexes are formed by reaction of the halides with amines, e.g. benzylamine,⁶⁹ azobenzene.⁷⁰ Hydrogen is eliminated as H^+ ;



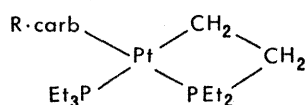
The structure of $PdCl(PEt_3)_2$ (azobenzene) has been confirmed by an X-ray analysis.⁷¹

A series of platinum complexes formed by the reaction:

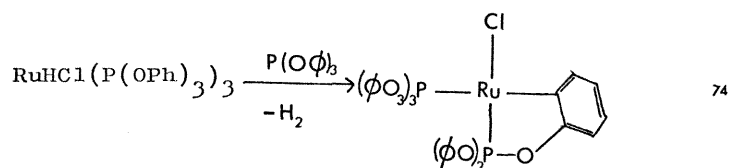
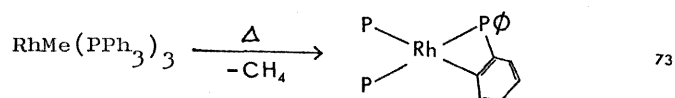


where (R-carb) is $R.C.B._{10}H_{10}$ or $R.C-\overset{\text{O}}{\underset{\text{B}_{10}H_{10}}{C}}-$ have

been shown to contain Pt-C bonds which complete the 4-coordination round Pt.⁷² Spectral data show the absence of M-H bonds, and the postulated structures are:-

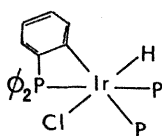


Further examples are:-



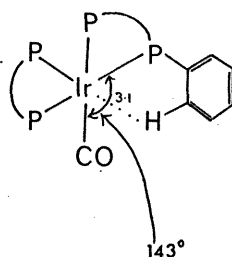
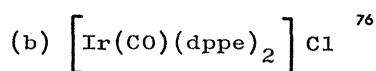
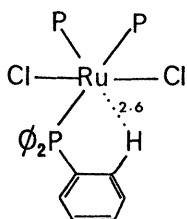
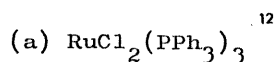
In these cases there is no change in formal oxidation state.

2. This is one case of oxidative addition (See Chapter 2.7), e.g. if benzene is added to $\text{IrCl}(\text{PPh}_3)_3$, a phenyl hydrogen is abstracted, irreversibly, to form the 6-coordinate Ir(III) complex whose structure is thought to be:-⁷⁵



This illustrates how very readily some hydrogen abstractions take place; similar behaviour is shown by other iridium compounds containing at least one phenyl group.

4. Two examples of complexes where X-ray structure determinations have shown that a phenyl hydrogen approaches a metal, making it pseudo 6-coordinate are:-



The closest approaches in $\text{RhCl}(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$ - 2.94 Å,⁷⁷ and $\text{RhHCl}(\text{SiCl}_3)(\text{PPh}_3)_2$ - 2.79 Å,⁷⁸ are attributed to packing rather than any actual interaction.

3. The largest class of hydride abstraction reaction is that in which the equilibrium is mobile, and further examples are continually being reported. This is also probably the most useful class of reactions from the catalytic point of view, in

Some examples are:-

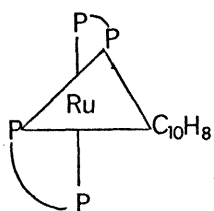


This example is examined later (See Chapter 2.5)

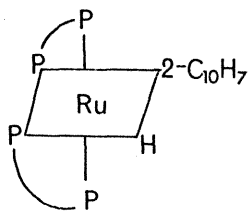


This last example constitutes an interrelated system since IIa is readily obtained by pyrolysis

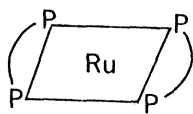
of Ia. The evidence given by Chatt and Davidson in their extremely thorough investigation of the tautomerism of (I),⁸² is that chemically the compound behaves as Ia, e.g. it loses naphthalene giving IIa. However, in the solid, there is a strong $\nu(\text{M-H})$ band in the IR at 1802 cm^{-1} . Also, the characteristic bands at $\sim 1600\text{ cm}^{-1}$ due to naphthyl, are observed, and those at $\sim 800\text{ cm}^{-1}$ for 2-naphthyls. The NMR shows the high-field group of bands, diagnostic of M-H, at 18.6τ . In the same way, the compound II contains $\nu(\text{Ru-H})$ at 1791 cm^{-1} , and it has been shown that the hydrogen originates from one of the phosphine methyl groups. The constancy of $\nu(\text{Ru-H})$ has been cited as good evidence of its complete transfer from carbon to ruthenium. An NMR spectrum could not be run on II, because of its insolubility and instability. The structures proposed by Chatt and Davidson were, on the basis of this and other evidence, e.g. deuteration studies:-



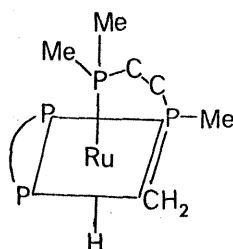
Ia



Ib



IIa

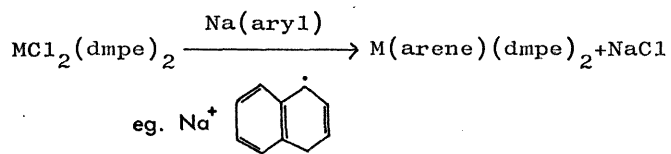


IIb

and it was suggested that the solid state structures are Ib and IIb, and that in solution these predominate, together with small amounts of the reactive Ia and IIa.

These two systems have been examined crystallographically; the naphthyl compound has been shown to have the proposed structure (See this Chapter), whereas the compound II appears to be disordered - no solution has been found. (See Chapter 2.3).

The naphthalene originates from the reductant, and the preparation of these compounds is as follows:-

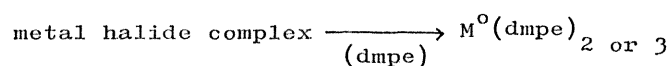


M = Ru, Os

aryl = naphthyl, phenyl, anthryl, phenanthryl

i.e. arene abstraction has taken place. All other metals form the predicted zerovalent

complexes without arene abstraction:-⁸³



M = Co, Ni, Pd, Pt tetrahedral

M = V, Cr, Mo, W octahedral

M = Fe sq. planar

Furthermore, dmpe is the only ditertiary phosphine for which this has been observed; the stabilisation of an M-C(σ) bond has in this case been attributed to the increased basicity of dmpe compared with dppe. i.e. the metal retains a high electron density which is not so easily delocalised within the phosphine d orbitals, and hence may be dispersed into the arene π^* orbitals by formation of a strong M-C bond. It will be seen later (Chapter 2.7) that dmpe is a unique ligand in several of its reactions.

The preparations of the osmium analogues of I and II were repeated; the structure of $\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ is found to be very similar to that of $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, (See Chapter 2.4), while $\text{Os}(\text{dmpe})_2$ proved too unstable to isolate. (See Chapter 2.4). The preparation of the iron analogue - $\text{Fe}(\text{dmpe})_2$ - was repeated by S D Ibekwe, but was also too unstable to crystallize.

Preliminary Observations

A crystalline sample of $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, prepared by J M Davidson in 1962, was available, and so these crystals were examined for their suitability for structure determination. They were large honey coloured prisms, bounded by several faces, and preliminary photography indicated that they had not decomposed. The IR spectrum of the sample contained the strong 1802 cm^{-1} band. The crystals were handled and mounted under nitrogen. The crystal used is shown in Figure 1.

Crystal Data

$\text{C}_{22}\text{H}_{40}\text{RuP}_4$, $M = 529.2$; monoclinic, $a = 15.234 \pm 0.002$, $b = 10.136 \pm 0.001$, $c = 18.729 \pm 0.002\text{ \AA}$, $\beta = 114.00 \pm 0.01^\circ$; $V = 2642.0\text{ \AA}^3$, $D_m = 1.30$ (floatation) $Z = 4$, $D_c = 1.30$, $F(000) = 1104$; Space Group $P2_1/c$ (C_{2h}^5 No.14), Mo-K α radiation (Nb filter), $\mu = 8.2\text{ cm}^{-1}$.

Data Collection

Temperature R.T; scan range -0.7° to $+0.6^\circ$;
Scan speed $2^\circ 2\theta/\text{minute}$; fixed time 10 seconds;
Standards (0 4 0) and (5 0 0) remaining constant to within $\pm 1\%$ of initial intensity; reflections measured in octants $\{\bar{h}\bar{k}l\}$ and $\{hk\bar{l}\}$, to a maximum $2\theta = 55^\circ$; cell dimensions from 19 reflections giving angles $\alpha = 89.98(1)^\circ$, $\gamma = 89.99(1)^\circ$; total number of independent structure amplitudes obtained after data reduction and collation of equivalent reflections 5451.

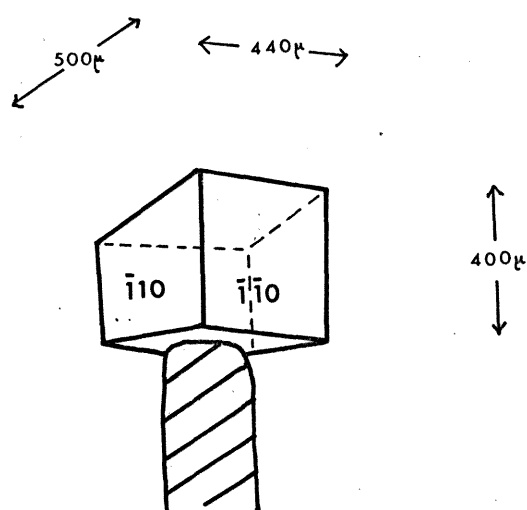


Figure 2.2.1
 $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ Crystal

The Equations of the Bounding Surfaces
of the Crystal

	l	m	n	p	(hkl)
1	0.8504	0.4840	-0.2063	-220.38	$\bar{1}10$
2	0.7646	-0.6274	0.1473	-247.50	110
3	0.6029	0.3678	0.7080	192.51	
4	-0.6783	0.7345	-0.0194	-263.80	$\bar{1}\bar{1}0$
5	0.8508	0.4580	-0.2578	222.25	$1\bar{1}0$
6	0.2028	-0.0478	0.9780	-218.283	

Structure Solution and Refinement

Formfactors for Ru and P were corrected for $\Delta f'$.

The Ru position was found by inspection of the Harker sections of the Patterson:-

$$\begin{array}{ccc} 2x & 2y & 2z \\ 0 & \frac{1}{2}-2y & \frac{1}{2} \\ -2x & \frac{1}{2} & \frac{1}{2}-2z \end{array}$$

which result from the vectors between the positions in $P2_1/c$:-

$$\begin{array}{l} \pm (x, y, z) \\ \pm (x, \frac{1}{2}-y, \frac{1}{2}+z) \end{array}$$

The initial position of (0.299 0.225 0.1205) was refined to $R=30.5\%$ (cycles 1-5), see accompanying table (Table 1). The corresponding $F(\text{obs})$ map showed four peaks in the expected positions for two cis diphosphine ligands. 450 extra terms were included in refining these positions, (cycles 6-8; $R=19.1\%$). An $F(\text{diff})$ map clearly revealed the naphthyl group, also all of the phosphine carbons, although some of these (C41 particularly) were not prominent, and many were elongated peaks, (e.g. C13, C12, C43). Accordingly, cycles 9-12 only included Ru, P1-4, naphthyl carbons, and some of the phosphine carbons. After cycle 12 the U values of the bridging carbons were all considerably higher than those for Ru and P, e.g. Ru 0.048, P2 0.077,

TABLE 2.2.1(a)
Refinement of the structure of $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

Cycle number	Number of terms	Criteria	R Value	Atoms included	Matrix type			Vibrations			Weight used		
					Ru	P	C(p)	C(nap)	Ru	P	C(p)	C(nap)	
1-5	981	min.amp.40	30.5	Ru	b	-	-	-	i	-	-	-	1
6-8	1430	min.amp.30	19.1	Ru, P1-P4	b	b	-	-	i	i	-	-	1
9-12	1430	min.amp.30	12.5	Ru, P1-P4 C(nap) some C(p)	b(1)	b(1) b(2)	b(1) b(2)	b(3)	i	i	i	i	1
13	1740	min.amp.25	14.0	Ru, P1-P4 C(nap) some C(p)	pb(1)	pb(1) pb(2)	pb(1) pb(2)	pb(3)	i	i	i	i	1
14, 15	1740	min.amp.25	10.8	all atoms	b(1)	b(1) b(2)	b(1) b(2)	b(3)	i	i	i	i	1
16, 17	3521	min.amp.10	11.7	all atoms	pb(1)	b(1) b(2)	b(1) b(2)	b(3)	a tb(1)	i	i	i	1

Matrix types: b = full block
pb = positional block
tb = vibrational block
c = contribution only
C(p) = C(phosphine)
C(nap) = C(naphthyl)

Thermal parameters: a = anisotropic
i = isotropic
c = constant

TABLE 2.2.1(b)
Refinement of the structure of RuH(C₁₀H₇)(dmpe)₂

Cycle number	Number of terms	Criteria	R Value	Atoms included	Matrix type		Vibrations		C(nap)	C(p)	C(nap)	C(p)	C(nap)	Weight used
					Ru	P	Ru	P						
18	3521	min.amp.10	10.0	all atoms	pb(1)	b(1) b(2)	b(1) b(2)	a tb(1)	b(3)	i	i	i	i	c ₁ = 25 c ₂ = 28 (2)
19-21	3521	min.amp.10	8.0	all atoms	pb(1)	pb(1) b(2)	b(1) b(2)	a tb(1)	b(3)	a	a	i	i	2
22	2573	min.amp./ deviation 20	13.5	all except C(p)	b(1)	b(1)	-	a	b(2)	a	a	-	i	1
23	3513	min.amp.10	12.8	disordered structure	c	c	c	a	c	a	a	i	i	2

Matrix types: b = full block
pb = positional block
tb = vibrational block
c = contribution only
C(p) = C(phosphine)
C(nap) = C(naphthyl)

Thermal parameters: a = anisotropic
i = isotropic
c = constant
Final scale = 0.83 (cycle 21)
Final convergence factor = 0.041 (cycle 21)

C11 0.371, C13 0.251.

In order to try and determine more precisely the positions of these ill-defined atoms, one cycle (13) was calculated in which Us were not refined (they were held at the refined values for Ru, P and naphthyl atoms and at 0.07 for C(phosphine) atoms), and only some of the phosphine carbons were included. The resulting F(diff) map again revealed the other carbon atoms; so it was decided to attempt to refine this structure. The centres of elongated peaks were chosen as atomic positions, and cycles 14 and 15 - all isotropic - and cycles 16 and 17 - Ru anisotropic - gave R=11.7%. The weighting scheme was now adjusted and refinement with Ru and P atoms anisotropic gave R=8.0% with this weighting scheme. During these calculations the isotropic Us of atoms C11, C12, C32, C33, C41 and C42 continued to rise, although at 8.0% (cycle 21) they had apparently converged at abnormally high values.

This behaviour was suggestive of disorder in the phosphine ligands, and so cycle 22 and an F(diff) map on Ru, P and naphthyl atoms was calculated, and the map was drawn out on perspex sheets. The superimposed contour maps are shown in Figure 2a and 2b. Peaks due to C21, C22, C23, C31, C32, C33 were compact and well shaped, though slightly elongated, but those for C12, C13, C42

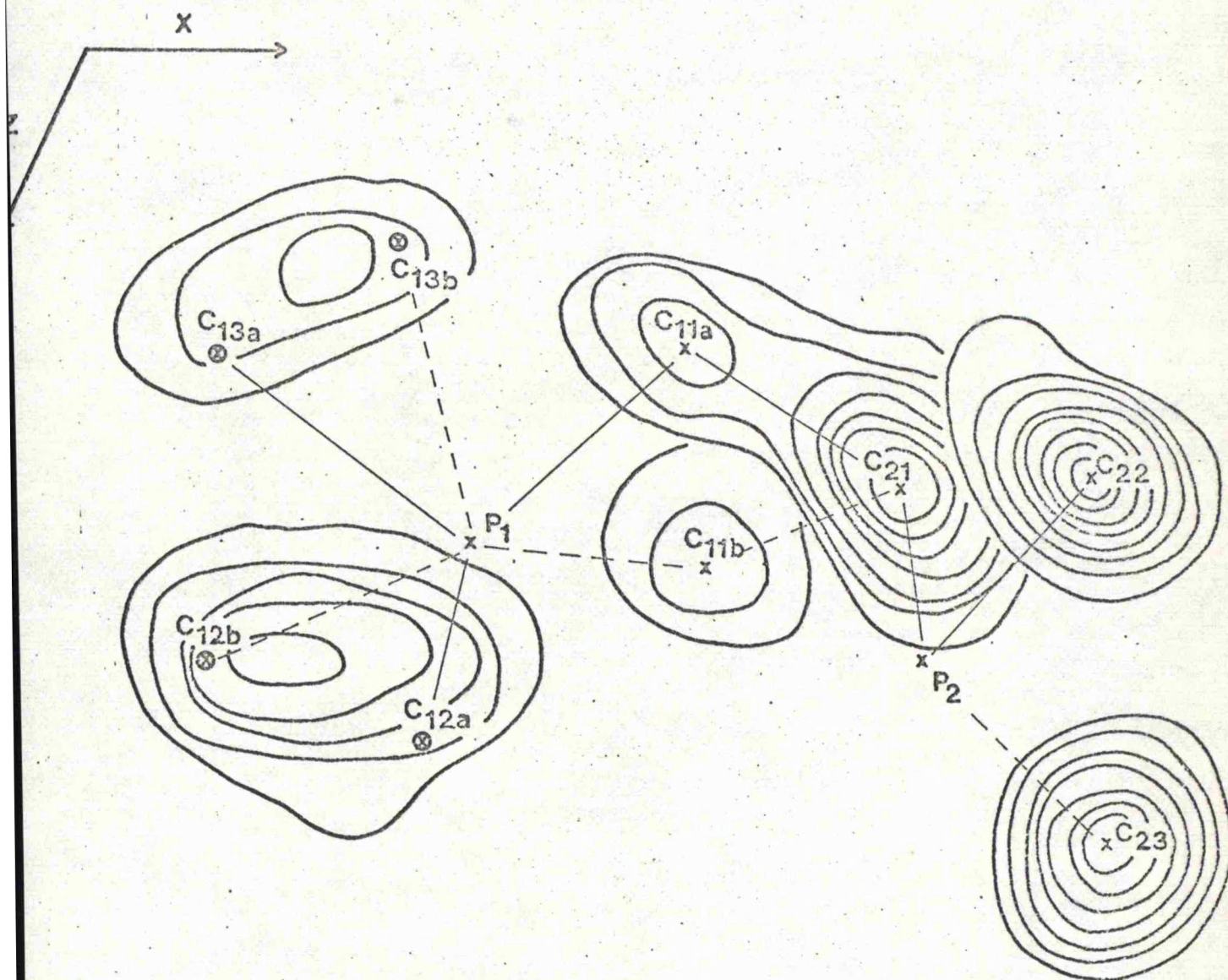


Figure 2.2.2a
 $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

Projection of $F(\text{diff})$ map phased on Ru, P atoms and naphthyl group, illustrating the disordered ligand P1.....P2. Contours at intervals of $0.35 \text{ e}/\text{\AA}^3$, lowest at $0.7 \text{ e}/\text{\AA}^3$. The calculated positions for terminal carbon atoms are indicated \otimes .

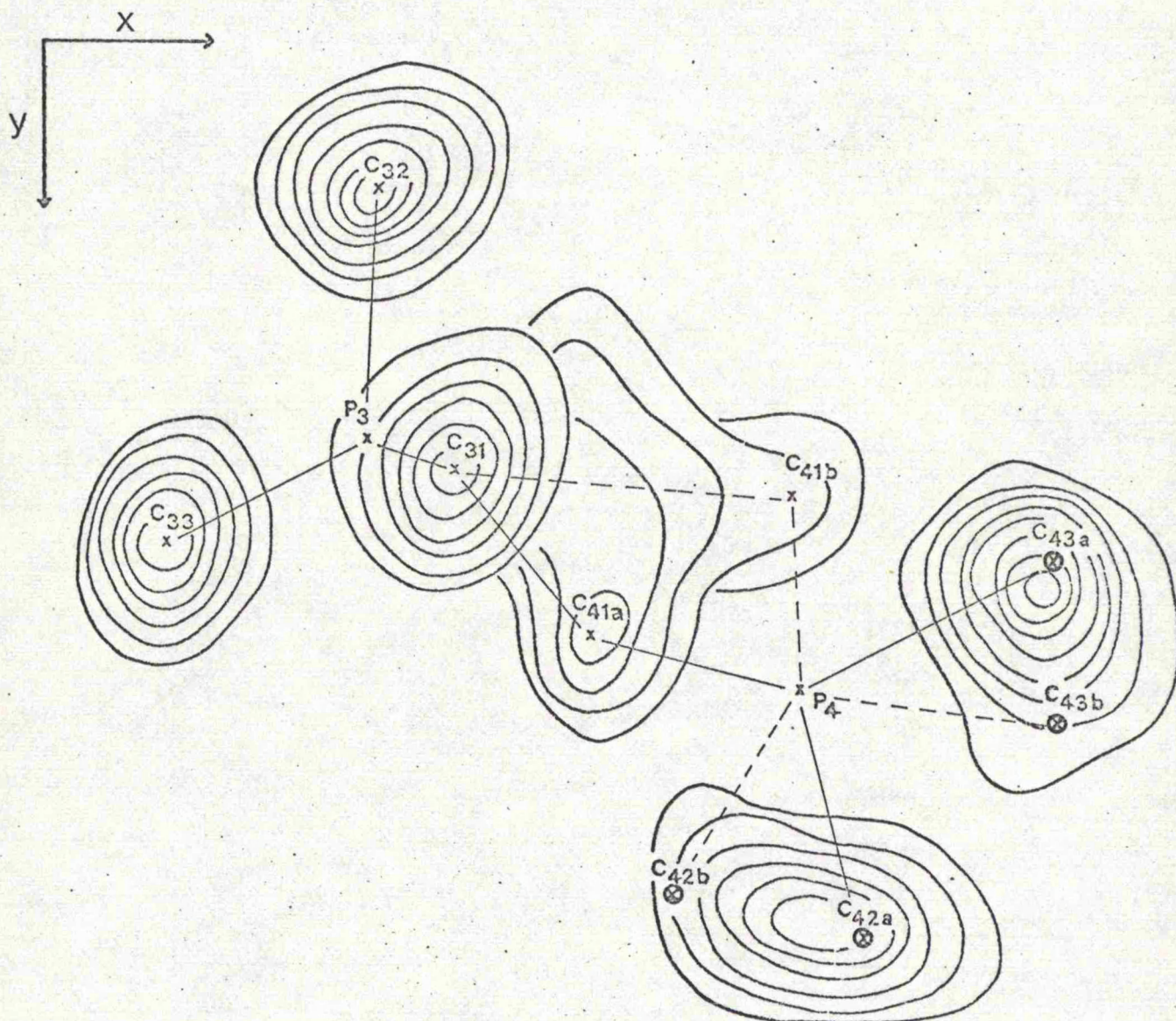


Figure 2.2.2b
 $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

Projection of $F(\text{diff})$ map phased on Ru, P atoms, and naphthyl group, illustrating the disordered ligand P3.....P4. Contours at intervals of $0.35 \text{ e}/\text{\AA}^3$, lowest at $0.7 \text{ e}/\text{\AA}^3$. The calculated positions for terminal carbon atoms are indicated \otimes .

and C43 were very elongated. In addition to C11 and C41 (labelled C11a and C41a) there were two other, smaller peaks (labelled C11b and C41b). C11b was well formed, but C41b was merely a suggestion of electron density. However, it was possible to visualise a type of disorder in which one end of each phosphine ligand remains fixed (P2 - C21 -) and (P3 - C31 -), while the other end is free to move (P1 - C11 -) and (P4 - C41 -). The splitting between C11a and b, C41a and b, is quite small. The corresponding splitting of C12, C13, C42 and C43 is consequently also small, and in these latter atoms, which additionally will be vibrating more vigorously, the two peaks have merged.

To test this hypothesis, the positions C11a and C11b, and C41a and C41b, were taken in turn, and the theoretical alternative terminal positions calculated, assuming an angle of 106° at phosphorus, and P-C distances of 1.82 \AA . In each case the theoretical positions fell within the elongated areas of electron density (see Figure 2). It was also noted that in the phosphine P1...P2, the positions C12 (a and b), C13 (a and b), were almost equally displaced from the observed centres of the peaks. In P3...P4, the C42a and C43a positions lay almost on the centres of their observed peaks, while C42b and C43b lay appreciably to one side. In both phosphines, this was consistent with the apparent heights of C11 and C41; C11a and b were almost of equal height, whereas the centre of C41b

was much less well-defined than that of C41a, and therefore its exact position was not easy to judge. Structure factors were calculated on the final parameters from cycle 21, including contributions from both conformations in a disordered structure, but without refining these parameters. Their relative contributions were estimated as C11a:b - 1:1, and C41a:b - 7:3, as a rough approximation. The R value was 12.8% (cycle 23), but, allowing for the fact that it was difficult to be precise in accounting for the disorder, and also that the disordered structure was not refined to convergence, this discrepancy in final R values is not unreasonable. Limitations on computer time prevented exhaustive trials of different disordered models from being practicable; the extra cost would have been out of all proportion to the probable value of the results.

All the tables therefore refer to the structure at 8.0%, in which only the predominating conformation is included, and so the geometry involving the phosphine carbon atoms is necessarily approximate. Unobserved reflections were calculated - none was greater than twice the minimum observed. The F(diff) map at R=8.0% showed all the H(naphthyl) atoms, as peaks of height 0.4 to 0.6 e/ \AA^3 at, or near, their calculated positions. (These were not refined). There was some residual electron density round Ru possibly due to unaccounted-for anisotropy

of vibration, but there was a distinct peak of height $\sim 0.4 \text{ e}/\text{\AA}^3$ in a position almost trans to P1, approximately 1.7\AA from the Ru atom.

Characterisation of Hydrogen Position

In order to test whether this peak did, in fact, represent the hydridic hydrogen, Ibers' method of calculating successive F(diff) maps on limited sets of data, was applied.⁸⁴ This is based on the fact that light atoms, in presence of heavy atoms, do not contribute significantly to the scattering at high theta. The suspected hydride peak remained reasonably constant in position, while other features round Ru shifted as the resolution was reduced.

The "noise level" (standard deviation of the electron density) increases with theta, and there exists an optimum limiting theta for characterising light atoms. Assuming that the data set is complete, the peak height of an atom is:-

$$\rho^c = \frac{1}{2\pi^2} \int_0^{s_0} (1 + a^2 s^2/4)^{-\frac{1}{2}} \exp. \left[\frac{-Bs^2}{16\pi^2} \right] s^2 ds$$

where a is the Bohr radius = 0.5292\AA

where $s = 4\pi \sin \theta / \lambda$

ρ^c approaches a limiting value as s_0 increases. The standard deviation of the electron density is given by:-

$$\sigma(\rho) = \left[\sum (F_o - F_c)^2 \right]^{1/2} / V$$

It follows that $\rho_H/\sigma(r)$ will pass through a maximum at some value of s . However, if a peak is spurious, it will vary randomly in position and height, as the number of terms (i.e. s) is varied. This criterion therefore provides a means of characterising a peak which is suspected to be caused by a hydrogen atom. Structure factors and an $F(\text{diff})$ map are calculated for data sets in which s_0 is gradually reduced. The 'best' map for obtaining an M-H distance is then that for which $\rho_H/\sigma(r)$ is a maximum. From Table 7 it can be seen that the map to $\sin \theta / \lambda = 0.5$ is best, giving Ru-H = 1.67\AA . No attempt was made to refine this position.

Results and Discussion

The final positional and vibrational parameters for the predominating structure are shown in the Appendix (Tables 2 and 3). Parameters affected by disorder are marked (*). The molecular geometry is shown in Table 4; there are no close intermolecular contacts. Table 5 lists some torsion angles. The final agreement analysis is listed in Table 6. Figure 3 is a drawing of one molecule, with the numbering system used and Figure 4 is a stereo pair of the crystal packing.

The coordination arrangement about Ru is slightly distorted octahedral, with the naphthyl group and hydridic hydrogen cis to each other in the plane defined

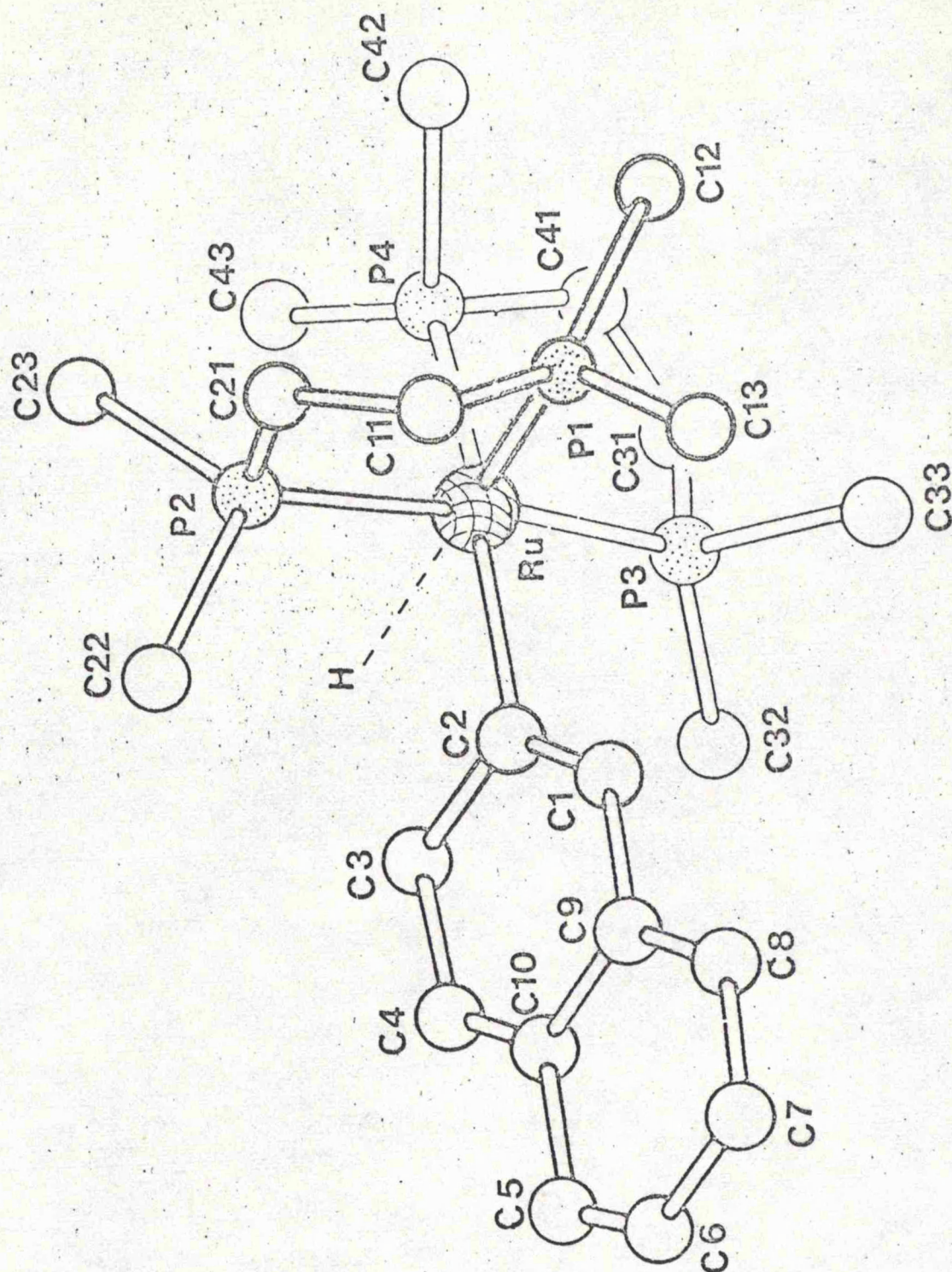


Figure 2.2.3
 $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

View of one molecule illustrating the numbering system used.

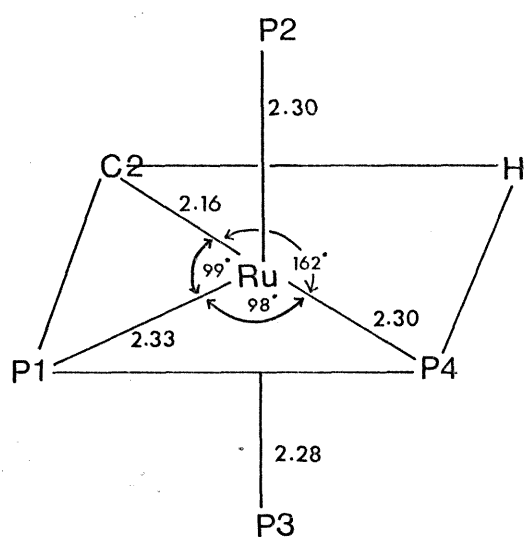


Figure 2.2.3(a)
 $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

The geometry round ruthenium

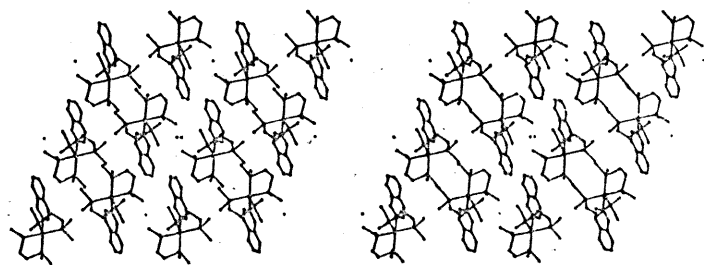


Figure 2.2.4
 $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

Stereo drawing of the packing viewed down y axis.

Table 2.2.4

Bond distances (\AA) and angles ($^{\circ}$), with their estimated standard deviations

Around Ruthenium

Ru-P(1)	2.333(3)	P(1)-Ru-P(2)	82.5(1)	P(1)-Ru-C(2)	99.3(3)
Ru-P(2)	2.303(3)	P(1)-Ru-P(3)	102.9(1)	P(2)-Ru-C(2)	88.7(3)
Ru-P(3)	2.280(3)	P(1)-Ru-P(4)	98.4(1)	P(3)-Ru-C(2)	85.9(3)
Ru-P(4)	2.301(3)	P(2)-Ru-P(3)	172.9(1)	P(4)-Ru-C(2)	161.6(3)
Ru-C(2)	2.160(10)	P(2)-Ru-P(4)	98.5(1)		
Ru...C(1)	3.161	P(3)-Ru-P(4)	85.4(1)		
Ru...C(3)	3.112				

Naphthyl Group

C(1)-C(2)	1.38(1)	C(1)-C(2)-C(3)	116(1)
C(2)-C(3)	1.43(2)	C(2)-C(3)-C(4)	120(1)
C(3)-C(4)	1.45(2)	C(3)-C(4)-C(10)	122(2)
C(4)-C(10)	1.28(2)	C(4)-C(10)-C(9)	121(1)
C(10)-C(5)	1.54(2)	C(9)-C(10)-C(5)	116(1)
C(5)-C(6)	1.30(2)	C(10)-C(5)-C(6)	116(2)
C(6)-C(7)	1.33(2)	C(5)-C(6)-C(7)	127(2)
C(7)-C(8)	1.41(2)	C(6)-C(7)-C(8)	123(2)
C(8)-C(9)	1.44(2)	C(7)-C(8)-C(9)	115(1)
C(9)-C(1)	1.44(2)	C(8)-C(9)-C(10)	123(1)
C(9)-C(10)	1.40(2)	C(10)-C(9)-C(1)	119(1)
		C(9)-C(1)-C(2)	122(1)
		C(1)-C(2)-Ru	125(1)
		C(3)-C(2)-Ru	119(1)
		C(1)-C(9)-C(8)	118(1)
		C(4)-C(10)-C(5)	123(1)

Table 2.2.4 (contd.)

Phosphine Groups

*P(1)-C(11)	1.93(4)	*C(11)-P(1)-C(12)	117(1)
*P(1)-C(12)	1.80(3)	*C(11)-P(1)-C(13)	76(1)
*P(1)-C(13)	1.88(3)	*C(12)-P(1)-C(13)	93(1)
P(2)-C(21)	1.82(2)	C(21)-P(2)-C(22)	103(1)
P(2)-C(22)	1.82(2)	C(21)-P(2)-C(23)	101(1)
P(2)-C(23)	1.83(2)	C(22)-P(2)-C(23)	98(1)
P(3)-C(31)	1.83(2)		
P(3)-C(32)	1.81(2)	C(31)-P(3)-C(32)	101(1)
P(3)-C(33)	1.80(2)	C(31)-P(3)-C(33)	105(1)
*P(4)-C(41)	1.87(3)	C(32)-P(3)-C(33)	101(1)
*P(4)-C(42)	1.84(2)	*C(41)-P(4)-C(42)	95(1)
*P(4)-C(43)	1.80(2)	*C(41)-P(4)-C(43)	99(1)
		*C(42)-P(4)-C(43)	99(1)
*C(11)-C(21)	1.50(3)		
*C(31)-C(41)	1.44(3)	*P(1)-C(11)-C(21)	106(2)
		*P(2)-C(21)-C(11)	114(2)
		*P(3)-C(31)-C(41)	113(2)
		*P(4)-C(41)-C(31)	118(2)
*Ru-P(1)-C(11)	108(1)	Ru-P(3)-C(31)	111(1)
*Ru-P(1)-C(12)	125(1)	Ru-P(3)-C(32)	118(1)
*Ru-P(1)-C(13)	130(1)	Ru-P(3)-C(33)	118(1)
Ru-P(2)-C(21)	112(1)	*Ru-P(4)-C(41)	108(1)
Ru-P(2)-C(22)	120(1)	*Ru-P(4)-C(42)	131(1)
Ru-P(2)-C(23)	121(1)	*Ru-P(4)-C(43)	119(1)

* involving atomic positions affected by disorder

Table 2.2.5

Selected Torsion Angles ($^{\circ}$), positive values
indicating clockwise rotation

* P(1)-C(11)-C(21)-P(2)	44
* P(3)-C(31)-C(41)-P(4)	-25
C(1)-C(2)-Ru-P(1)	-20
C(1)-C(2)-Ru-P(2)	-102
C(1)-C(2)-Ru-P(3)	83

* involving atomic positions affected by disorder

Table 2.2.7

Hydrogen peak heights and related quantities for the
hydride searching maps

Cut-off ($\lambda^{-1} \sin \theta$)	Number of terms	$\rho^E(e.\text{\AA}^{-3})$	$\sigma(\rho)(e.\text{\AA}^{-3})$	$\rho^E/\sigma(\rho)$	Ru-H(\AA)
0.3	539	0.25	0.072	3.44	1.59
0.4	1208	0.30	0.080	3.68	1.72
0.5	2189	0.40	0.088	4.54	1.67
0.63 (all data)	3513	0.40	0.090	4.49	1.64

Reference 84 explains the meaning of the quantities
presented in this table.

by Ru-P1-P4-C2. As is commonly observed in hydride complexes, e.g. $\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$,⁸⁵ $\text{RhH}(\text{CO})(\text{PPh}_3)_3$,⁸⁴ the other ligands are bent towards the hydride position, i.e. P1-Ru-P4 98° , C2-Ru-P4 162° , probably as a steric effect of the small hydride ligand.

The Ru-P bonds (2.28 to 2.33\AA) are similar to, or perhaps slightly shorter than, those in other ruthenium phosphines, through there is often quite a large variation in the individual Ru-P lengths in one molecule. Table 8 shows reported Ru-P distances. Ru-P1, trans to hydride, is the longest (2.33\AA), presumably by a slight trans effect of hydride. (However, in $\text{RuCl}_2(\text{PPh}_3)_3$ Ru-P trans to the hydrogen from a phenyl group is considerably shorter than the others.)¹²

Within each phosphine, the ordered atoms have a reasonable geometry, the P-CH₂ and P-CH₃ distances, average 1.82\AA , being similar to those observed in other phosphine complexes. Because of the disorder, it is difficult to comment meaningfully on the conformations of the phosphines. The bridging systems in both groups have staggered conformations about the C-C bond, as is generally observed in complexes with bidentate phosphines. In each case, one C(methylene) - C21 and C41 - lies nearly in the Ru-P plane, while the other - C11 and C31 - lies out of this plane.

Table 5 shows some torsion angles. The conformations of ordered (dmpe) are discussed further in Chapter 2.7.

TABLE 2.2.8

Ru-P Distances

	<u>Ru-P</u>	<u>Reference</u>
$\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	2.28-2.33	
$\text{RuCl}_2(\text{PPh}_3)_3$	2.23-2.41	a
$\text{RuHCl}(\text{PPh}_3)_3$	2.21-2.36	b
$\text{RuH}(\text{acetate})(\text{PPh}_3)_3$	2.23-2.36	c
$\text{RuCl}_2(\text{PhMe.P.C}_2\text{H}_4\text{.P.MePh})_2$	2.34	d
$\text{Ru}_2\text{Cl}_5(\text{PBu}_3^{\text{n}})_4$	2.32-2.36	e
$\text{Ru}_2\text{Cl}_4(\text{PEt}_2\text{Ph})_5$	2.26-2.34	f
$\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6 + \text{RuCl}_3(\text{PEt}_2\text{Ph})_3 -$	2.26-2.39	g

- a. S J LaPlaca & J A Ibers, Inorg.Chem., 1965, 4, 778
- b. A C Skapski & P G H Troughton, Chem.Comm., 1968, 1230
- c. A C Skapski & F A Stephens, JCS(D), 1969, 1008
- d. I Kawada, Tetrahedron Letters, 1969, 793
- e. G Chioccola, J J Daly & J K Nicholson, Angew.Ch.Int.Ed., 1968, 7, 131
- f. N W Alcock & K A Rasper, JCS(A), 1968, 2108
- g. K A Rasper, JCS(A), 1969, 461

The electron density contours of the phosphine ligands show that for each ethane bridge there are two possible conformations differing only in the positions of C11 and C41. The conversion from one isomer to the other can be achieved by a rotation of approximately 50° about the Ru-P bond. The position of the phosphorus atom in the crystal remains constant whereas the carbon atoms bonded to that phosphorus move. Both conformations probably have similar energies, as the partial conformation about the C-C bridge remains staggered. It is noticeable that both Ru-P bonds involved in the disorder lie in the plane of the naphthyl ring. In contrast the intermolecular packing perpendicular to the aromatic ring is apparently sufficient to determine the positions of the methyl groups C22, C23, C32 and C33. This flexibility of the molecule, observed even in the solid state, may be related to the ease of losing naphthalene from the complex.

The Ru-H distance, 1.7\AA , deduced from the 0.5\AA^{-1} map, agrees with other known Ru-H distances, i.e. 1.7\AA in $\text{RuHCl}(\text{PPh}_3)_3$ ⁸⁶ and in $\text{RuH}(\text{acetate})(\text{PPh}_3)_3$.⁸⁷ The significance of this distance will be discussed later, in Chapter 2.10.

The Ru-C2 distance, 2.16\AA , is slightly longer than is usual for M-C(aryl) bonds (see Table 9), but is within

the range of observed distances. If the octahedral radius of Ru(II) is taken as 1.33\AA , and allowance is made for sp^2 hybridisation of carbon, then the theoretical Ru-C length is 2.07\AA . The lengthening observed in the present structure may not be significant, but the ready loss of naphthalene by heating to 150°C , supports the suggestion of a long, weak M-C bond.

The bond lengths in the coordinated naphthyl group range from 1.28 to 1.54\AA , but the variation is not systematic as it is, for example, in free C_{10}H_8 .⁸⁸ The standard deviations are too large to make a meaningful comparison with the geometries of other beta-substituted naphthalenes. However, the angle C1-C2-C3 (116°), agrees with other observations that this angle in M-C(aryl) complexes is generally nearer 115° than 120° , e.g. 114° in $\text{CrCl}_2(\text{p-tolyl})(\text{THF})_3$,⁸⁹ 116° in $\text{Ni}(\pi\text{Cp})(\text{PPh}_3)(\sigma\text{-C}_6\text{H}_5)$.⁹⁰

The torsion angle C1-C2-Ru-P1 is 20° . This rotation of the naphthyl group out of the plane Ru.P1.P4 is probably caused by the presence of the Ru-H bond of 1.7\AA ; the contact distance H(C31)...H(Ru) is 2.3\AA , which is just the van der Waal's radius sum. If the naphthyl group were to lie in the coordination plane (symmetrically positioned between C22 and C32), then this contact would be extremely short ($\sim 2\text{\AA}$).

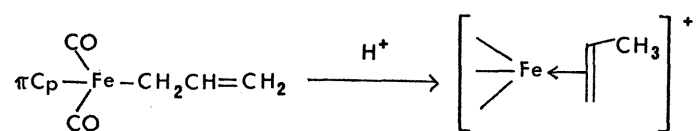
TABLE 2.2.9
M-C(aryl) Distances

	M-C	Reference
Cr(p-tolyl)Cl ₂ (THF) ₃	2.01	a
Mo(C ₆ F ₅)(CO) ₂ (π C ₇ H ₇)	2.24	b
W(C ₆ H ₅)(CO) ₃ (π C ₅ H ₅)	2.32	c
Re(p-C ₆ H ₄ Cl)(CO) ₅	2.28	d
Fe(C ₆ H ₅)(CO)(PPh ₃)(π C ₅ H ₅)	2.11	e
Ru(C ₁₀ H ₇)(H)(dmpe) ₂	2.16	f
Os(C ₁₀ H ₇)(H)(dmpe) ₂	2.13	g
Co(mesityl) ₂ (PEt ₂ Ph) ₂	1.96	h
Co(C ₆ H ₅)(C ₁₂ N ₂ H ₁₈ O ₂)(H ₂ O)	1.93	i
Rh(C ₆ H ₅)Cl(tetraphenylporphine)	2.05	j
Ni(C ₆ H ₅)(PPh ₃)(π C ₅ H ₅)	1.90	k
Ni(C ₆ F ₅)(PPh ₃)(π C ₅ H ₅)	1.91	l
Ni(C ₆ F ₅)(C ₆ Cl ₅)(PPh ₂ Me) ₂	1.91, 1.98	m
Pd(azobenzene)Cl(PEt ₃) ₂	2.00	n
Hg(p-tolyl) ₂	2.08	o

- a. J J Daly & R P A Sneed, JCS(A), 1967, 736
b. M D Rausch et al., JACS, 1968, 90, 3242
c. V A Semion et al., Chem.Comm., 1968, 666
d. Yu T Struchkov, 4th International Conference on Organometallic Chemistry, Bristol 1969 (abstract A15)
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g. See Chapter 2.4
h. P G Owston & J M Rowe, JCS, 1963, 3411
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o. M Mathew & N R Kunchur, Canad.J.Chem., 1970, 48, 429

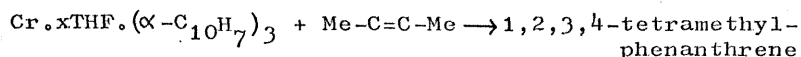
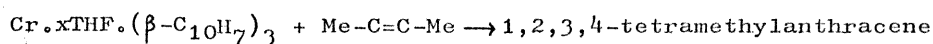
Sigma-pi Equilibrium

$\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ has been shown to contain an $\text{Ru-C}(\sigma)$ bond; the naphthalene molecule in $\text{Ru}(\text{C}_{10}\text{H}_8)(\text{dmpe})_2$ is probably attached in some manner involving pi-bonding. There has been much discussion recently^{91,92} about the mechanism of such Sigma-pi shifts, in view of their probable catalytic importance (Chapter 1.1), but little is known for certain about whether the shifts occur by a concerted or a multi-step mechanism. The earliest reported example is:-⁹³



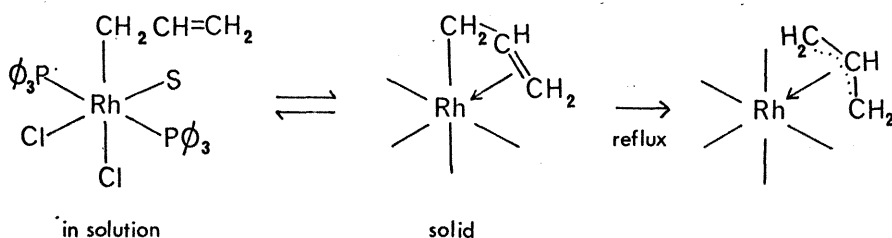
The most studied system is claimed to be that of 'Hein's complexes', but this is just one of several well-authenticated cases, and the mechanism does not seem to have been any more thoroughly rationalised than in others. Hein's complexes are chromium π -arene species, e.g. $[\text{Cr}(\text{Ph})(\text{Ph-Ph})]^+\text{I}^-$, from PhMgBr and CrCl_3 , and intermediates, e.g. $\text{Cr.3THF.}(\sigma\text{-Ph})_3$, have been isolated. The mechanism proposed for these rearrangements involves radical ions.⁹⁴ The sigma complexes undergo a great variety of reactions which are presumed to involve hydrogen abstraction from the

aromatic ligands, e.g.:⁹⁵



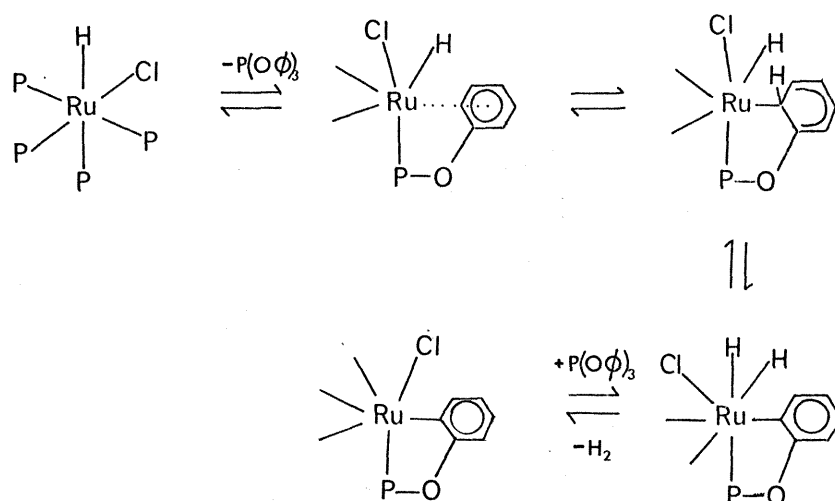
Aryne intermediates were postulated for the above reactions. The π -arene complexes are very readily formed, but no structural results are reported so that it is not known how they are bonded. However, the crystal structure of one of the intermediates, $\text{CrCl}_2 \cdot 3\text{THF}(\text{ptolyl})$ confirms that it contains σ -bonded tolyl. ($\text{Cr-C} = 2.10\text{\AA}$).⁸⁹

Sigma-pi rearrangements have also been extensively studied in metal-allyl systems, particularly using variable temperature NMR, which can detect changes in conformational and rotational freedom by observing changes in the equivalence of protons, e.g.:⁹⁶

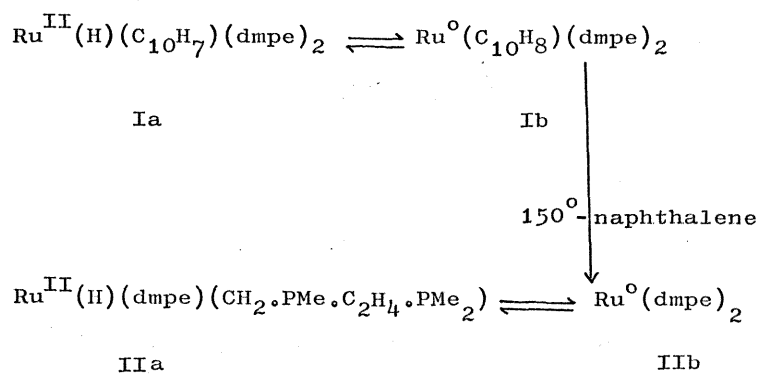


Sigma-pi rearrangement is often induced by protonation, e.g. as above, as well as by the presence of a strongly trans-weakening ligand in a σ -bonded complex.

Tsutsui⁹¹ has discussed these at length, but without suggestions as to mechanisms. Parshall, in a related review,⁹² proposes a mechanism for the hydrogen abstraction reaction of $\text{RuHCl}(\text{P}(\text{OPh})_3)_4$:-

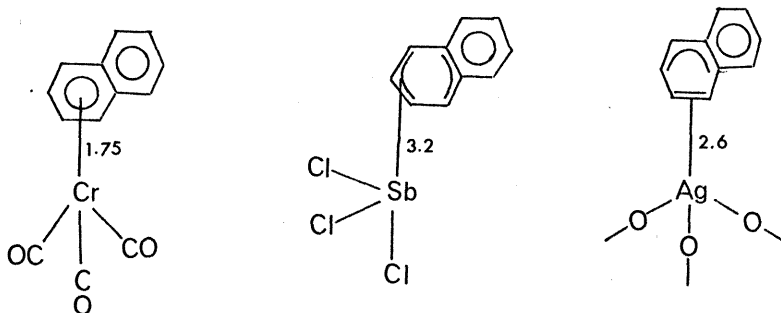


In the present system:-

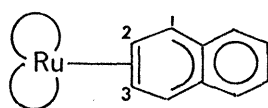


Ia tautomerises to a small extent, in solution, to Ib, its chemical properties being consistent with Formula Ib. For example, it readily loses naphthalene to give IIb. However, this in turn is also in tautomeric equilibrium with an Ru(II) hydride, IIa. Since naphthalene cannot be added to II, this equilibrium probably also favours the Ru(II) hydride; physical measurements support its formulation as IIa, e.g. the IR contains $\nu(\text{Ru-H})$ at 1791 cm^{-1} . The conversion is intramolecular as the hydrogen has been shown to come from the naphthalene, and also since naphthalene cannot be added to IIb to give Ib.

A mechanism analogous to Parshall's seems unlikely, as the phosphine groups would themselves need to undergo considerable rearrangement to accommodate a naphthalene ring system either as a 'half sandwich' as in $\text{Cr}(\text{CO})_3(\text{naphthalene})$,⁹⁷ or a pi-allyl as in $2\text{SbCl}_3(\text{naphthalene})$:⁹⁸



It is more likely that an olefine bond is formed, as in $4\text{AgClO}_4(\text{naphthalene})$.⁹⁹ This would only necessitate a slight shift of the naphthalene rings to bring one of the aromatic C-C bonds to a coordinating position. It is significant that the disorder in the phosphine ligands is connected with the two atoms, P1 and P4, in the equatorial plane; flexibility about these atoms would facilitate this type of shift. The distance from Ru to the midpoint of C1-C2, i.e. Ru-(C1-C2), in the σ complex is 3.07\AA ; Ru-(C2-C3), though, is only 2.65\AA , so that the movement necessary is slight if the π complex is:-

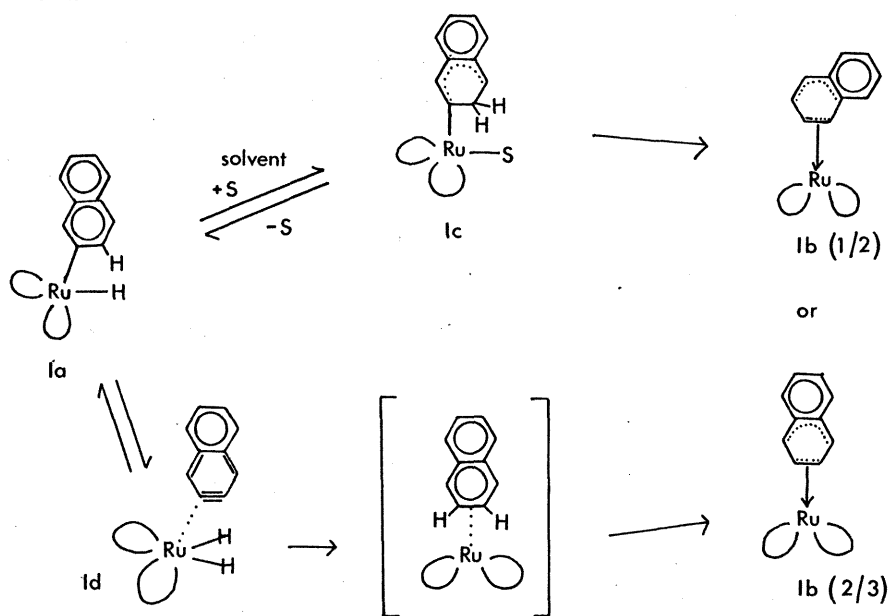


(2/3)

The hydridic hydrogen has, however, to move onto C2, and a simple concerted mechanism for this is not easy to visualise. This hydride shift would be easier if the ring rotates in the opposite direction, when a $1/2$ complex could result; either structure would be analogous to complexes of silver and copper:-

Complex	M - (C-C)	Reference
$\text{AgClO}_4(\text{benzene})$	2.55	100
$\text{AgAlCl}_4(\text{benzene})$	2.57	101
$\text{AgClO}_4(\text{m-xylene})_2$	2.55	102
$4\text{AgClO}_4(\text{naphthalene})$	2.60	99
$\text{AgClO}_4(\text{cyclohexylbenzene})_2$	2.48	103
$\text{CuAlCl}_4(\text{benzene})$	2.13	104

If, on the other hand, the conversion is two-step, either of these could be formed, via a solvated intermediate, possibly Ic. Similarly, if an aryne Id is formed, either a 1/2 or a 2/3 complex could be formed.



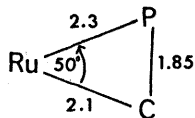
Unfortunately, the form Ib is too unstable, and probably exists in too small amounts, for this to be tested.

CHAPTER 2.3

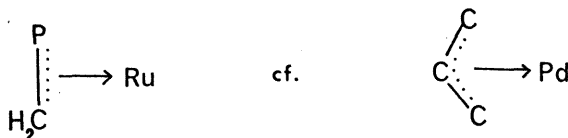
THE ATTEMPTED STRUCTURE ANALYSIS OF Ru (dmpe)₂

The product, Ru⁰ (dmpe)₂, (II), of pyrolysis of Ru⁰(C₁₀H₈)(dmpe)₂, (I), is also postulated to have an Ru(II) hydride structure in the solid. The tautomerism was demonstrated, as for (I), by reaction with HCl and DCl, which gave mixtures of products corresponding to reaction of both tautomers. The hydrogen was shown to have come from a phosphine methyl group, by deuteration studies using C₁₀D₈ and Me₂P.C₂D₄.PMe₂. $\nu(\text{Ru-H})$ occurs at 1791 cm⁻¹ (shoulder at 1815 cm⁻¹); no NMR could be obtained.

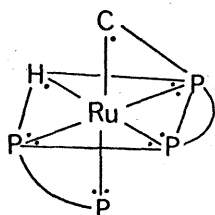
The structure postulated by Chatt and Davidson is analogous to that of cis-RuH₂(dmpe)₂, but is highly strained; the angle P-Ru-C is ~50°.



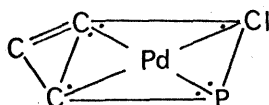
It may be compared to the π -allyl type of structure:-



ie Here we have a 10e system:-



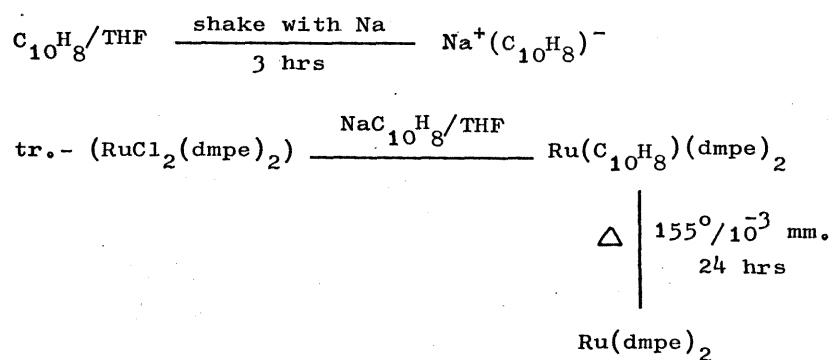
cf. the 6e system:-



If true, this would be a highly novel structure, and so a crystal structure analysis was attempted.

Preparation

Crystals of the complex had been prepared by Chatt and Davidson :-



The crystals were large yellow prisms which came down rapidly on recrystallisation from pentane. A sealed sample of the original preparation was available, and

so these crystals were examined. At first sight they presented no apparent difficulties, as they gave excellent photographs showing triclinic symmetry, and were not too unstable in air. Crystals were, however, mounted under nitrogen in tubes.

Crystal Data

$C_{12}H_{32}RuP_4$, $M = 401.7$; triclinic, $a = 10.035 \pm 0.005$,
 $b = 10.724 \pm 0.005$, $c = 9.716 \pm 0.005$ Å, $\alpha = 94.32 \pm 0.04$,
 $\beta = 114.84 \pm 0.03$, $\gamma = 96.22 \pm 0.04^\circ$; $V = 934.9$ Å³,
 $D_m = 1.43$ (floatation), $Z = 2$, $D_c = 1.43$, $F(000) = 416$;
 Space Group $P\bar{1}$ (C_2 , no. 2) probably, $MoK\alpha$ radiation
 (Zr filter), $\lambda = 0.7107$ Å, $\mu = 10.87$ cm⁻¹.

Data Collection

Temperature R.T.; scan range -0.6° to $+0.6^\circ$;

Scan speed 2° 20/minute; fixed time 10 seconds for
 shell to $2\theta = 30^\circ$,

Scan speed $\frac{1}{2}^\circ$ 20/minute, fixed time 20 seconds for
 remainder;

Standards (0 7 0) and (6 0 0) falling to 92% and 73%

of initial intensity; reflections measured in the

hemisphere $\left\{ \begin{smallmatrix} -++ \\ hkl \end{smallmatrix} \right\}$, to a maximum $2\theta = 54^\circ$;

cell dimensions from 12 reflections;

total number of independent structure amplitudes obtained

after data reduction and collation of equivalent

reflections, assuming Space Group $P\bar{1}$, 2764.

The crystal used is shown in Figure 1.

Attempted Solution of Structure

A Patterson map was first calculated, over half the unit cell, (this is necessary for either P1 or $P\bar{1}$), at a resolution of $\sim \frac{1}{4} \text{ \AA}$ in each direction. The projection of the main features of this map is shown in Figure 2.

For $P\bar{1}$, the expected vector pattern is formed by combination of Ru-Ru, Ru-P, P-P vectors. If Ru is at $\pm x_1, \pm y_1, \pm z_1$, and P is at $\pm x_2, \pm y_2, \pm z_2$; then if $\delta = (x_2 - x_1)$ and $\sigma = (x_2 + x_1)$, the cross vectors are:-

	$x_1 \ y_1 \ z_1$	$-(x_1 \ y_1 \ z_1)$	$x_2 \ y_2 \ z_2$	$-(x_2 \ y_2 \ z_2)$
$x_1 \ y_1 \ z_1$	0 0 0	$2x_1 \ 2y_1 \ 2z_1$	$-(\delta \ \delta \ \delta)$	$\sigma \ \sigma \ \sigma$
$-(x_1 \ y_1 \ z_1)$	$-(2x_1 \ 2y_1 \ 2z_1)$	0 0 0	$-(\sigma \ \sigma \ \sigma)$	$\delta \ \delta \ \delta$
$x_2 \ y_2 \ z_2$	$\delta \ \delta \ \delta$	$\sigma \ \sigma \ \sigma$	0 0 0	$2x_2 \ 2y_2 \ 2z_2$
$-(x_2 \ y_2 \ z_2)$	$-(\sigma \ \sigma \ \sigma)$	$-(\delta \ \delta \ \delta)$	$-(2x_2 \ 2y_2 \ 2z_2)$	0 0 0

and the relative expected peak heights will be:-

$$2x \ 2y \ 2z \quad \text{Ru} - \text{Ru} \sim 9$$

$$\left. \begin{matrix} \sigma \ \sigma \ \sigma \\ \delta \ \delta \ \delta \end{matrix} \right\} \quad \text{Ru} - \text{P} \sim 3$$

$$2x \ 2y \ 2z \quad \text{P} - \text{P} \sim 1$$

One would therefore expect to see a Ru-Ru vector peak in a general position in the Patterson cell $(2x_1 \ 2y_1 \ 2z_1)$, surrounded by $(\sigma \ \sigma \ \sigma)$ type peaks from intermolecular Ru-P vectors. These Ru-P peaks should be confirmed by the occurrence of Ru-P peaks $(\delta \ \delta \ \delta)$ of intramolecular type, round the origin peak. Of the 3 highest peaks (1, 4, 12) - see Figure 2 - 2 were too near the origin

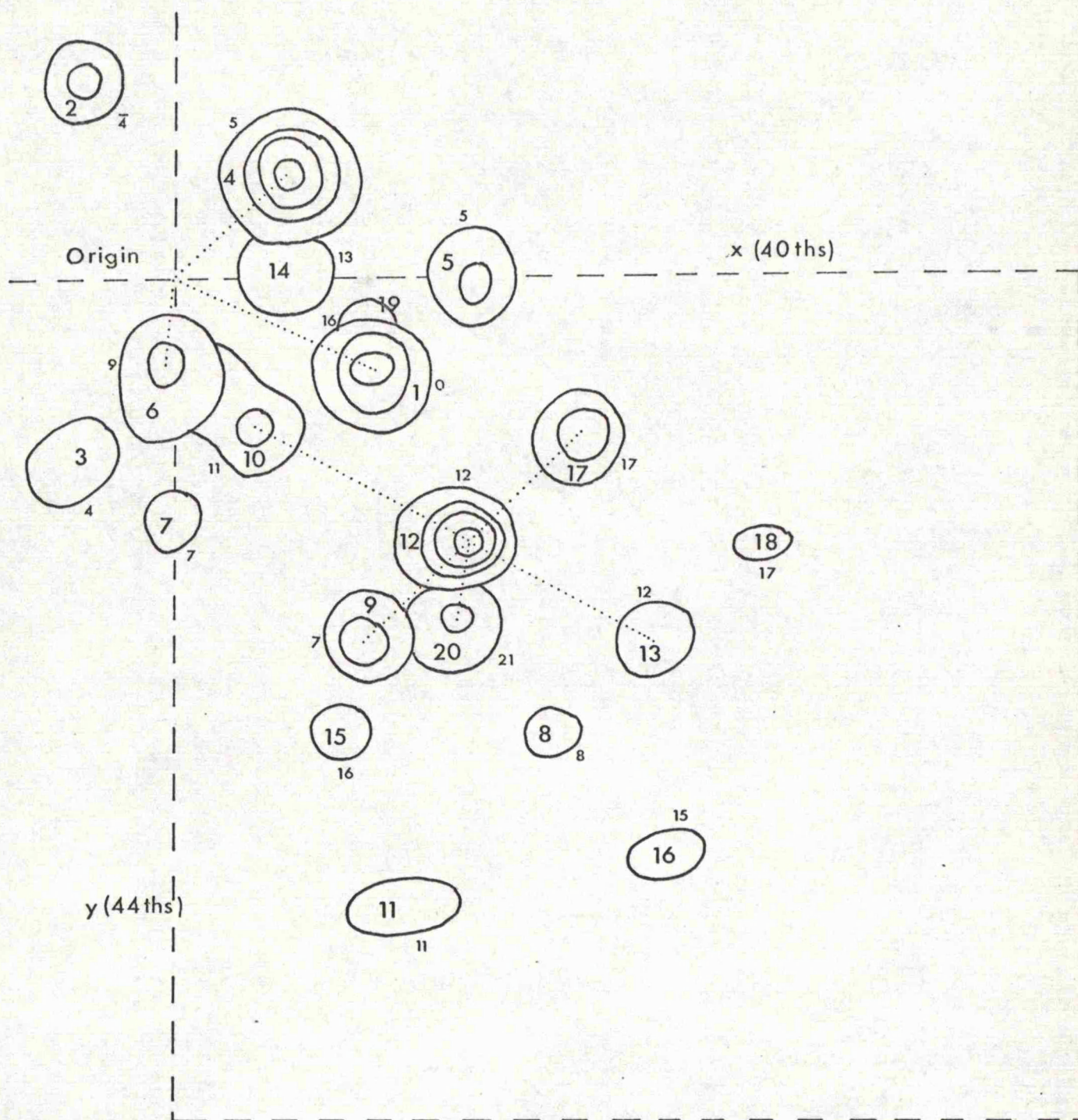
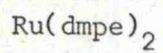


Figure 2.3.2

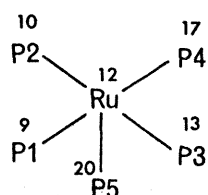


Projection of the Patterson map down the z axis. (In this, and all other projections in this chapter, no correction is made for non orthogonality of the unit cell.) z heights (40ths) shown in small type, numbering of peaks in larger type.

to be Ru-Ru vector peaks, (Ru-Ru distances of 1.95 and 2.3 \AA respectively). Interpretation of either of these as Ru-Ru vectors would have raised difficulties in accounting satisfactorily for the many peaks in the vicinity of peak 12, in the centre of the cell. This peak was at $(13/40, 14/44, 12/40)$, and it appeared to correspond to the most reasonable Ru-Ru vector. It was surrounded by 5 ($\sigma\sigma\sigma$) type peaks, whose positions, heights and distances from the central peak, are shown; also their approximate positions in the real cell, assuming a Ru position of $\sim(7/40, 7/44, 6/40)$.

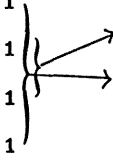
Peak	Atom	Hgt.	Patterson position			Ru-pk.	Real position		
12	Ru	13	13/40	14/44	12/40		7	7	6
9	P1	7	8	19	7	1.9	2	12	1
10	P2	6	4	8	11	2.4	-2	1	5
13	P3	5	21	19	12	2.3	15	12	6
17	P4	7	18	9	17	1.9	12	2	11
20	P5	6	13	18	21	2.3	7	11	15

The disposition of peaks being:-



2 distances (Ru-P1, P4) seemed very short, and more

plausible as Ru-C vectors. However, if these are genuine Ru-P vectors, then one expects (*ddd*) peaks as follows:-

<u>Peak</u>	<u>Position</u>	<u>Weight</u>	<u>Giving</u>
Ru-P1	5 -5 5	1	
Ru-P2	9 6 1	1	
Ru-P3	-8 -5 0	1	
Ru-P4	-5 5 -5	1	
Ru-P5	0 -4 -9	1	1 —————> 1 pk.wgt. 1

Because peaks from P1 to P4 are nearly centrically arranged around Ru, these will superpose to give double weight peaks since the Patterson cell always has a centre of symmetry at the origin.

These (*ddd*) peaks were observed, at approximately their expected heights:-

<u>Peak</u>	<u>Vector</u>	<u>Height</u>	<u>Position</u>	<u>(0 0 0)-(pk)</u>
1	Ru - P2,P3	11	-8 -5 0	2.3
4	Ru - P1,P4	15	5 -5 5	1.9
6	Ru - P5	7	0 5 8	2.3

The majority of the other peaks were accounted for by P-P vectors, and this accounted for all the highest peaks on the map (1, 2, 3, 4, 5, 6, 9, 10, 11, 12, 13, 14, 17, 20). At this stage there was no evidence to

suggest that the true space group might be $P1$, as the three strong vectors round the origin were the only peaks near the origin. The Patterson map of a $P1$ crystal would be expected to be much less clear-cut. The appearance of theoretical Patterson maps for various triclinic crystals is summarised in Table 1.

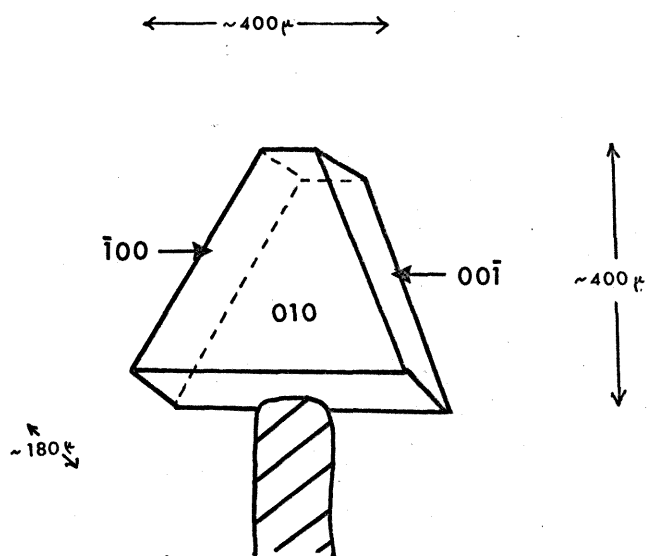


Figure 2.3.1

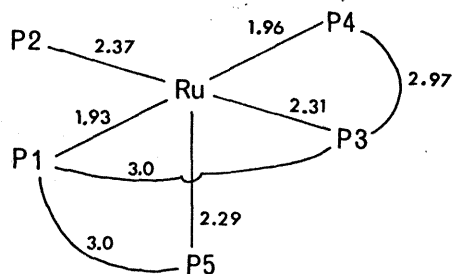
$\text{Ru}(\text{dmpe})_2$ Crystal

Space Group	Number of Molecules	Relationship	Expected Peaks Round (0,0,0)	Weight	Expected Peaks Round M-M Vector	Weight
1 P1	2 acentric	noncentrically	8	1	8	1
2 P1	2 centric	noncentrically	4	2	8	1
3 $\overline{P1}$	2 acentric	centrically	4	2	4	2
4 $\overline{P1}$	2 centric	centrically	2	4	4	2
3a $\overline{P1}$	1 dimer	centred round origin	4	2	4	2
2a $\overline{P1}$	2 crystallographically centric	noncentrically (as 2 but in $P1$) asymmetric unit has $2\frac{1}{2}$ molecules.	4	2	8 (at $\frac{1}{2}, 0, 0$)	1

TABLE 2.3.1

Case 3a is equivalent to 3 but in this case the link between Ru1 and Ru2 should be apparent. This possibility was considered very carefully; of the 3 peaks round (0,0,0), peak 4 would correspond to a very short (1.95 \AA) metal-metal bond, peak 1 to a fairly short (2.3 \AA) bond, and no peaks would be observed in the centre of the Patterson cell; peak 12 would arise from a metal-metal bond of $\sim 5 \text{ \AA}$, so that the link would have to be through phosphine bridges.

Summarising, the evidence all seemed to support a transplanar symmetrical arrangement of four ligand atoms, plus one atom in one of the two octahedral positions. At this stage, these all looked like P atoms, as the distances between peaks were all rather long for P-C bonds. (Distances not shown are $> 3 \text{ \AA}$.)



Attempts to Refine Trial Structure

Formfactors were not initially corrected for $\Delta f'$.

The position (peak 12) 0.1617 0.1589 0.15 was chosen for the Ruthenium atom, and after cycles 1-3 (see Table 2), an F(obs) map showed the same pattern of five peaks round Ru, as the Patterson. Their heights and positions were:-

<u>Peak</u>	<u>Height</u>	<u>x</u>	<u>y</u>	<u>z</u>
Ru	99			
P1	38	0.0445	0.2744	0.0222
P2	26	-0.0490	0.0368	0.1333
P3	25	0.3665	0.2791	0.1667
P4	34	0.2830	0.0392	0.2665
P5	23	0.1625	0.2610	0.3625

Apart from the many peaks round the assumed Ru position, large parts of the cell were quite devoid of density, and all electron density seemed to be concentrated round the origin. Three cycles (4-6) of refinement of Ru and P1-P4 positions led to $R = 30.7\%$, with acceptable position and temperature factor shifts. In this, and all subsequent calculations on this compound, full matrix refinement was used. The F (diff) map phased on this set of planes appeared reasonable (See Figure 3), except that again, all density was concentrated in the first octant of the unit cell. P1 and P4 positions were in slight troughs; P2 and P3 approximately on points of zero electron density. P5 came up strongly, as did several possible carbon atom positions, but these latter lay on

TABLE 2.3.2(a)
Calculations on Ru(dmpe)₂ in P₁

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Initial Positions			Initial Vibrations		Final Vibrations		Maps
					Atom	x	y	z	Atom	U	Atom	U
1-3	2729	min.amp.10	47.3	Ru	Ru	.162	.159	.150	Ru	.04	Ru	.028
												obs.
4-6	2729	min.amp.10	30.7	Ru Pl-4	Ru	.160	.158	.150	Ru	.028	Ru	.034
					P1	.044	.274	.022	Pl-4	.040	P1	.033
					P2	-.049	.037	.133			P2	.043
					P3	.366	.279	.167			P3	.053
					P4	.283	.039	.266			P4	.038
7-9	2729	min.amp.10	31.2	Ru P1,P3 P4,P5	Ru	as above (for cycle 4)			Ru	.028	Ru	.034
					P1,3,4,5				all		P1	.036
									Ps	.040	P3	.038
						.162	.261	.362			P4	.039
											P5	.050
10-12	2729	min.amp.10	35.5	Ru P1,P4,P5	Ru	as for cycle 4			Ru	.028	Ru	.031
					P1,4,5				all		P1	.039
									Ps	.040	P4	.044
											P5	.052
13-15	2729	min.amp.10	26.3	Ru Pl-5	Ru	as for cycle 4			Ru	.028	Ru	.033
					Pl-4,5				all		P1	.033
									Ps	.040	P2	.045
											P3	.055
											P4	.038
											P5	.046
												diff. after cycle 13 (R=28.1)

TABLE 2.3.2(b)
Calculations on Ru(dmpe)₂ in P1

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Initial Positions Atom x y z	Initial Vibrations Atom U	Final Vibrations Atom U	Maps
16,17	2729	min.amp.10	24.2	Ru, P1-5 C21,32,31	(as refined in cycle 15): Ru .159 .158 .151 P1 .042 .278 .022 P2 .950 .032 .131 P3 .369 .276 .162 P4 .291 .039 .261 P5 .163 .262 .366 C21 .837 .143 .022 C31 .255 .388 .056 C32 .481 .170 .272	Ru .033 P1 .033 P2 .045 P3 .055 P4 .038 P5 .046 C21 .040 C31 .040 C32 .040	Ru .033 P1 .036 P2 .046 P3 .062 P4 .036 P5 .046 C21 .022 C31 .020 C32 .052	obs.
18-20	2729	min.amp.10	27.2	Ru, P1-5	as above (cycle 15)	as above	not refined	-
21-23	499	min.amp.80	21.9	Ru, P1,P2	as above (cycle 15)	all 0.04	Ru .018 P1 .055 P2 .073	obs.
24-27	499	min.amp.80	23.1	Ru, P1,P3	as cycle 15	all 0.04	Ru .015 P1 .056 P3 .109	-
28-31	499	min.amp.80	22.1	Ru, P1,P4	as cycle 15	all 0.04	Ru .015 P1 .078 P4 .098	-

TABLE 2.3.2(c)
Calculations on Ru(dmpe)₂ in P1

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Atom	Initial Positions x y z	Initial Vibrations Atom	Final Vibrations Atom	Maps
32	499	min.amp.80	21.7	Ru,P11,P2 Ru P3,P41,P5 P2 P3 P5 C11,12 P11 C31,32 P41 C41,51 C11	as cycle 15		Ru .033 P2 .045 P3 .055 P5 .046 P11 .033 P41 .038 C11 .04 C12 .04 C31 .04 C32 .04 C41 .04 C51 .04	Ru .009 P2 .034 P3 .134 P5 .099 P11 .073 P41 .075 C11 -.019 C12 .045 C31 -.067 C32 -.058 C41 .052 C51 .010	-
33-35	499	min.amp.80	13.8	Ru, P1-5 Ru C21,22, C25 C33	from Patterson		Ru .033 P1 .04 P2 .045 P3 .055 P4 .04 P5 .046 C21 .04 C22 .04 C25 .04 C33 .04	Ru .022 P1 .035 P2 .062 P3 .070 P4 .041 P5 .041 C21 .011 C22 .050 C25 .046 C33 .120	diff.
36	2133	min.amp.25	25.6	as above					diff.
37-39	1848	min.amp.30	31.4	Ru,P2,3,5	as cycle 15		Ru .033 P2 .045 P3 .055 P5 .046	Ru .024 P2 .054 P3 .086 P5 .055	diff.

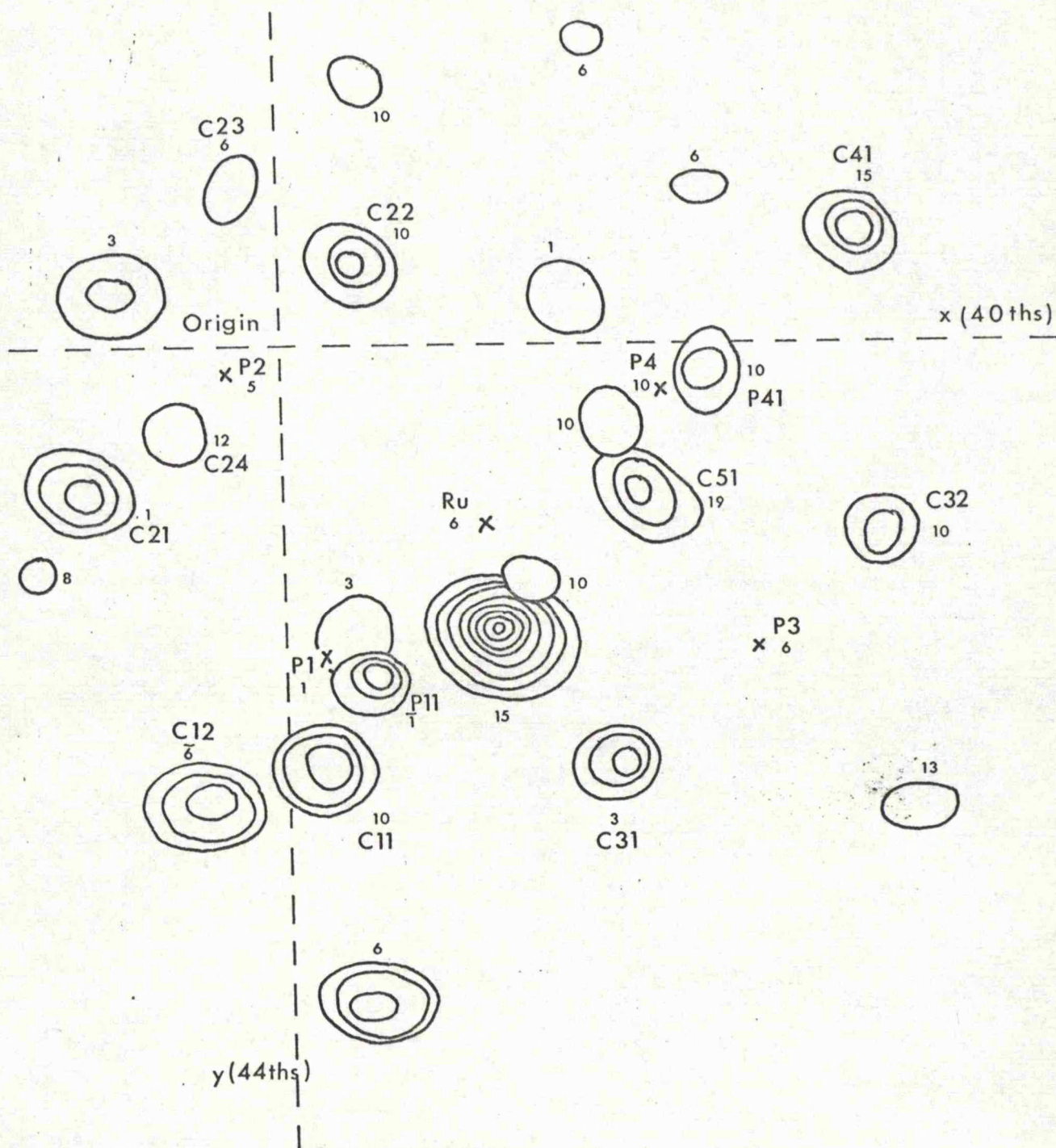
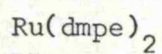


Figure 2.3.3



Projection down z of $F(\text{diff})$ map at cycle 6. Input atoms marked x ; contours at intervals of $2 \text{ e}/\text{\AA}^3$ (lowest at $4 \text{ e}/\text{\AA}^3$). z heights (40ths) shown in small type.

a suspiciously regular grid (C11, C51, C21, C22, C31, C32.). Since P2 seemed to lie too near to its centrically related atom, it was omitted from the next calculation. (Cycles 7-9 on Ru, P1, P3-P5, taking initial positions from the first F (obs) map). R was reduced to 31.2% and, again, all the vibrations were reasonable. (See table)

Ruthenium formfactors were now corrected for $\Delta f'$.

The four phosphorus atoms in Chatt and Davidsons' postulated structure were unlikely to occupy a square plane, so there were grounds for believing that some of the positions P1 to P4 might be spurious, whereas P5 probably represented a genuine phosphorus atom. Of the four planar atoms, P2 and P3 always came up lowest on maps, so refinement was attempted on Ru, P1, P4 and P5 only. Cycles 10 to 12 gave $R = 35.5\%$. However, P2 and P3 reappeared on the corresponding F (obs) map.

The peak heights were:	Ru	99 *	
	P1	34 *	(*input atoms)
	P2	25	
	P3	22	
	P4	31 *	
	P5	23 *	

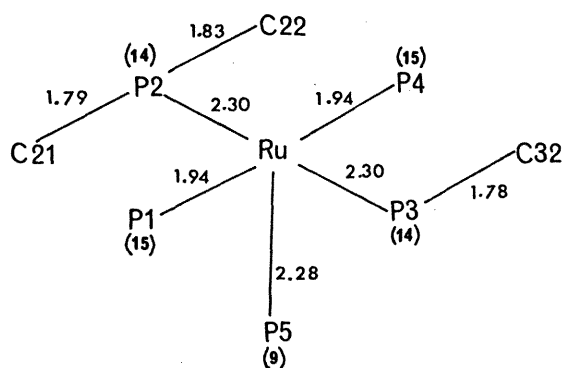
This suggested that possibly P5 might really be a carbon atom; also suggested by its (relatively) high U value (0.052). The molecular geometry now calculated still indicated two very short bonds, and the distance from P2 to the centrically related P2' was rather short, $\sim 3\text{\AA}$. Possible phosphine links were suggested by the angles, eg P2-Ru-P5 86° . Cycle 13 and an F (diff) map were now computed on Ru and all five possible P positions.

The three highest 'carbon' peaks were chosen:-

<u>Peak</u>	<u>Height (electrons)</u>	<u>P-C</u>
C21	8	1.71
C31	7	1.68
C32	6	1.68

and these were added to the refined positions after two more cycles (14 and 15). After cycles 16 and 17, the U values of these 'carbons' were widely different, and on the corresponding F (obs) map, the only other peak to come up was 'C22'. (All these 'carbon' peaks are indicated as they occurred on the first F (diff) map, in Figure 3). A slightly different approach was next tried; cycles 18 to 20 were calculated in which only occupation numbers were refined. However, no definite conclusion could be drawn from the refinement.

An F (diff) map was next computed, based on the Ru position found on the Patterson, in which it was hoped to cut out everything except contributions from Ru. The criteria reject if $F_o < 15$, and if amplitude/deviation < 0.5 , were set. This gave a planes list of 1772 terms. The same pattern of peaks was observed, but P5 came up weaker than the others.



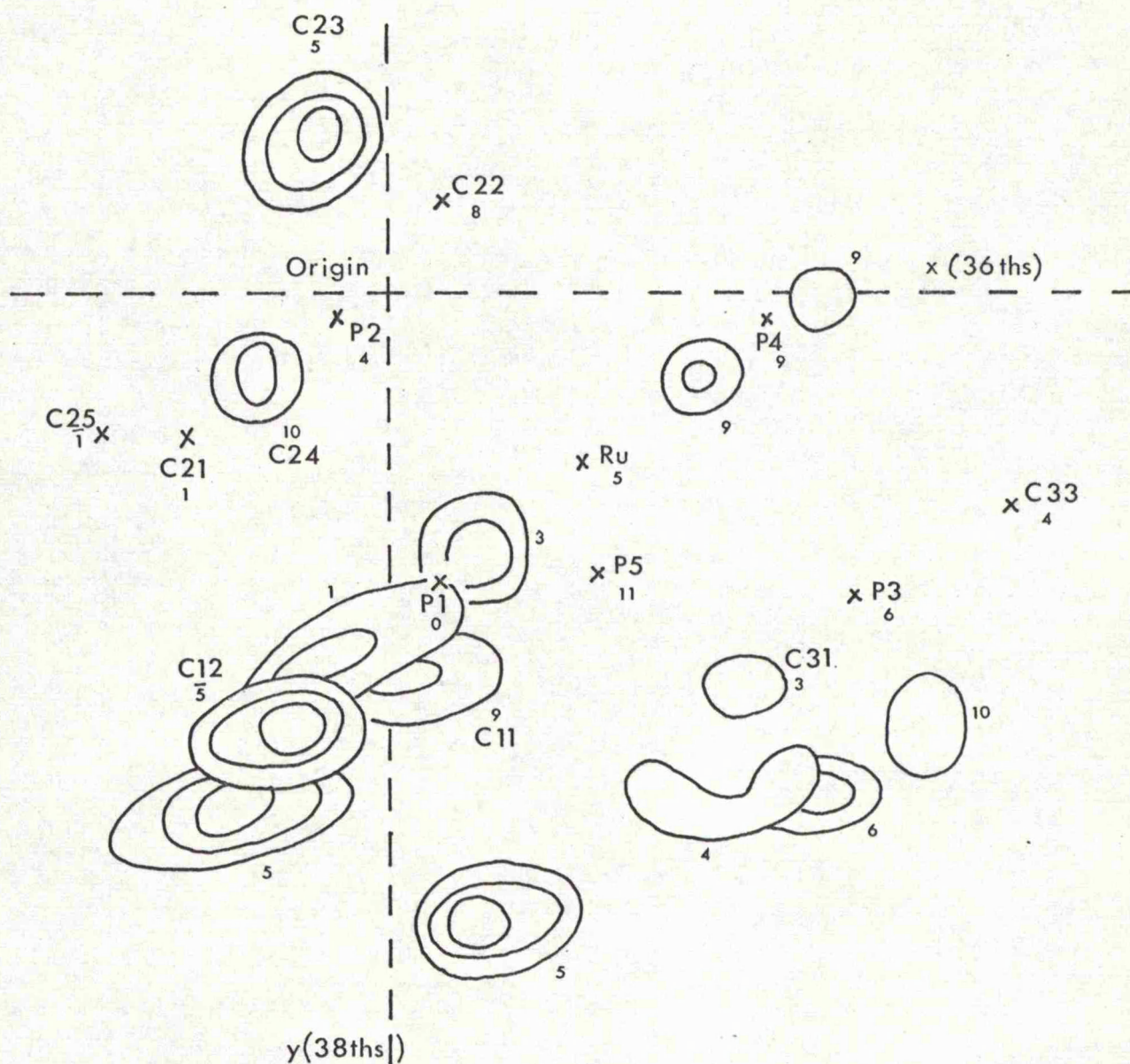
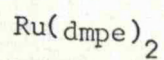


Figure 2.3.4



Projection down z of $F(\text{diff})$ map at cycle 35. Input atoms marked x ; contours at intervals of $0.4 \text{ e}/\text{\AA}^3$ (lowest at $0.8 \text{ e}/\text{\AA}^3$). z heights (36ths) shown in small type.

Since P1 held a strong claim to be a genuine P atom, it was decided to systematically test the various combinations of P1 with other atoms:-

Ru P1 P2 (Cycles 21-23)
then Ru P1 P3 (Cycles 24-27)
& then Ru P1 P4 (Cycles 28-31)

The calculations, which were inconclusive, are shown in Table 2.

A molecular geometry was now calculated on two, more reasonable, positions for P1 and P4 (P11 and P41), together with several possible carbons. P11 and P41 are at peaks on the far side (from Ru), of P1 and P4, on the first F (diff) map. In other words, if P1 and P4 are disordered, then P11 and P41 correspond to atoms at the most chemically sensible distances from Ru. Ru, P11, P2, P3, P41, P5, C11, C12, C31, C32, C41, C51 were put into one cycle (cycle 32), but the resulting U values were nonsensical, some of those for 'carbon' atoms being negative (see table).

Next, four different 'carbon' atoms were tried; C21, C22, C25, C33 - three of these had appeared on the Patterson map as peaks 3, 17 and 9 - but after 3 cycles (33-35), the U values were again meaningless. An F (diff) map (see Figure 4) after cycle 35 showed no new, sensible peaks round any of the P positions. One cycle (36) on these same parameters, setting the minimum amplitude as 25 (2133 terms) gave $R = 25.6\%$ and the corresponding

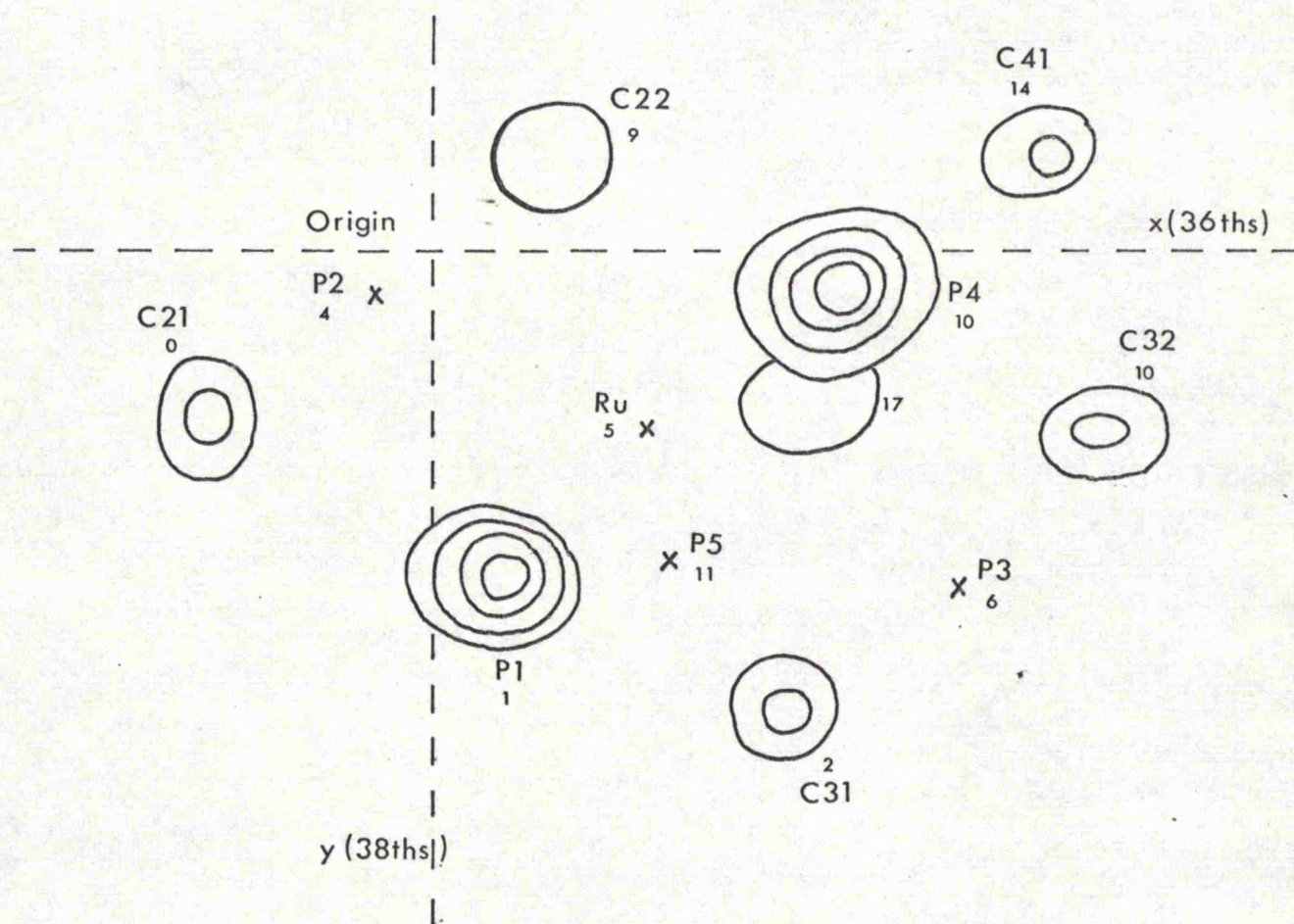
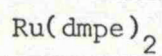


Figure 2.3.5



Projection down z of $F(\text{diff})$ map at cycle 39. Input atoms marked x ; contours at intervals of $3 \text{ e}/\text{\AA}^3$ (lowest at $3 \text{ e}/\text{\AA}^3$). z heights (36ths) shown in small type.

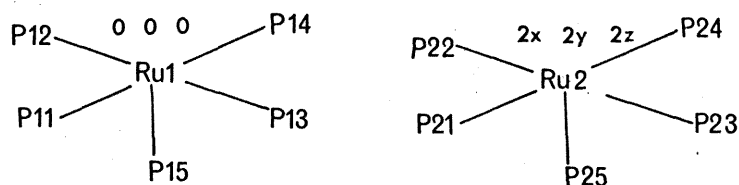
F (diff) map was very similar to the previous one.

Finally, three cycles (37-39), were calculated on Ru, P2, P3 and P5, all of which have reasonable Ru-P lengths; the F (diff) map is shown in Figure 5.

Nothing new appeared, and there was nothing abnormal about any of the input atom peaks. P1 and P4 still appeared at distances 1.97 and 1.99 Å from Ru.

Calculations in P1

Concurrently with attempted refinement in $\bar{P}1$, the alternative solution, in P1, was tested. The atoms were renumbered:-



Initially, four cycles (1-4) of refinement were computed for Ru1 (fixed at 0,0,0), Ru2 (at 2x,2y,2z, where x,y,z was the Ru position in $\bar{P}1$), and P13 and P21. The temperature factors refined to widely differing values (see Table 3). The F (obs) map computed over the whole cell, is shown in Figure 6. A large part of the cell was again empty. The heights at which peaks

came up were:	Ru1	80 *	Ru2	99 *
	P11	29	P21	66 *
	P12	16	P22	14
	P13	38 *	P23	22
	P14	11	P24	19
	P15	15	P25	15

TABLE 2.3.3

Calculations on Ru(dmpe)_2 in P1

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Initial Positions				Initial Vibrations		Final Vibrations		Maps
					Atom	x	y	z	Atom	U	Atom	U	
1-4	2729	min.amp.10	39.2	Ru1,P13	Ru1	0	0	0	all	.04	Ru1	.057	obs.
				Ru2,P21	Ru2	.323	.318	.300		Ru2	.032		
					P13	.217	.118	.017		P13	.011		
					P21	.200	.427	.183		P21	-.010		
5,6	499	min.amp.80	25.1 diverged	Ru1,P13	Ru1	0	0	0					-
				C131,132	Ru2	.323	.318	.300					
					P13	.217	.118	.017	all	.04			
				Ru2,P22	P22	.106	.202	.278					
				C222	C222	.222	.086	.389					
					C131	.096	.235	.908					
					C132	.320	.024	.116					
7-9	499	min.amp.80	19.6	Ru1,P11, P13	Ru1	0	0	0	Ru1	.057	Ru1	.009	obs.
				Ru2,P21, P24	Ru2	.320	.316	.300	Ru2	.033	Ru2	.080	
					P11	.875	.117	.883	P11	.040	P11	.029	
					P13	.206	.127	.016	P13	.011	P13	-.012	
					P21	.199	.434	.181	P21	-.010	P21	.004	
					P24	.451	.196	.414	P24	.040	P24	.024	
10,11	499	min.amp.80	25.1 diverged	Ru1,P12	Ru1	0	0	0	Ru1	.009	Ru1	.007	-
				P13	Ru2	.323	.315	.314	Ru2	.080	Ru2	.073	
				Ru2,P21-P24	P12	.795	.880	.990	P12	.040	P12	.010	
					P13	.214	.126	.021	P13	-.012	P13	-.053	
					P21	.197	.439	.164	P21	.004	P21	-.003	
					P22	.113	.191	.285	P22	.040	P22	.233	
					P23	.530	.435	.317	P23	.040	P23	.192	
					P24	.471	.181	.418	P24	.024	P24	-.004	

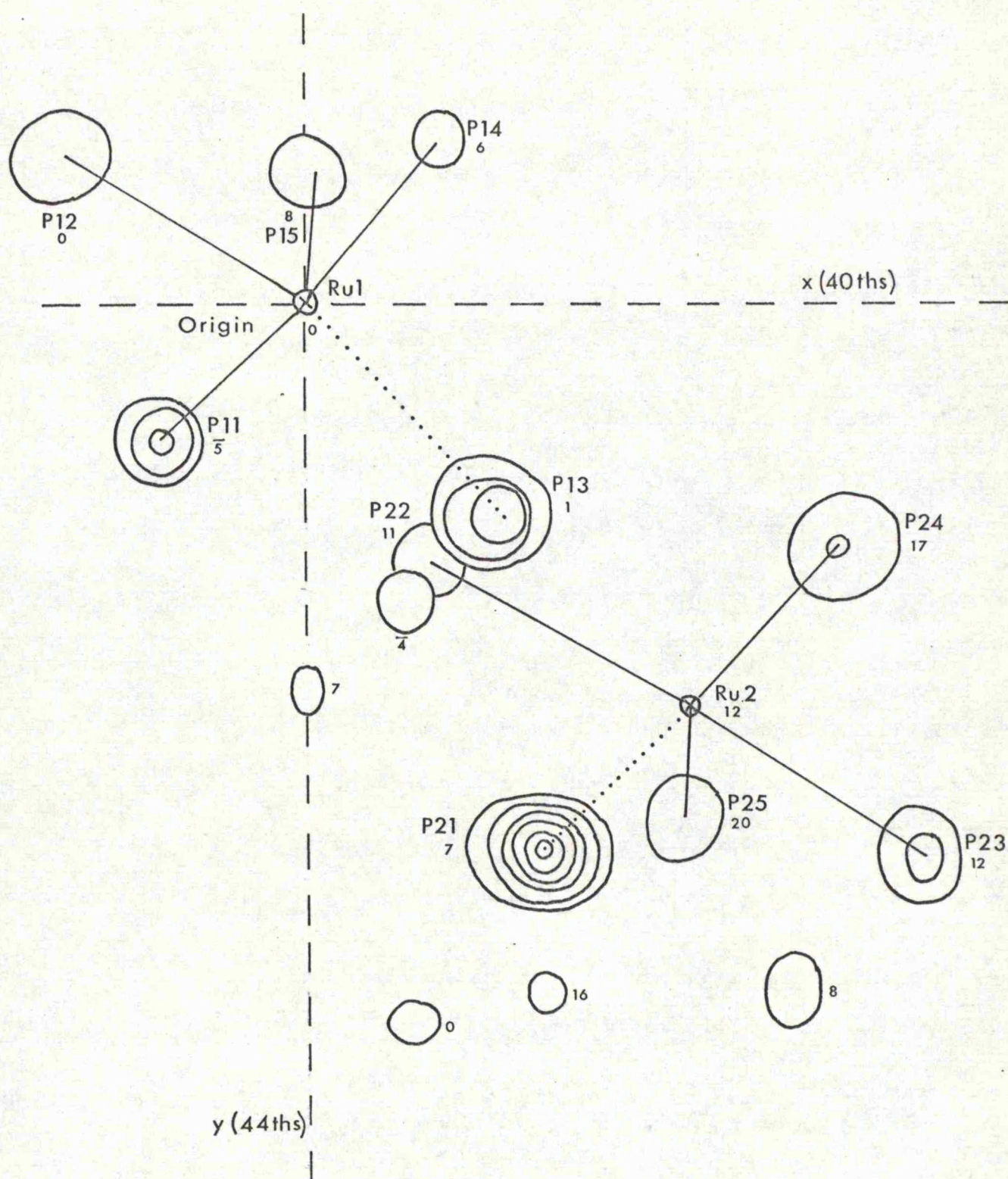


Figure 2.3.6

Ru(dmpe)₂

Projection down z of $F(\text{obs})$ map in $P1$, at cycle 4. Input atoms marked x ; contours at intervals of $10 \text{ e}/\text{\AA}^3$ (lowest at $10 \text{ e}/\text{\AA}^3$). z heights (40ths) shown in small type.

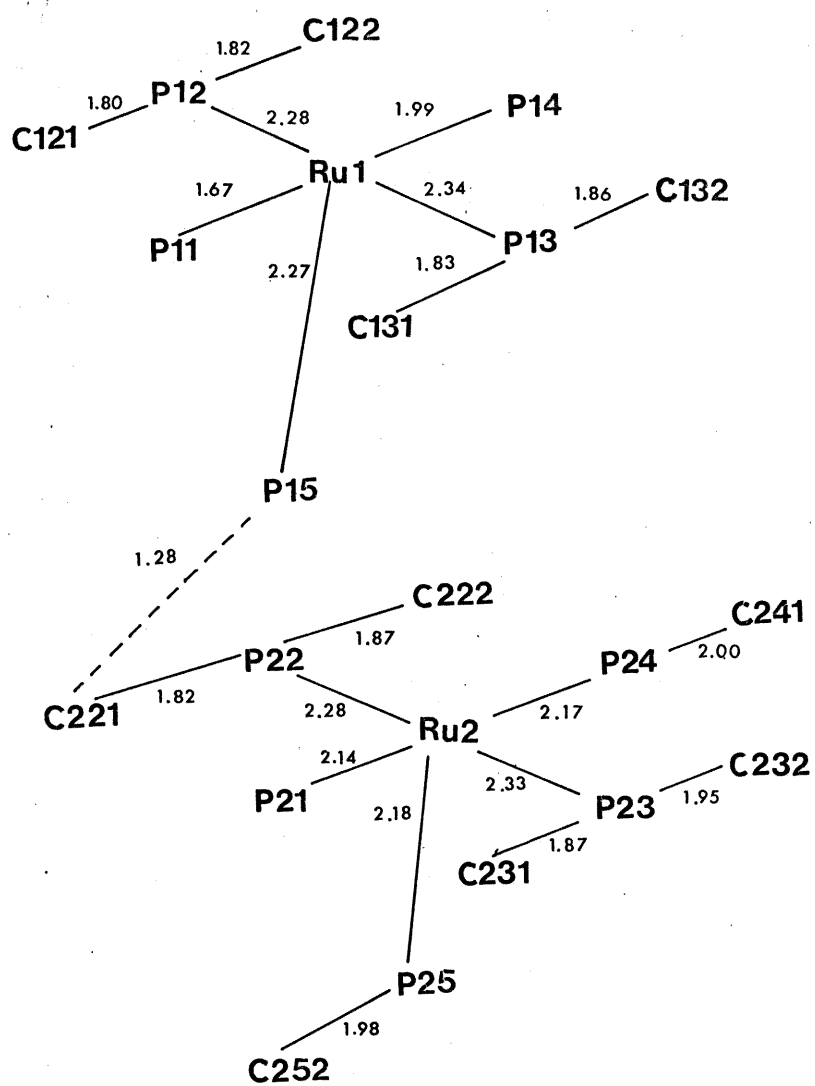


Figure 2.3.7

 $\text{Ru}(\text{dmpe})_2$

Schematic drawing of F(obs) map at cycle 9.

Two peaks came up near P13 - at distances 1.71 and 1.77 Å, corresponding to C31 and C32 in P1, and these were called C131 and C132. Similarly, a peak 1.87 Å from P22 was named C222, and structure factors were computed for all these atoms. Refinement proved impossible, as the temperature factors of the carbon atoms increased rapidly, and the refinement diverged. Three cycles (7-9) on Ru1, P11, P13, Ru2, P21, P24 led to R = 19.6%, with very improbable U values. The corresponding F (obs) map, had the geometry shown in Figure 7.

The heights were:-

Ru1	39 *	Ru2	37 *
P11	23 *	P21	24 *
P12	15	P22	13
P13	24 *	P23	17
P14	18	P24	19 *
P15	7	P25	13

Since P11 and P14 were both too close to Ru1, whereas all the P atoms round Ru2 were at reasonable distances, cycles 10 and 11 were calculated on Ru1, P12, P13, Ru2, P21-4. This reduced R to 25.1%, but the refinement diverged. No further calculations were made in P1.

Direct Methods

A direct methods package⁴⁶ for centrosymmetric structures, which uses the symbolic addition method, see Appendix,

was used in an attempt to solve this structure.

(The space group $P\bar{1}$ was assumed.)

The statistical tests for centrosymmetry are:-

	<u>Centro-</u>	<u>Noncentro-</u>	<u>Found</u>
$\langle E ^2 \rangle$	1.0	1.0	1.030
$\langle E \rangle$	0.798	0.886	0.745
$\langle E^2 - 1 \rangle$	0.968	0.736	1.058
	<u>% data with</u>	<u>Calc.</u>	<u>Found</u>
	$ E > 1$	32.0	31.4
	$ E > 2$	5.0	5.88
	$ E > 3$	0.3	0.3

These together suggested that the original choice of $P\bar{1}$ was correct and that a well behaved set of E values had been generated by the program.

Two hundred and fifty (250) of the largest E values are chosen, and, by symbolic addition of the arbitrary signs given to six of these E values, a trial set of the most probable signs is obtained.

In triclinic symmetry, there are insufficient sign relationships to determine a unique most probable set of signs. In the present case, only three signs could be assigned and this gave eight equally probable sets followed by three groups of eight sets, of lower probability, and it was necessary to compute E maps for these lower probability sign sets as well as for those in the most probable group.

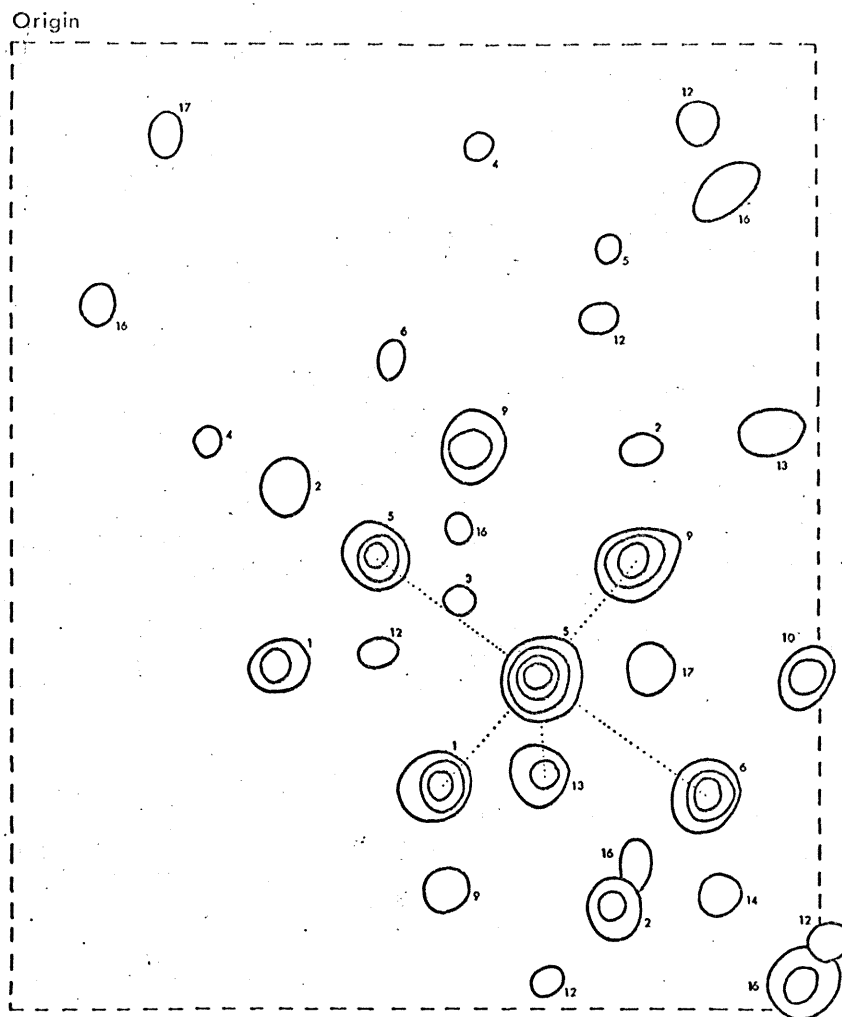


Figure 2.3.8

$Ru(dmpe)_2$

Projection down z of 11th E map, showing the origin shift.
 z heights are shown in small type.

The eight first sets were each tried, but in every case there was no sensible structural unit, and all 'peaks' were of approximately the same height. Generally the pattern of peaks was similar to that observed in all the F maps already calculated. The Patterson solution corresponded to the 11th set of signs, in the 2nd most probable group, with an origin shift to $\frac{1}{2}, \frac{1}{2}, 0$. This E map showed the regular grid of peaks seen on all F maps (see Figure 8 for a projection of the E map).

Further Attempts

Apart from the attempts to refine trial structures, the following tests and calculations were performed:-

1. Delaunay Reduction. This was done on the triclinic cell that had been chosen, to check that no symmetry was hidden by the author's choice of axes. No relation was found between any of the cell parameters.
2. A sharpened Patterson was calculated, using appropriate factors to give point atoms ($M = 1.0$), and reducing the U values by 0.02 ($U = 0.02$). The sharpening function used was:-

$$\exp.(8\pi^2 U \sin^2 \theta / \lambda^2) / [c + \sum_{i=1}^4 a_i \exp.(-b_i M \sin^2 \theta / \lambda^2)]$$

c , a_i and b_i are normalized exponential form-factors for Iridium; this map was not significantly different from the unsharpened map.

3. The photographs were checked for signs of crystal decomposition or disorder. No evidence was found to support this.
4. A new sample of the complex was kindly prepared by J M Davidson at Cambridge; crystals from this batch gave photographs identical to the original set, so it was decided not to re-collect any data.
5. An analysis was performed on the original sample to check the chemical composition.

Results - found P 27.8 C 36.26 H 8.38%

Calc. for $C_{12}H_{32}P_4Ru$ P 30.9 C 35.9 H 8.05%

6. To check the probable number of $Ru(dmpe)_2$ units in the cell, Kitaigorodskii's formula¹⁰⁵ for molecular packing was calculated:-

$$k = z \cdot \frac{V_o}{V}$$

where V_o is the molecular volume

V is the cell volume

z is the number of molecules/cell

k is the coefficient of molecular packing.

The cell volume for $Ru(C_{10}H_8)(dmpe)_2 \sim 2580$

∴ 1 molecule occupies 645

The cell volume for $Ru(dmpe)_2 \sim 935$

for $(C_{10}H_8)$, $k \sim 0.7$, and the volume occupied
by $(C_{10}H_8) \approx 70 \cdot 10^6$

$$\therefore \text{ in Ru } (C_{10}H_8)(dmpe)_2 \quad 0.7 = \frac{4 \times V_o}{2580}$$

\therefore the volume of 1 molecule, $V_o \approx 450$

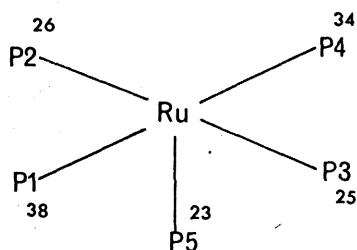
Subtracting 70 for a naphthalene fragment,
gives 380

V for $Ru (dmpe)_2 \sim 380 \times 1/0.7 \sim 540$ for
1 molecule

\therefore 2 molecules require ~ 1080 , and so the
chosen cell probably contains two
 $Ru (dmpe)_2$ units.

Possible Structures

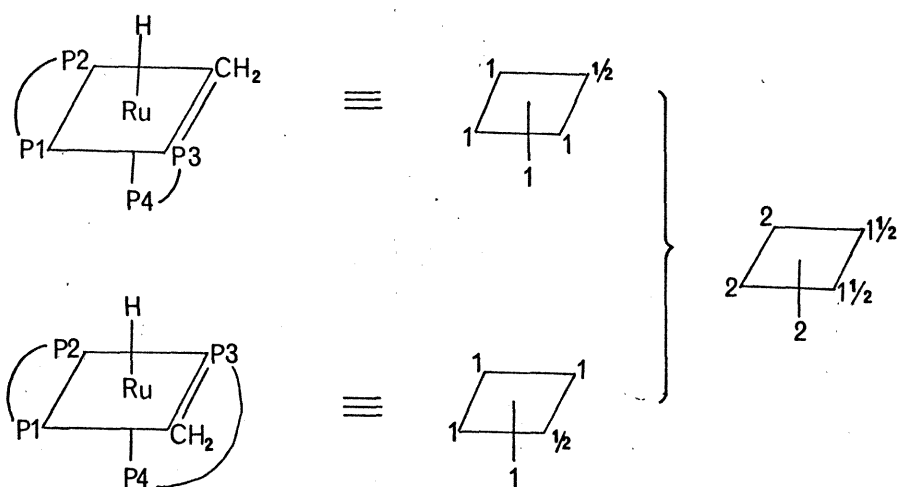
Considering the structure as a monomer, with possible
disorder affecting all atoms, this would explain the
persistent appearance of five peaks; their observed
weights are generally (relative to Ru height 99)



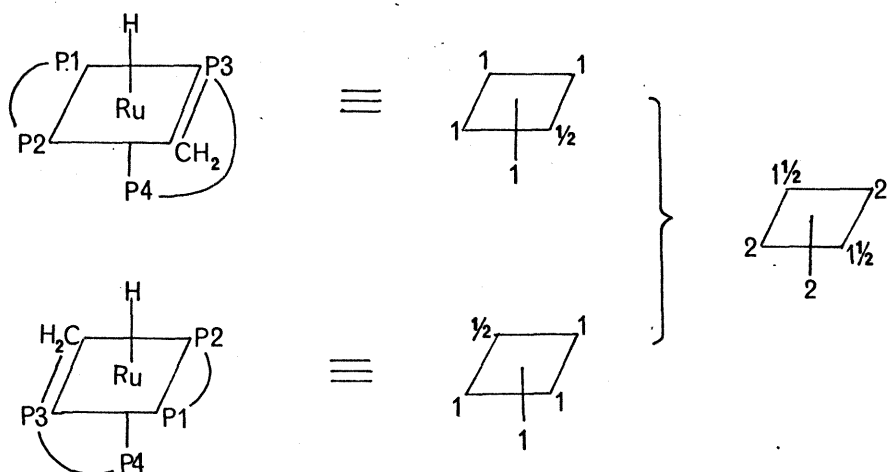
but it is not clear what combination of structures

would give rise to this pattern, as three of the five peaks would be predicted to be stronger than the other two:-

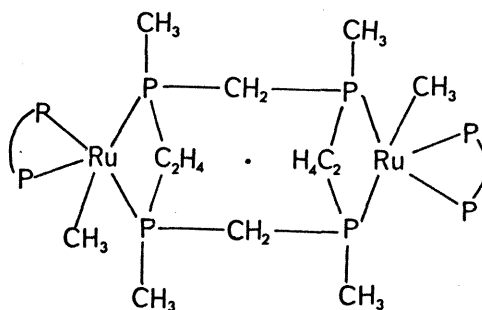
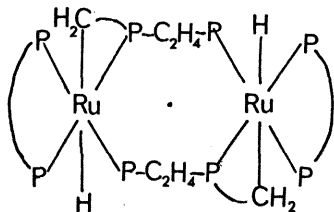
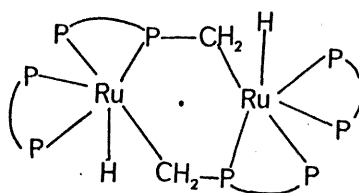
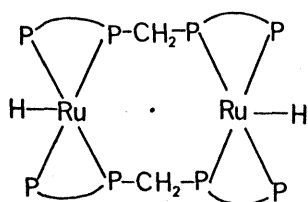
For example:



or:



Considering a dimeric structure, some possibilities are:-



However, the very careful and detailed chemistry which was carried out by the original authors, apparently ruled out the possibility of a dimer, and it does not seem likely that one of the above, elaborate, structures exists, only in the crystalline state.

A long time was spent trying to solve the structure of $\text{Ru}(\text{dmpe})_2$, because it describes, with that of $\text{Ru}(\text{C}_{10}\text{H}_8)(\text{dmpe})_2$ a novel type of tautomerism. The difficulties

have been described in this chapter, but it is worthwhile summarising here their possible explanations and the reasons for eventually abandoning the problem. When a structure cannot be solved, the crystal used may be disordered, so that discrete atomic positions no longer exist. In such cases, disorder is sometimes detected on photographs, as blurred spots, and on a diffractometer trace as broad peaks. Also, characteristically, attempts to refine disordered atoms lead to artificially high U values, and the disorder causes blurred, elongated peaks on Fourier maps, in which it is impossible to locate atomic centres. In the present case, this is not observed. All the peaks are very well shaped, and sharply defined; there are no banana-shaped peaks spanning possible phosphorus atom positions, and no indication whatever that the observed peaks are not genuine atomic peaks. Even if there is only partial disorder, such that, say, two distinct orientations of the molecule exist, in $P\bar{1}$, one would expect some indication of this on the maps. The fact that five peaks always come up round Ru, almost necessitates an explanation in terms of disorder, as there is no evidence that the assumed composition of the crystals is wrong.

If the crystals had, even partly, decomposed during the four year period prior to X-ray work, this should have been obvious from initial photographs, and certainly from the first electron density maps. The new batch of

crystals was closely examined and the photographs compared with those of the original crystals; they were identical. Also, the chemical analyses were the same.

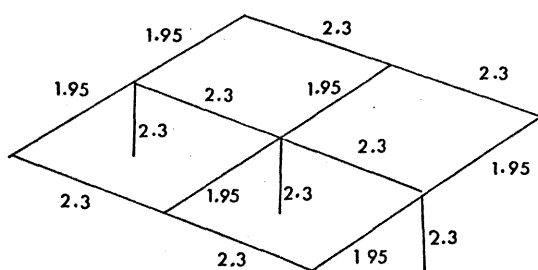
If, on the other hand, the crystal is not disordered, but twinned, it has not been possible to detect it. There are no pseudo-symmetry elements on any of the Weissenberg photographs - indeed, what twinning could give rise to a pseudo-triclinic cell? Examination of the reflections, by sine theta, showed no regularities, and the Delaunay reduction confirmed the original choice of axes.

Possibly the wrong space group was chosen. However, all calculations in $P1$ (and this should give a solution, even if the symmetry is really $P\bar{1}$) led to erratic U value shifts, and refinements were impossible because of divergence. Refinements in $P\bar{1}$ generally led to very reasonable U values.

Finally, the suspicious features of the apparent structure are:-

1. The Patterson of a triclinic crystal has no Harker vectors apart from $2x, 2y, 2z$, to make interpretation difficult. The R_u position chosen seems the only reasonable solution, but is suspect in the light of having failed to lead to a complete structure.

2. All maps show the almost regular grid of peaks:-



3. P1 and P4 are too close to Ru to be phosphorus atoms. They each have satellite peaks that may be the result of disorder, but P1 and P4 have sensible U values.
4. P2 is too near to its symmetry-related position at $-x, -y, -z$.
5. The whole structure lies too close to the origin, leaving a large part of the cell empty.
6. Four planar P atoms do not correspond to the likely structure, but P5 always comes up lower than the other P atoms.
7. P1 always comes up too high in relation to the Ru peak height. (Atomic numbers : Ru44, P15), whereas P3 is always low relative to other 'P' peaks.
8. There is no electron density between any of the peaks, and the possible carbon atom peaks also lie on the grid, rather than at tetrahedral

angles to the P atoms.

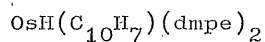
E.g. $C31 - P3 - C32 = 176^{\circ}$.

9. The angles between peaks make it impossible to reconcile the observed and the model structure, as all peak-peak distances are too long for P-C bonds.
10. Direct methods failed to give an independent solution, and even the Patterson solution was only one of the 2nd most probable.

CHAPTER 2.4

THE PREPARATION OF $\text{Os}(\text{C}_{10}\text{H}_8)(\text{dmpe})_2$ AND $\text{Os}(\text{dmpe})_2$:



THE CRYSTAL AND MOLECULAR STRUCTURE OF



After prolonged attempts at solving the structure of $\text{Ru}(\text{dmpe})_2$, various possible analogues of this system were considered:-

1. The closest analogues may be the corresponding osmium complexes mentioned briefly by Chatt and Davidson.⁸² However, only $\text{Os}(\text{C}_{10}\text{H}_8)(\text{dmpe})_2$ was reported, not $\text{Os}(\text{dmpe})_2$. It was likely that the two naphthyls would be isomorphous, in which case $\text{Os}(\text{dmpe})_2$ might be as difficult to solve as $\text{Ru}(\text{dmpe})_2$, if it exhibited similar disorder.
2. The corresponding iron complexes could not be isolated by Chatt and Davidson. The preparation had been repeated by S. D. Ibekwe, who obtained black oils. It is possible that naphthalene is too bulky to coordinate to the much smaller iron, and that reduction proceeds direct to the expected planar $\text{Fe}^0(\text{dmpe})_2$. This would be interesting in its own right if it were planar $\text{Fe}(0)$. Another possibility might be to try and reduce $\text{FeCl}_2(\text{dmpe})_2$ with $\text{K}^+\text{C}_6\text{H}_6^-$, which contains a smaller organic part.
3. The formation of these σ -naphthyl complexes appears to be unique to dmpe. This may be a steric effect of the ligand having exactly the right 'bite' to form a

hydride, and also small terminal groups; or it could be the increased stabilisation of $M-C(\sigma)$ by the ligand, which withdraws less electron density from the metal than other phosphines, e.g. $Ph_2P.C_2H_4.PPh_2$ (dppe). It might be possible to 'tailor' a ligand to give similar behaviour:

- (a) $(Et_2P.C_2H_4.PEt_2)$ (depe). This has very nearly equivalent electronic properties, but is decomposed by $Na^+ C_{10}H_8^-$.
- (b) $(MePhP.C_2H_4.PMePh)$. The phenyl groups might have steric requirements which make the overall geometry unsuitable for hydride formation.
- (c) $(Me_2P.C_2H_2.PMe_2)$  P. This would probably be too rigid.
- (d) $(Me_2P.C_6H_{10}.PMe_2)$  P. This retains the conformation about the central C-C bond, and would be expected to behave similarly to dmpe.
- (e) $(Me_2As.C_2H_4.AsMe_2)$. This is a yellow crystalline solid. As some crystals were available, a reduction was attempted, but the ligand decomposed (sodium naphthalene is well known as an extremely powerful reducing agent).

It was decided to reprepare $Os(C_{10}H_8)(dmpe)_2$, and prepare $Os(dmpe)_2$. This work was done by myself with S D Ibekwe.

Preparations

The reaction scheme is shown in Figure 1. Either the cis or trans dichloride may be used, but reduction of the cis form gave the cis-dihydride (mp. 199°), $\nu(\text{Os-H})$ 1980; 2020 cm^{-1}). Analysis confirmed the product which came down as large pale rhombs, mp. 186° . Found, C 41.1%, H 6.7% Calculated for $\text{C}_{22}\text{H}_{40}\text{P}_4\text{Os}$; C 42.8%, H 6.5%.

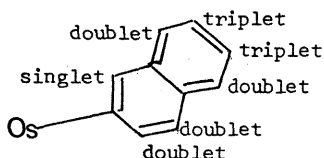
The IR in nujol showed $\nu(\text{Os-H})$ at 1880 cm^{-1} , $\nu(\text{C-C})$ (naphthyl) at $1570, 1610\text{ cm}^{-1}$, $\nu(\text{C-H(naphthyl)})$ at $740, 815\text{ cm}^{-1}$.

$\text{Os}(\text{dmpe})_2$ could be obtained as a white feathery solid by prolonged heating to 220° . $\nu(\text{Os-H})$ had shifted to 1860 cm^{-1} , and complete loss of naphthalene was indicated by the disappearance of the aromatic bands. The reaction always involves substantial losses, and there was not enough product to recrystallize, even after combining the yields from several preparations (eventually some fine needles were obtained from pentane, but these were very fragile); it has therefore not been possible to study the structure, though it appears that $\text{Os}(\text{dmpe})_2$ is very similar to $\text{Ru}(\text{dmpe})_2$ from comparison of IR traces. (See Figure 2)

NMR of $\text{Os}(\text{C}_{10}\text{H}_8)(\text{dmpe})_2$

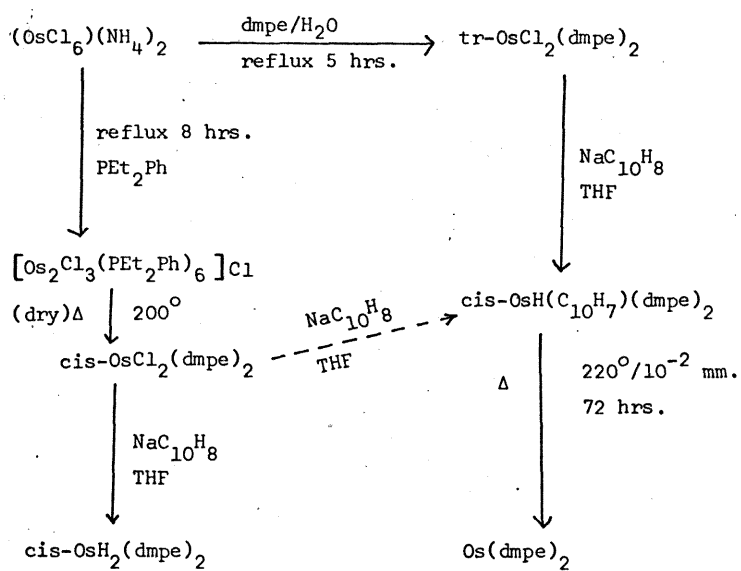
The NMR was run, in C_6D_6 , to confirm that the complex exists as a hydride. A doublet of quartets was observed at 19.1 and 19.4 τ , which was interpreted as coupling of the hydridic hydrogen to three equivalent cis phosphorus

atoms, (quartet), plus coupling to the trans P atom giving a doublet. $J(P-H) = 70$ cycles, (typical of cis phosphines). In the phosphine region ($\sim 8.5\tau$), the spectrum was complex; all CH_2 groups are equivalent; each CH_2 couples strongly to its nearest P atom, and weakly to the other P in the same ligand. This gives a doublet of doublets. Six CH_3 groups are equivalent with respect to the electron density in the naphthyl group. Each couples strongly to its P atom, and weakly to the two other P atoms in its plane giving a doublet of triplets. The methyl groups on P^4 , trans to naphthyl, only couple appreciably to the nearest P atom, giving a doublet. The ratio of these splittings indicated that the three P atoms were not quite symmetrical with respect to the naphthyl, and thus the phosphorus skeleton is very similar to that of $RuH(C_{10}H_7)(dmpe)_2$. In the naphthyl region ($\sim 2\tau$), β -attachment was confirmed by the presence of one singlet, corresponding to the C1 proton which has no α -protons to couple with, as well as doublets from all those protons with one neighbouring α -proton, and two triplets from the two protons with two neighbouring α -protons;



It was therefore expected that the crystal structure would be closely analogous to that of $RuH(C_{10}H_7)(dmpe)_2$.

Figure 2.4.1



- 1) $[\text{Os}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ mpt. $178-180^\circ$ recryst. EtOH.
- 2) $\text{cis-OsCl}_2(\text{dmpe})_2$ mpt. 312° . sticky solid, extracted EtOH.
- 3) $\text{tr-OsCl}_2(\text{dmpe})_2$ mpt. 300° . eluted over $\text{Al}_2\text{O}_3/\text{C}_6\text{H}_6$ with 1:9 $\text{Et}_2\text{O}/\text{C}_6\text{H}_6$, recryst. methylcyclohexane.
- 4) $\text{cis-OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ mpt. 186° . recryst. n-heptane.
- 5) $\text{Os}(\text{dmpe})_2$ recryst. pentane.

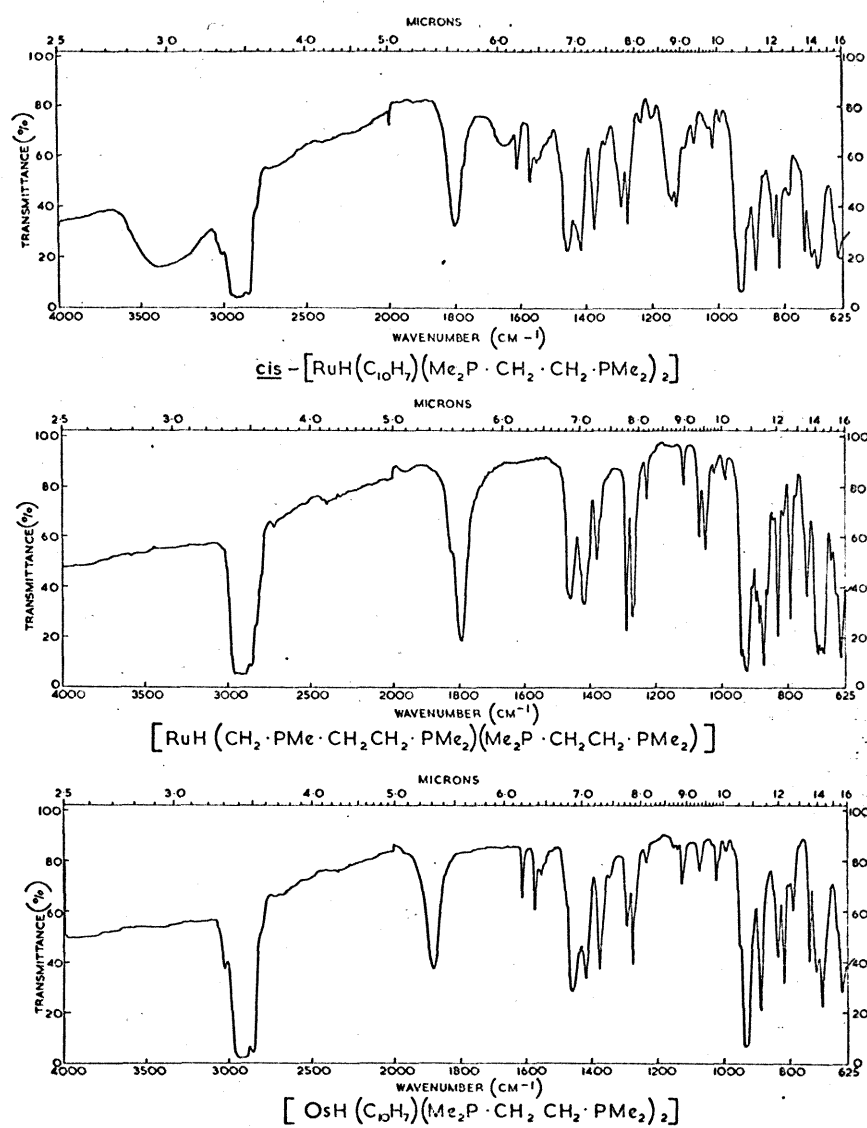


Figure 2.4.2

Infra Red Spectra of the related ruthenium and osmium compounds.

Preliminary Photography

Initial photography showed the long, honey-coloured prisms to be isomorphous with the Ru analogue; the crystal used for collecting data, mounted about the *b* axis, is shown in Figure 3.

Crystal Data

$C_{22}H_{40}OsP_4$, $M = 618.3$; monoclinic, $a = 15.339 \pm 0.010$,
 $b = 10.136 \pm 0.006$, $c = 18.709 \pm 0.010$ Å, $\beta = 114.14 \pm$
 0.04° ; $V = 2654$ Å³, $D_m = 1.52$ (floatation), $Z = 4$,
 $D_c = 1.52$, $F(000) = 1232$; Space Group $P2_1/c$ (C_{2h}^5 No.14),
 Mo-K α radiation (Nb filter), $\lambda = 0.71070$ Å, $\mu = 52.4$ cm⁻¹.

Data Collection

Temperature R.T; scan range -0.8° to $+0.7^\circ$;
 Scan speed 2° 2 θ /minute; fixed time 20 seconds;
 Standards (0 4 0) and (0 0 8) falling to 100% and
 82% of initial intensity; reflections measured in
 octants $\{\bar{h}kl\}$ and $\{h\bar{k}l\}$, to a maximum $2\theta = 47^\circ$;
 cell dimensions from 3 reflections (12 measurements)
 giving angles $\alpha = 90.00(5)^\circ$, $\gamma = 90.03(5)^\circ$,
 total number of independent structure amplitudes
 obtained after data reduction and collation of equivalent
 reflections 3965.

Each reflection was measured twice, in two positions,
 giving a total of 8460 measurements, which were then
 combined. Absorption corrections were applied to all
 reflections with $|F| > 5 |\sigma F|$ using a 0.055 cm mesh
 (222 points).

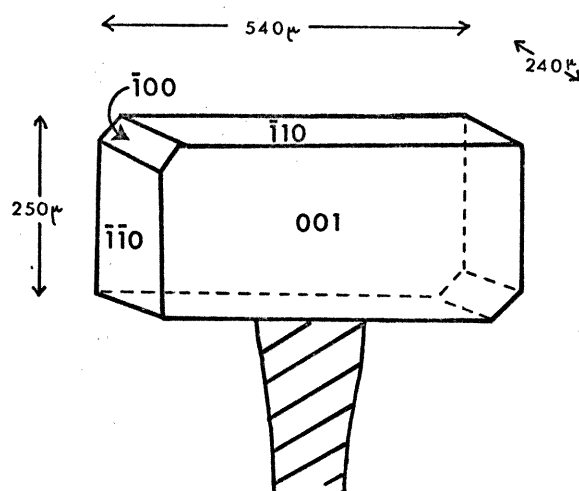


Figure 2.4.3

$\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ Crystal

The Equations of the Bounding Surfaces
of the Crystal

	l	m	n	p	(hkl)
1	-0.3221	-0.9302	0.1759	119.704	001
2	0.3060	0.9517	0.0259	124.357	00 $\bar{1}$
3	0.7909	-0.0738	-0.6075	309.379	100
4	0.8638	-0.2056	0.4599	268.236	110
5	-0.0612	-0.0742	0.9954	126.604	$\bar{1}10$
6	-0.7431	0.1780	0.6451	309.945	$\bar{1}00$
7	-0.8864	0.2447	-0.3931	271.573	$\bar{1}\bar{1}0$
8	0.0645	0.1138	-0.9914	131.217	1 $\bar{1}0$

Solution and Refinement of Structure

Since it appeared that $\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ might be isostructural with $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, the refined coordinates for the Ru complex (at $R=8\%$), were input as initial parameters for the Os complex. Details of the structure factor calculations and refinements are given in Table 1. The atoms which had been disordered, or affected by the disorder, in $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ - C11, C21, C31, C41, C12, C13, C42, C43 - were omitted from the first few cycles; unit scale factor and weighting were used.

At $R=9.8\%$, an $F(\text{diff})$ map was calculated. The scale of this map was 3.2 so that the C(phosphine) atoms were appearing at up to three electrons. It was apparent that C11 was disordered, as in the Ru complex, but that C41 was only slightly disordered:-

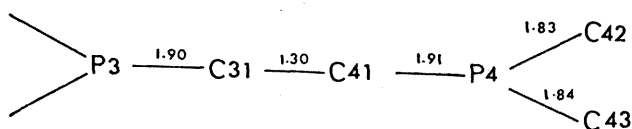
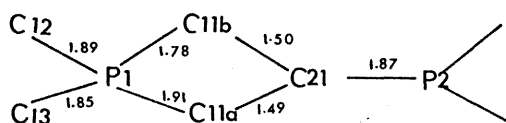


TABLE 2.4.1

Refinement of the structure of OsH(C₁₀H₇)(dmpe)₂

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Matrix type			Vibrations			Weights used		
					Os	P	C(p)	C(nap)	Os	P		C(p)	C(nap)
1,2	3044	min.amp.10	11.1	all except some C(p) (see text)	pb(1)	pb(1)	b(1)	b(2)	a	a	i	i	1
3	3044	min.amp.10	9.8	all except some C(p)	pb(1)	pb(1)	b(1)	b(2)	a	a	i	i	c ₁ = 3(c ₂ = 3(
4-8	3044	min.amp.10	7.2	all atoms	pb(1)	pb(1)	b(1)	b(3) b(2)	a	a	i	i	c ₁ = 4(c ₂ = 3((3)
9	3044	min.amp.10	10.3	all except C(p)	b(1)	b(1)	-	b(2)	a	a	-	i	3

Matrix types:

b = full block
 pb = positional block
 tb = vibrational block
 c = contribution only
 C(p) = C(phosphine)
 C(nap) = C(naphthyl)

Thermal parameters:

a = anisotropic
 i = isotropic
 c = constant
 Final scale = 1.008 (cycle 8)
 Final convergence factor = 0.001 (cycle 8)

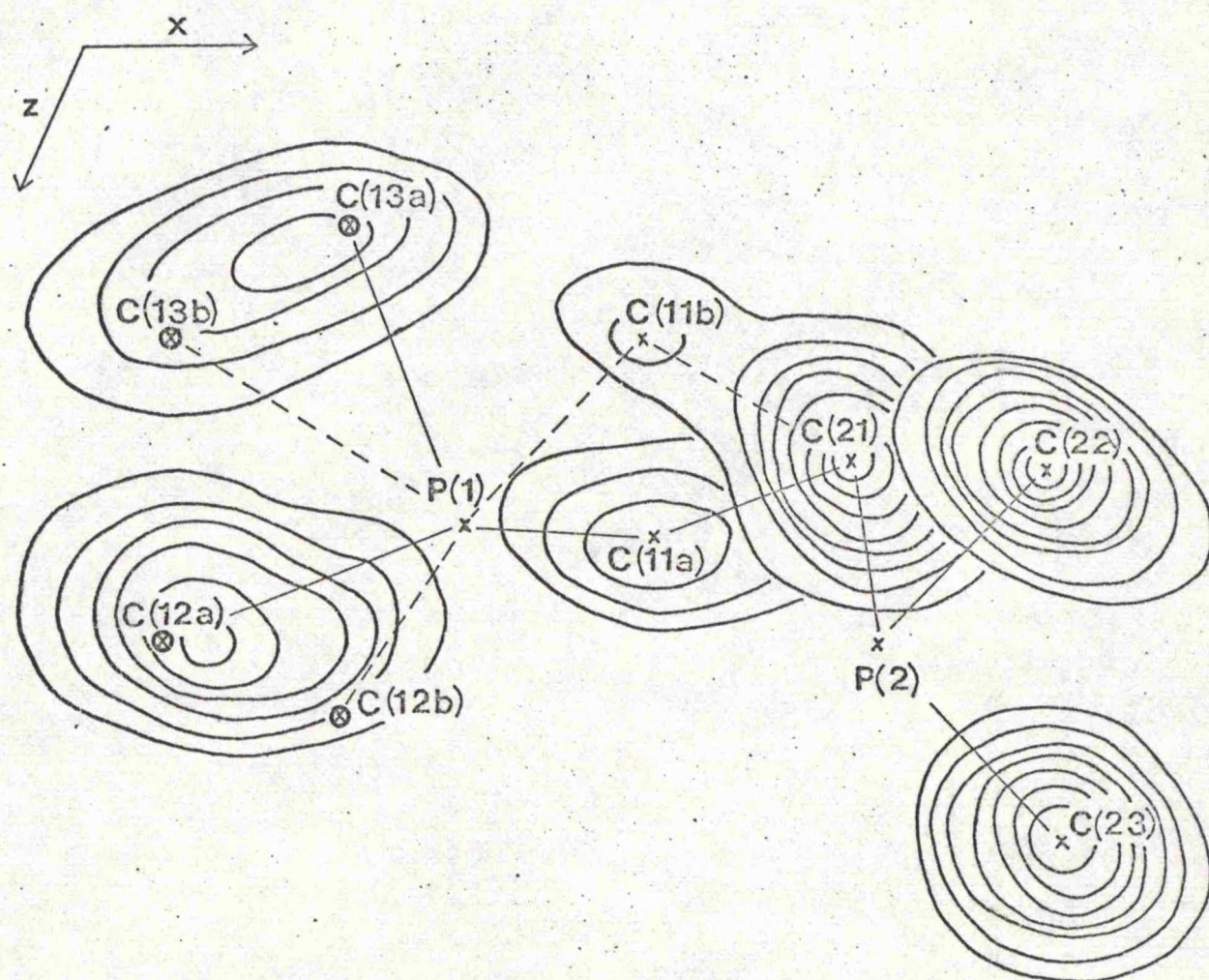


Figure 2.4.4a
 $\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

Projection of $F(\text{diff})$ map phased on Os, P atoms, and naphthyl group, illustrating the disordered ligand $\text{P1} \dots \text{P2}$. Contours at intervals of $0.35 \text{ e}/\text{\AA}^3$, lowest at $0.7 \text{ e}/\text{\AA}^3$. The calculated positions for terminal carbon atoms are indicated \otimes .

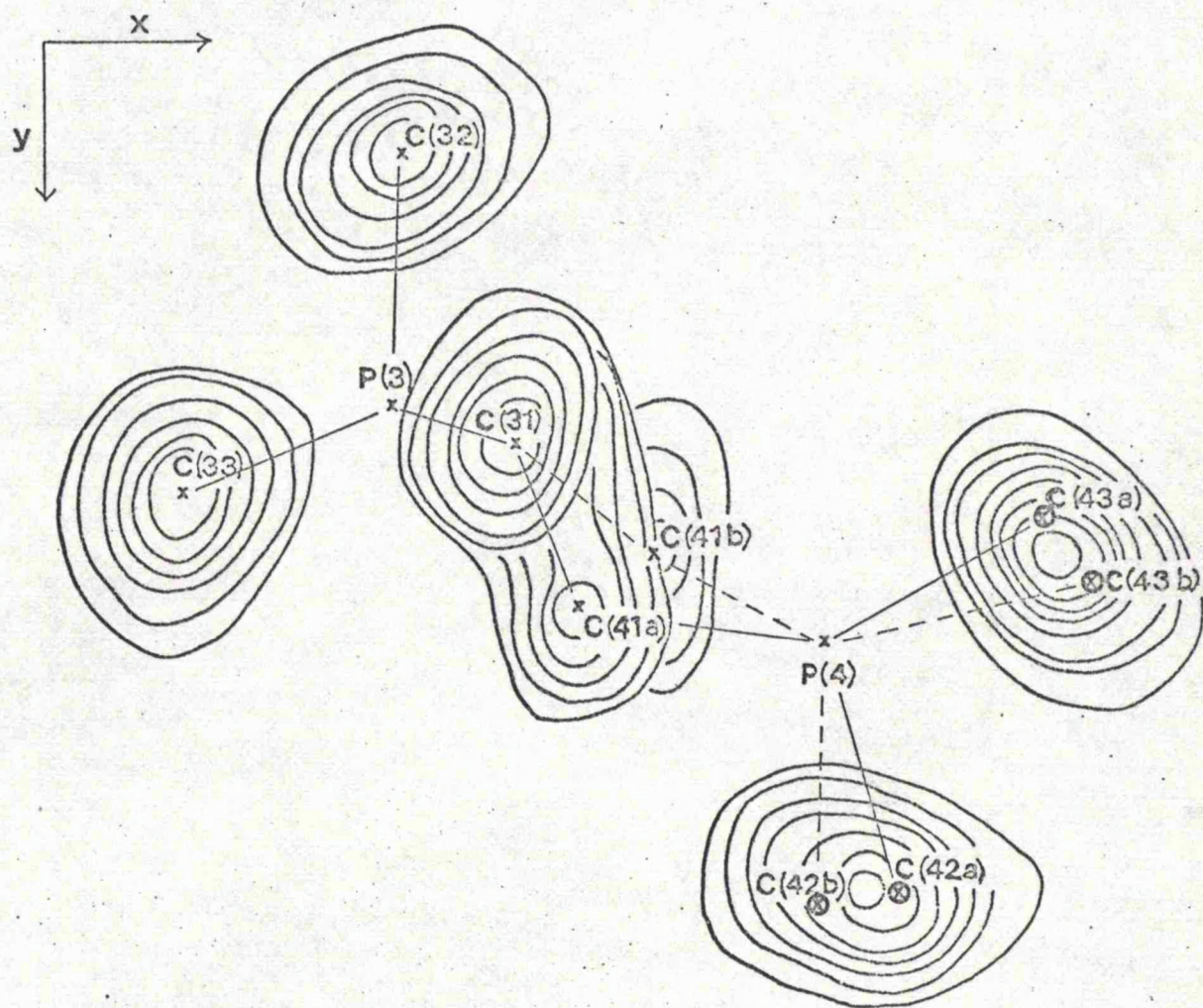


Figure 2.4.4b
 $\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

Projection of $F(\text{diff})$ map phased on Os, P atoms, and naphthyl group, illustrating the disordered ligand P3.....P4. Contours at intervals of $0.35 \text{ e}/\text{\AA}^3$, lowest at $0.7 \text{ e}/\text{\AA}^3$. The calculated positions for terminal carbon atoms are indicated \otimes .

The appearance of this map was very similar to the corresponding map of the ruthenium complex. All atoms (taking C11a and the 'average' C12 and C13 positions) were now included in the final refinement - cycles 4 to 8 - which reduced R to 7.2%. (See Table 1) The final scale was 1.0; an F(diff) map revealed the positions of all but one of the H(naphthyl) atoms, at heights of 0.5 to 0.9 e/ \AA^3 , near their calculated positions. No attempt was made to search for the hydridic hydrogen, which did not show on this map, because of considerable residual electron density round the osmium position. Structure factors for the unobserved reflections (amplitude $< 10e$) were calculated - the highest calculated as 26, most others being $< 20e$.

Finally, structure factors were calculated, omitting the entire phosphine ligands and using the refined parameters for the remaining atoms (cycle 9). The corresponding F(diff) maps for the two phosphines are shown in Figures 4a and 4b. These are comparable to Figures 2.2.2 a and b for the ruthenium analogue, and illustrate the disorder.

Results and Discussion

The final parameters are given in the Appendix (Tables 2 and 3), while the molecular geometry is

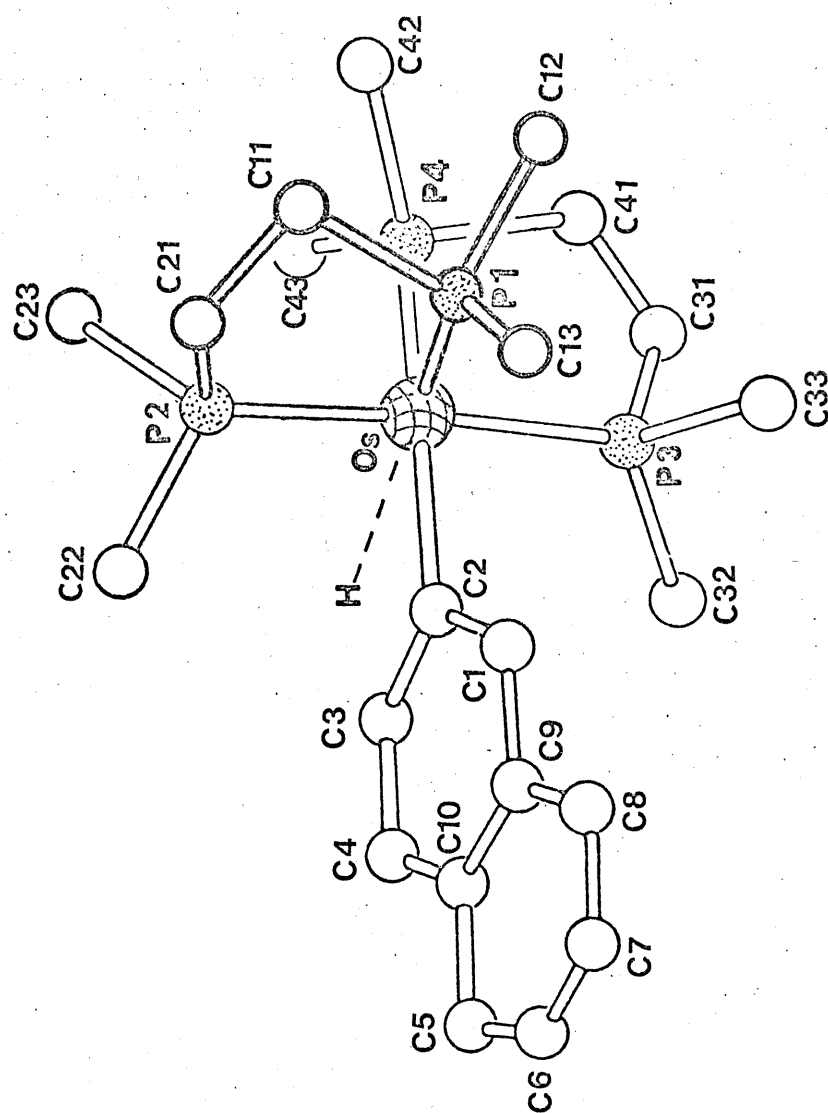


Figure 2.4.5
 $\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$

View of one molecule, illustrating the numbering system used.

Table 2.4.4

Bond distances (\AA) and angles ($^\circ$), with their estimated standard deviations

Around Osmium

Os-P(1)	2.325(6)	P(1)-Os-P(2)	82.4(2)	P(1)-Os-C(2)	99.5(5)
Os-P(2)	2.297(5)	P(1)-Os-P(3)	102.3(2)	P(2)-Os-C(2)	88.6(5)
Os-P(3)	2.285(5)	P(1)-Os-P(4)	97.8(2)	P(3)-Os-C(2)	87.0(5)
Os-P(4)	2.301(5)	P(2)-Os-P(3)	173.9(2)	P(4)-Os-C(2)	162.1(5)
Os-C(2)	2.134(17)	P(2)-Os-P(4)	98.2(2)		
Os...C(1)	3.13	P(3)-Os-P(4)	84.9(2)		
Os...C(3)	3.12				

Naphthyl Group

C(1)-C(2)	1.37(2)	C(1)-C(2)-C(3)	116(2)
C(2)-C(3)	1.47(3)	C(2)-C(3)-C(4)	118(2)
C(3)-C(4)	1.50(3)	C(3)-C(4)-C(10)	122(2)
C(4)-C(10)	1.33(3)	C(4)-C(10)-C(9)	121(2)
C(10)-C(5)	1.52(4)	C(9)-C(10)-C(5)	123(2)
C(5)-C(6)	1.39(4)	C(10)-C(5)-C(6)	108(3)
C(6)-C(7)	1.27(4)	C(5)-C(6)-C(7)	133(3)
C(7)-C(8)	1.44(4)	C(6)-C(7)-C(8)	121(3)
C(8)-C(9)	1.44(3)	C(7)-C(8)-C(9)	114(2)
C(9)-C(1)	1.49(3)	C(8)-C(9)-C(10)	122(2)
C(9)-C(10)	1.35(3)	C(10)-C(9)-C(1)	120(2)
		C(9)-C(1)-C(2)	123(2)
		C(1)-C(2)-Os	125(1)
		C(3)-C(2)-Os	118(1)
		C(1)-C(9)-C(8)	118(2)
		C(4)-C(10)-C(5)	117(2)

Table 2.4.4 (contd.)

Phosphine Groups

*P(1)-C(11)	1.87(4)	*C(11)-P(1)-C(12)	89(2)
*P(1)-C(12)	1.81(4)	*C(11)-P(1)-C(13)	105(2)
*P(1)-C(13)	1.79(4)	*C(12)-P(1)-C(13)	92(2)
P(2)-C(21)	1.87(3)	C(21)-P(2)-C(22)	103(1)
P(2)-C(22)	1.90(3)	C(21)-P(2)-C(23)	100(1)
P(2)-C(23)	1.90(3)	C(22)-P(2)-C(23)	100(1)
P(3)-C(31)	1.92(3)		
P(3)-C(32)	1.82(4)	C(31)-P(3)-C(32)	98(2)
P(3)-C(33)	1.79(3)	C(31)-P(3)-C(33)	102(1)
*P(4)-C(41)	1.93(4)	C(32)-P(3)-C(33)	100(2)
*P(4)-C(42)	1.83(3)	*C(41)-P(4)-C(42)	99(1)
*P(4)-C(43)	1.83(3)	*C(41)-P(4)-C(43)	105(2)
		*C(42)-P(4)-C(43)	96(1)
*C(11)-C(21)	1.61(4)		
*C(31)-C(41)	1.45(4)	*P(1)-C(11)-C(21)	103(2)
		*P(2)-C(21)-C(11)	108(2)
		*P(3)-C(31)-C(41)	105(2)
		*P(4)-C(41)-C(31)	118(3)
*Os-P(1)-C(11)	109(1)	Os-P(3)-C(31)	113(1)
*Os-P(1)-C(12)	126(1)	Os-P(3)-C(32)	120(1)
*Os-P(1)-C(13)	128(1)	Os-P(3)-C(33)	121(1)
Os-P(2)-C(21)	111(1)	*Os-P(4)-C(41)	106(1)
Os-P(2)-C(22)	119(1)	*Os-P(4)-C(42)	129(1)
Os-P(2)-C(23)	121(1)	*Os-P(4)-C(43)	119(1)

* involving atomic positions affected by disorder

Table 2.4.5

Selected Torsion Angles ($^{\circ}$), positive values
indicating clockwise rotation

* P(1)-C(11)-C(21)-P(2)	- 52
* P(3)-C(31)-C(41)-P(4)	- 40
C(1)-C(2)-Os-P(1)	- 25
C(1)-C(2)-Os-P(2)	-107
C(1)-C(2)-Os-P(3)	77

* involving atomic positions affected by disorder

shown in Table 4. Parameters marked (*) correspond to atoms affected by the disorder. The standard deviations are larger than in the Ru complex.

Selected torsion angles are listed in Table 5; the only intermolecular contact (other than those between hydrogens) is C41-C8, 3.55\AA . The final agreement analysis is listed in Table 6. Figure 5 shows one molecule, with the numbering system; as the intermolecular packing is essentially identical to that of $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, no diagram is given.

The complex is almost exactly iso-structural with its Ru analogue; the only difference occurring in the conformation of the disordered phosphines.

From a comparison of Figures 2.2.2 and 2.4.4, it can be seen that the dominant conformation about P1 is reversed in the osmium complex, and that there is much more disorder about P4 in the ruthenium complex. The observation that the torsion angles about C-C in the phosphines (both -ve, i.e. as defined in reference 218) allow one of the ligands to adopt the opposite conformation relative to $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, confirms that dmpe has minimal steric requirements, even when two dmpe groups are cis to one another.

This contrasts with dppe, which is much less flexible.

The Os-P distances (average 2.30\AA), are slightly shorter than other measurements of Os-P (see Table 7). The P-C and C-C parameters are almost identical in

TABLE 2.4.7

Os-P Distances

	<u>Os-P</u>	<u>Reference</u>
$\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	2.29-2.33	
$\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$	2.34-2.56	a
$\text{OsCl}_2(\text{NO})(\text{HgCl})(\text{PPh}_3)_2$	2.39, 2.40	b
$\text{OsCl}_3(\text{NH}_3)(\text{PPh}_3)_2$	2.41	c
$\text{Os}(\text{CO})_3(\text{PPh}_3)_2$	2.32-2.42	d
$\text{OsCl}_4(\text{PMe}_2\text{Ph})_2$	2.45	e
$\text{OsCl}_3(\text{PMe}_2\text{Ph})_3$	2.35-2.41	e
$\text{OsH}_4(\text{PEt}_2\text{Ph})_3$	2.30-2.34	f

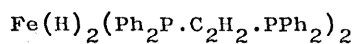
- a. P L Orioli & L Vaska, Proc.Chem.Soc., 1962, 333
- b. G A Bentley et al., JCS(D), 1970, 998
- c. D Bright & J A Ibers, Inorg.Chem., 1969, 8, 1078
- d. J K Stalick & J A Ibers, Inorg.Chem., 1969, 8, 419
- e. L Aslanov et al., JCS(D), 1970, 30
- f. quoted by L Aslanov et al., JCS(D), 1970, 30
(unpublished data of R Mason & P O Whimp)

both complexes; plainly the effect of changing Ru to Os is negligible on the structure in the solid. This accords with the well known observation that second and third row complexes often have very similar properties, differing from their first row analogues. (In this case, $\text{FeH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ has not been isolated, if indeed it exists.)

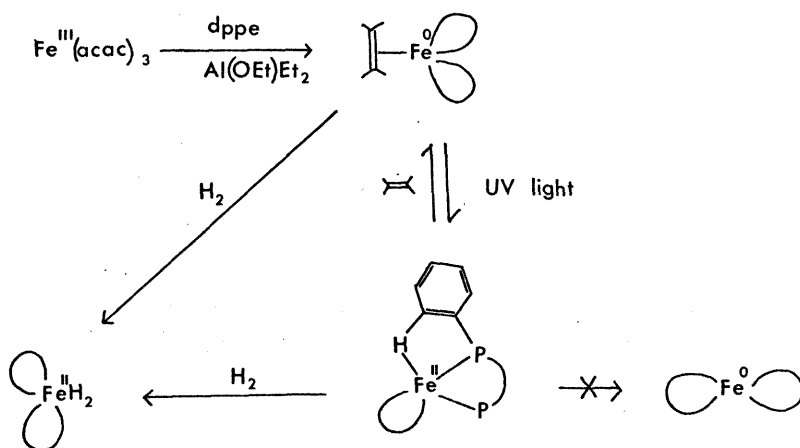
The Os-C length ($2.13(2) \text{ \AA}$) is not significantly different from Ru-C ($2.16(1) \text{ \AA}$), and almost certainly insufficient to account for the fact that the naphthalene is much more tightly held in the Os complex. If these are assumed to be pure sigma bonds, these distances give values for covalent Ru(II) and Os(II) radii of $1.39 - 1.42 \text{ \AA}$ (sp^2 carbon 0.74 \AA). They are thought to be the first measurements of Ru-C(σ) and Os-C(σ) bonds.

CHAPTER 2.5

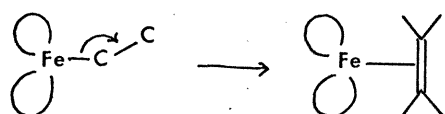
THE ATTEMPTED STRUCTURE ANALYSIS OF

Iron Dihydride Complexes

The system $\text{Fe}^0(\text{dppe})_2 \rightleftharpoons \text{Fe}^{\text{II}}\text{H}(\text{C}_6\text{H}_4 \cdot \text{PhP} \cdot \text{C}_2\text{H}_4 \cdot \text{PPh}_2)(\text{dppe})$ was reported by Hata⁸¹ as an example of a complex containing a labile ligand hydrogen which reversibly forms an Fe-H bond. IR and NMR spectra were given as evidence for the M-H bond:- $\nu(\text{Fe-H})$ 1893 cm^{-1} , $\delta(\text{Fe-H})$ 24.2τ . Whereas $\text{Ru}^0(\text{dmpe})_2$, - and probably $\text{Os}^0(\text{dmpe})$ - exhibits this type of tautomerism, attempts to prepare the iron complex, failed.⁸³ $\text{Fe}^0(\text{dppe})_2$ is thus the nearest analogue. The complex is formed by UV irradiation of $\text{Fe}^0(\text{dppe})(\text{ethylene})$:-



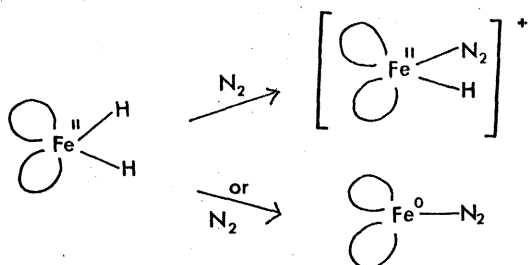
The coordinated ethylene was thought to be derived from homolytic fission of the Fe-C bond of an Fe ethyl intermediate, cf. the reduction of Ni(acac)₂:¹⁰⁷



Fe⁰(dppe)₂ is very unstable; it reacts with hydrogen to give a solvated dihydride, for which the only evidence is an IR band at 1850 cm⁻¹. This is within the range for ν(Fe-H) for monohydride complexes, cf:-¹⁰⁸

tr- FeHCl(dmpe) ₂	1810 cm ⁻¹
tr- FeHCl(depe) ₂	1849 cm ⁻¹
tr- FeHI(depe) ₂	1872 cm ⁻¹

and is ~100 cm⁻¹ higher than the only previously reported iron dihydride FeH₂(o-C₆H₄(PEt)₂)₂ which has been assigned a trans structure because of the low stretching frequency (ν(Fe-H) 1725 cm⁻¹). It was therefore suggested that FeH₂(dppe)₂ might be a cis dihydride complex. The preparation was repeated by A H Mawby, using different reducing systems; he could not isolate Fe⁰(dppe)₂ but he obtained a dihydride as an intermediate in the preparation of a nitrogen complex, which also suggested that the configuration might be cis:-



The nitrogen complex is always formed as a red oil, from which crystals could not be isolated. $\nu(\text{N}\equiv\text{N})$ was observed at $\sim 2100 \text{ cm}^{-1}$. Nitrogen complexes of iron with ditertiary phosphines have been reported,¹⁰⁹ in which Fe is coordinated to N_2 and H, e.g. trans- $[\text{FeH}(\text{N}_2)(\text{depe})_2]^+ \text{BPh}_4^-$, where depe is $(\text{Et}_2\text{P}\cdot\text{C}_2\text{H}_4\cdot\text{PEt}_2)$. These are crystalline solids with $\nu(\text{N}\equiv\text{N})$ at 2090 cm^{-1} , $\nu(\text{Fe}-\text{H})$ at 1870 cm^{-1} , $J(\text{Fe}-\text{H})$ at 28.2τ . Green has reported¹¹⁰ the preparation of black oily Fe- (N_2) complexes, e.g. $\text{Fe}^0(\text{N}_2)(\text{PEt}_3)_4$ and these are probably not hydrides; $\nu(\text{N}\equiv\text{N})$ 2100 cm^{-1} . This lends support to the idea of an $\text{Fe}(0)$ complex in the present case, since there is no reaction with anions such as BPh_4^- .

The bidentate phosphines: dppe ($\text{Ph}_2\text{P}\cdot\text{C}_2\text{H}_4\cdot\text{PPh}_2$)
 dppm ($\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{PPh}_2$)
 dpp ($\text{Ph}_2\text{P}\cdot\text{C}_2\text{H}_2\cdot\text{PPh}_2$)(cis form)

were used in these experiments, and the dihydrides obtained are listed on the next page.

Complex	Colour	Stability to light	$\nu(\text{Fe-H})$
$\text{FeH}_2(\text{dppe})_2$	yellow	unstable, turning brown	1850
$\text{FeH}_2(\text{dpp})_2$	golden-yellow	unstable, not much colour change	1860
$\text{FeH}_2(\text{dppm})_2$	red	stable	1710

Only two crystal structures are known for iron-group dihydrides; $\text{FeH}_2(\text{P}(\text{Ph}(\text{OEt})_2)_4)^{111}$ and $\text{IrH}_2(\text{CO})(\text{PPh}_3)_2(\text{GeMe}_3)^{112}$ and it seemed worthwhile to make a structural comparison to determine whether the difference in $\nu(\text{Fe-H})$ is related to cis-trans isomerism. The trans octahedral configuration of $\text{FeH}_2(\text{o-C}_6\text{H}_4(\text{PEt})_2)_2$ is assumed from IR data; an alternative structure (but less likely in view of the known steric requirements of hydride) is a tetrahedral metal phosphine skeleton with the small hydrogen atoms occupying the spaces. This type of structure was suggested¹¹³ from powder photographs of $\text{Pd}(\text{PPh}_3)_4$, $\text{RhH}(\text{PPh}_3)_4$, and $\text{RuH}_2(\text{PPh}_3)_4$, which indicated possible isomorphism. $\text{Pd}(\text{PPh}_3)_4$ is thought to be tetrahedral; the tetrahedral geometry of $\text{RhH}(\text{PPh}_3)_4$ was confirmed,¹¹⁴ and although the hydrogen was not located, it was required by symmetry to lie on one of the threefold axes through Rh and each phosphorus atom, and is probably disordered between these four positions. It is not known whether $\text{FeH}_2(\text{P}(\text{Ph}(\text{OEt})_2)_2)_2$ is octahedral or tetrahedral; however, by analogy with trans hydrido halides, $\text{FeH}_2(\text{diphosphine})_2$ might reasonably be expected

to be octahedral. As these are first row complexes, there would be a reasonable chance of locating the hydridic hydrogens, and therefore of measuring a trans effect of hydride, on phosphorus, if these are cis complexes. No trans effect was noted in $\text{ReH}_3(\text{PPh}_3)_2(\text{dppe})$.¹¹⁵ There is also the possibility that these are not genuine dihydrides, rather that there is once again an interaction between the metal and a phenyl hydrogen.

Because of the very poor photographs obtained from $\text{FeH}_2(\text{dppe})_2$, even from quite large crystals (0.5 mm across), $\text{FeH}_2(\text{dpp})_2$ was chosen for detailed study, though in this case also the photographs were very weak, and disorder was suspected.

Preliminary Observations

Photography indicated the coexistence of two crystalline forms. One was very unstable indeed; oscillation photos showed a long axis ($\sim 25\text{\AA}$). Possibly there is an equilibrium $\square(\text{stable}) \rightleftharpoons \square(\text{unstable})$, similar to that for $\text{FeH}(\text{dppe})_2$. The more stable form was monoclinic with the a and c axes inclined to the crystal faces. The largest possible crystal was selected for data collection, mounted about the b axis (See Figure 1).

Crystal Data

$\text{C}_{52}\text{H}_{46}\text{FeP}_4$, $M = 850.3$; monoclinic, $a = 14.226 \pm 0.013$,
 $b = 12.219 \pm 0.025$, $c = 28.321 \pm 0.034 \text{\AA}$, $\beta = 99.20 \pm 0.09^\circ$;
 $U = 4860.0 \text{\AA}^3$, $D_m \approx 1.3$, $Z = 4$, $D_c = 1.16$, $F(000) = 1776$,
 Space Group $P2_1/c$, (C_{2h}^5 No.14), $\text{MoK}\alpha$ radiation (Nb filter),
 $\lambda = 0.71070 \text{\AA}$, $\mu = 4.82 \text{ cm}^{-1}$.

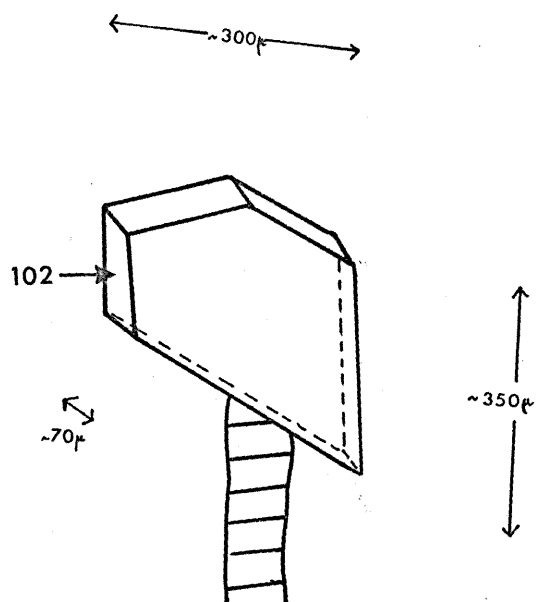


Figure 2.5.1
 $\text{Fe}(\text{H})_2(\text{Ph}_2\text{P.C}_2\text{H}_2.\text{PPh}_2)_2$ Crystal

Data Collection

Temperature R.T.; scan range -0.8° to $+0.5^{\circ}$;
 Scan speed 2° /minute; fixed time 20 seconds;
 Standards (0 0 $\bar{4}$) and (0 3 $\bar{1}$) both falling to 70%
 of initial intensity; reflections measured in
 octants {hkl} and $\{\bar{h}kl\}$, to a maximum $2\theta = 30^{\circ}$;
 cell dimensions from 3 reflections (12 measurements)
 giving angles $\alpha = 90.03(13)^{\circ}$, $\gamma = 89.84(14)^{\circ}$;
 total number of independent structure amplitudes
 obtained after data reduction and collation of
 equivalent reflections 1519.

Attempted Structure Determination

Formfactors for Fe and P were corrected for $\Delta f'$.
 All measured intensities were processed, but only
 353 had observed amplitudes $> 5\sigma$ on the initial scaling.
 A Patterson map was calculated on these 353 terms only,
 since many of the remainder were statistically insigni-
 ficant and could lead to confusion in interpretation.
 The map did not contain much detail, but a consistent
 solution could be found, involving the highest peaks,
 and giving an Fe and one P position:-

Fe	0.281	0.014	0.113
P1	0.344	0.111	0.167

However, refinement of a trial structure phased on these
 two atoms led to widely different temperature factors,

TABLE 2.5.1
Refinement of the structure of $\text{FeH}_2(\text{Ph}_2\text{P}(\text{C}_2\text{H}_5)_2)_2$

Cycle number	Number of terms	Criteria	R Value	Atoms included	Matrix type	Vibrations	Weighting used
					Fe P C	Fe P C	
1-3	353	min.amp.5	42.2	Fe,P1	b b -	i i -	1
4-6	353	min.amp.5	42.4	Fe,P1-P3	b b -	i i -	1

```
Matrix types:  b = full block      Thermal parameters:  i = isotropic
               Final scale          = 9.32
```

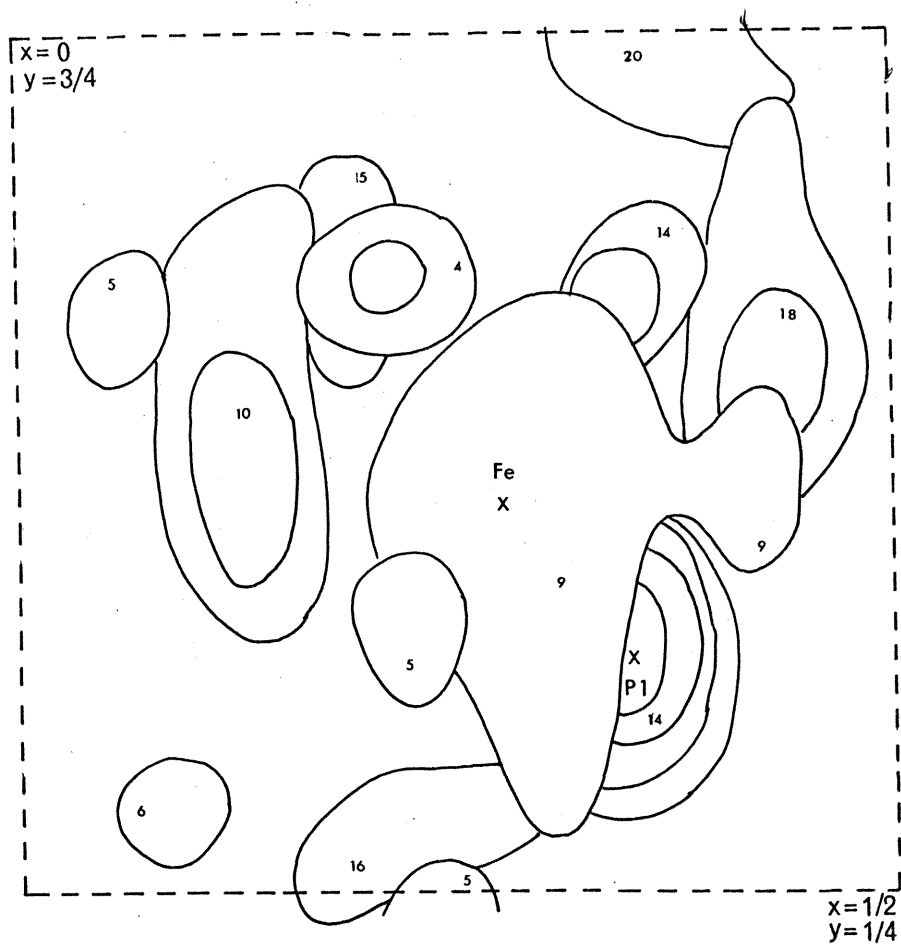


Figure 2.5.2

Projection down z of $F(\text{obs})$ map at cycle 3. Input atoms marked x ; contours at intervals of $0.8 \text{ e}/\text{\AA}^3$ (lowest at $0.8 \text{ e}/\text{\AA}^3$). z heights (84ths) shown in small type.

(0.021 and 0.095), and a high R value. (See Table 1)

The Fe-P distance from the F(obs) map calculated on these planes was 1.82 \AA ; there were pseudo-mirror effects about $y=0$ but there were other peaks round the Fe atom. Although the positions of these seemed chemically reasonable, the overall appearance of the map was very ill-defined. (See Figure 2). The scale was very high, so that the Fe integrated peak height was only $8\frac{1}{2} \text{ e/\AA}^3$, P1 was $3\frac{3}{4} \text{ e/\AA}^3$. Two of the highest peaks were chosen as P atoms:-

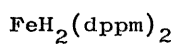
Peak	<u>x</u>	<u>y</u>	<u>z</u>	<u>Fe-peak</u>	<u>Height</u>
P2	0.348	-0.099	0.171	2.37	$2\frac{1}{4}$
P3	0.217	-0.101	0.053	2.42	2

After three cycles (4-6), the refinement had not reduced R, and Fe had a negative U (-0.036). The geometries were also somewhat uncertain:-

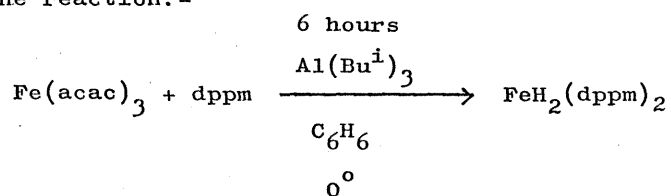
	<u>After Cycle 5</u>	<u>After Cycle 6</u>
Fe-P1	1.36	1.29
Fe-P2	2.55	2.63
Fe-P3	2.68	2.61
P1-Fe-P2	83°	87°
P1-Fe-P3	168°	157°
P2-Fe-P3	98°	93°

At this point it was decided that further refinement would be pointless, unless better data became available,

and so this structure was abandoned.



Very small crystals of $\text{FeH}_2(\text{dppm})_2$ were obtained by the reaction:-



These were red hexagonal plates and photography gave the following cell data:-

$$\begin{array}{ll} a = 18.54 \text{ \AA} & \beta = 90^\circ \\ b = 10.08 & \\ c = 22.52 & P2_1/c \end{array}$$

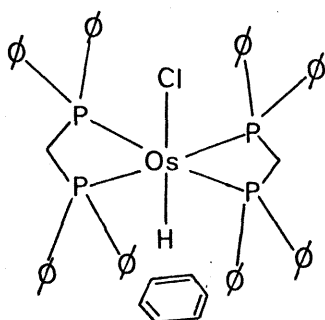
However, in common with the other dihydrides, the photographs were very weak indeed, and after the failure to solve the structure of $\text{FeH}_2(\text{dpp})_2$, it seemed unlikely that this complex would provide better data, so the problem was abandoned.

CHAPTER 2.6

THE PREPARATION AND CHARACTERISATION OF TRANS- OsHCl(dppm)_2 AND TRANS- $\text{OsH}_2(\text{dppm})_2$

The trans- MX(PP)_2 hydrides, where $\text{M} = \text{Ru, Os}$;
 $\text{X} = \text{Cl, Br, I, CN}$; PP = bidentate ditertiary phosphine,
 can be prepared from the corresponding cis- $\text{MX}_2(\text{PP})_2$
 complexes by LiAlH_4 reduction.⁵⁸ The osmium complexes
 tend to be more stable thermally than the ruthenium
 complexes, but less stable in air; they also show a
 tendency to solvate, particularly with benzene. In the
 case of trans- OsHCl(dppm)_2 , where dppm is $\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{PPh}_2$,
 the characteristic Os-H stretching vibration at $\sim 2000\text{ cm}^{-1}$
 was reported to be completely suppressed when the complex
 was crystallised from benzene. It appeared that one
 molecule of solvent was bound in some way to the hydride
 complex, as it could not be removed except under vigorous
 conditions. (50% remained even after evacuation at 100°
 for 48 hours, after which a weak $\nu(\text{Os-H})$ band appeared at
 2077 cm^{-1} .) With ethyl acetate as solvent, no abnormal
 behaviour was noted.

This suggested the possibility that a weak steric inter-
 action is taking place, whereby the benzene in some manner
 'blocks' movement of the hydridic hydrogen and hence
 partially suppresses the Os-H vibration. This could be
 caused by tight locking of ligand phenyl groups trapping
 the benzene molecule:-



If current theories of transition metal catalysis are correct, and a sigma-pi equilibrium is a vital part of many mechanisms, then one might expect a continuous gradation in structure from:-

1. metal hydride cis to a σ -bonded carbon in
e.g. $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, through
2. π -bonded complexes, e.g. $\text{Cr}(\text{CO})_3 \cdot \text{C}_6\text{H}_6$,¹¹⁶ to
3. complexes which contain benzene or toluene of crystallisation, where the aromatic molecule is entirely independent of the complex, e.g. $\text{RhI}_2\text{Me}(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_6$,¹¹⁷
e.g. $\text{IrCl}(\text{CO})_2(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_6$ ¹¹⁸

The anomalous properties of $\text{OsHCl}(\text{dppm})_2$ suggested that a structure analysis might be worthwhile, giving information about the extreme case of a very weak ring-hydride interaction, on the borderline between 2 and 3.

Experimental Work

The preparation was repeated, by S D Ibekwe and myself, following Chatt and Watson's method,¹¹⁹ and it was soon realised that the product depends critically on the exact amount of excess LiAlH_4 used in the final reduction. The reaction scheme is shown in Figure 1.

$[\text{Os}_2\text{Cl}_4(\text{Et}_2\text{PhP})_6]$ was prepared by adding the phosphine in EtOH to the dark red solution of ammonium chlorosmate in water. The mixture was refluxed for 6 hours by which time the solution had turned yellow. The product came down overnight; washing in petroleum ether removed any excess phosphine, followed by washing with benzene. The second stage is a dry reaction between (dppm) and the osmium salt, in a Schlenck tube under nitrogen. A brown colour developed at $\sim 140^\circ\text{C}$: otherwise the only visible indication of reaction was condensation of (PEt_2Ph) on the sides of the tube. The mixture fused at 200° , and after cooling, excess phosphine was removed with petroleum ether; the pale yellow feathery crystals were recrystallised from nitrobenzene, and washed with MeOH. The far IR spectrum showed two broad bands due to cis chlorines. The reduction was performed in dry THF under nitrogen, using 2x excess LiAlH_4 . The crude product showed a band at $\sim 2070\text{ cm}^{-1}$. Recrystallisation from EtOAc gave fine yellow needles, mpt. $273-274^\circ$, with sharp bands for $\nu(\text{Os-H})$ at 2074 cm^{-1} , $\nu(\text{C}\equiv\text{O})$ at 1735 cm^{-1} and $\nu(\text{acetate})$ at $1235, 1048\text{ cm}^{-1}$. The other portion, after recrystallisation from benzene, gave

$$\begin{array}{ccc} (\text{OsCl}_6)(\text{NH}_4)_2 & \xrightarrow{\text{PEt}_2\text{Ph}} & \left[(\text{PEt}_2\text{Ph})_3 - \text{Os} \begin{array}{c} \diagup \text{Cl} \diagdown \\ \diagdown \text{Cl} \diagup \end{array} - \text{Os} - (\text{PEt}_2\text{Ph})_3 \right] \text{Cl} \\ & & \downarrow \text{dppm} \\ \text{tr-OsHCl(dppm)}_2 & \xleftarrow[\text{THF}]{\text{LiAlH}_4} & \text{Cis-OsCl}_2(\text{dppm})_2 \end{array}$$

Analytical Figures for Osmium Complexes

			<u>found</u>			<u>calc.</u>		
			C	H	Cl	C	H	Cl
OsHCl(dppm) ₂ · ½C ₆ H ₆	C ₅₃ H ₄₈ OsP ₄ Cl		61.8	4.75	4.17	61.6	4.7	3.44
OsDC1(dppm) ₂ · ½C ₆ H ₆	C ₅₃ H ₄₇ DOsP ₄ Cl		61.5	4.78	3.13	61.6	4.7	3.44
OsHCl(dppm) ₂ · ½EtOAc	C ₅₂ H ₄₉ OsP ₄ ClO		60.1	4.92	3.25	60.1	4.75	3.42
OsH ₂ (dppm) ₂	C ₅₀ H ₄₆ OsP ₄		63.1	4.92	-	62.5	4.8	-
OsHCl(dppm) ₂ · C ₆ H ₆	C ₅₆ H ₅₁ OsP ₄ Cl		62.3*	4.9*		62.7	4.75	3.31
OsHCl(dppm) ₂	C ₅₀ H ₄₅ OsP ₄ Cl					60.3	4.52	3.57

(* determined by Chatt and Hayter)

large yellow prismatic needles mpt. $286-288^{\circ}$ with a single sharp band for $\nu(\text{Os-H})$ at 2088 cm^{-1} . There were no indications of any bands due to benzene in this spectrum; the intense normal frequencies should be present, only very slightly shifted, if there is an interaction with the metal.¹²⁰ The far IR of both ethylacetate and benzene solvates showed three bands, at 40.0 , 42.0 , 43.5μ . The NMR showed $\delta(\text{Os-H}) = 27\tau$ (quintet) with $J(\text{P-H}) = 15\text{ cps.}$, typical of coupling to four equivalent phosphorus atoms cis to hydride. The phosphorus methylene resonances appeared at 6.5τ and the phosphorus phenyls at $2.4-3.2\tau$. The corresponding deuteriochloride was also prepared, using LiAlD_4 as reducing agent to test Chatt's suggestion¹²¹ that the 2088 cm^{-1} band might be a benzene vibration.

On recrystallisation from benzene, pale yellow crystals of $\text{trans-OsDCl(dppm)}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$, mp. 280° , were obtained. $\nu(\text{Os-D}) = 1494\text{ cm}^{-1}$. The ratio $\nu(\text{Os-H})/(\text{Os-D}) = 1.398$ which is close to the theoretical value of $\sqrt{2}$.

If a large (tenfold) excess of LiAlH_4 is used (as in our early attempts to reproduce Chatt and Hayter's results), pale yellow brittle hexagons of $\text{trans-OsH}_2(\text{dppm})_2$ mp. 255° , are formed with $\nu(\text{Os-H})$ at 1712 cm^{-1} . This was confirmed by preparation of the dideuteride, $\text{trans-OsD}_2(\text{dppm})_2$ mp. 226° , $\nu(\text{Os-D})$ at 1228 cm^{-1} . ($\nu(\text{Os-H})/(\text{Os-D}) = 1.394$). A trans assignment is probable from the occurrence of only one Os-H stretching frequency;

this is thought to be the first preparation of

$\text{OsH}_2(\text{dppm})_2$ and compares with $\text{trans-OsH}_2(\text{Et}_2\text{P-oC}_6\text{H}_4\text{-PEt}_2)$ which has $\nu(\text{Os-H})$ at 1720 cm^{-1} . No NMR spectrum could be obtained because of the insolubility of the dihydride in C_6D_6 or DMSO. Analytical details for the various complexes are summarised in Table 1.

The original work reported anomalous behaviour which our work has shown to be incorrect.¹²² Possibly Chatt and Hayter obtained a different solvate, with 1 molecule C_6H_6 , which did have $\nu(\text{Os-H})$ suppressed; however, their analytical figures are not significantly different from ours (see Table 1). We can therefore re-affirm the generalisation that $\nu(\text{M-H})$ is always observed for metal-hydrogen bonds, unless it is masked by $\nu(\text{C}\equiv\text{O})$ or $\nu(\text{N}\equiv\text{N})$.

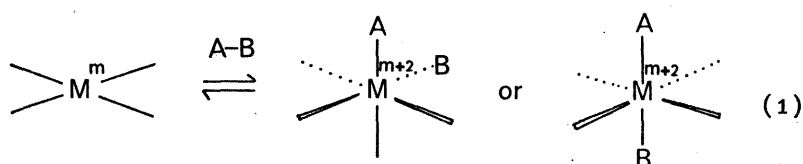
However, the corollary to this is that the complex was no longer directly relevant to X-ray studies on catalytically interesting hydrides. Although the structure might show cis effects due to hydride ligands, a full structure analysis was not undertaken. The crystals of $\text{OsHCl}(\text{dppm})_2$ were, however, photographed and found to be orthorhombic; $a = 21.10\text{ \AA}$, $b = 10.05\text{ \AA}$, $c = 42.46\text{ \AA}$.

CHAPTER 2.7

THE CRYSTAL AND MOLECULAR STRUCTURE OF

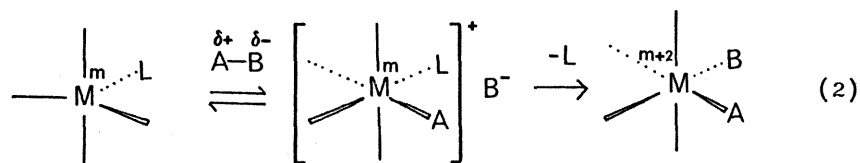
TRANS-(Ir(H)(COOMe)(dmpe)₂)BPh₄

The important step of activation may take place by addition of a substrate molecule to a metal in a low formal oxidation state. Coordinatively unsaturated planar d^8 complexes add polar or homonuclear molecules e.g. H_2 , HCl , O_2 , C_2H_4 , to give d^6 complexes (in the case of addition of O_2 , C_2H_4 , the complex remains formally d^8 .)¹²³



The products may be either cis or trans.

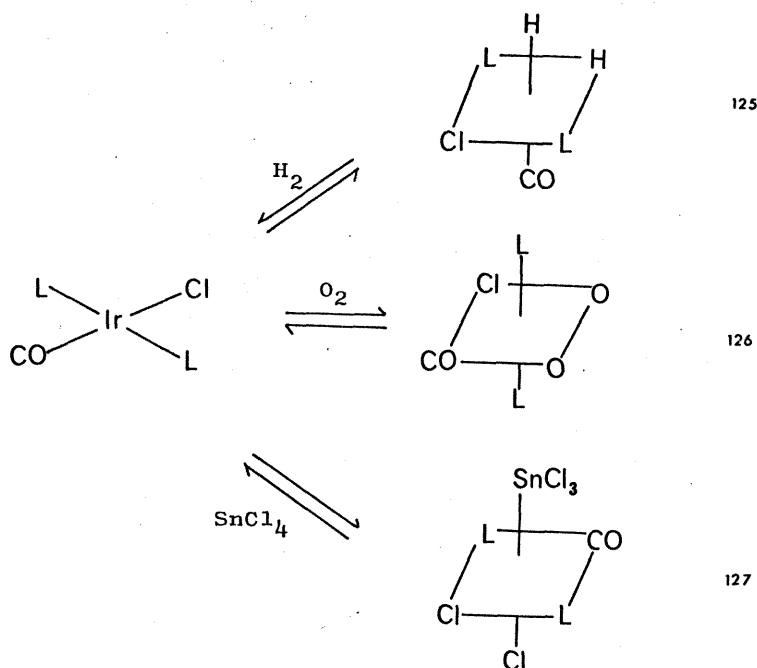
Coordinatively saturated 5-coordinate complexes add polar molecules either by a two-step mechanism:-



or by initial dissociation (by heat or light), to form

a reactive 4-coordinate complex. The products are always cis.

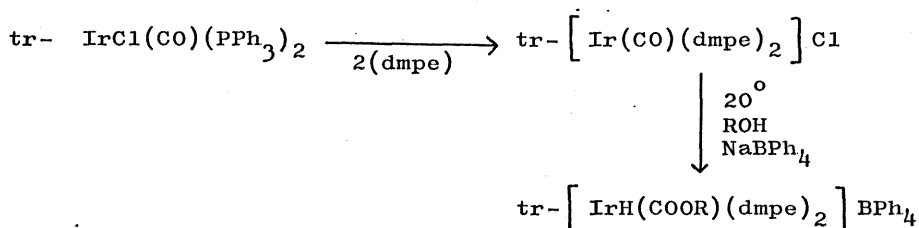
This type of reaction is commonly referred to as oxidative addition. Reactions of type 1 have been exhaustively studied particularly with Vaska's compound, ¹²⁴ IrCl(CO)(PPh₃)₂, which is a typical Ir(I) complex, e.g. (L = PPh₃):-



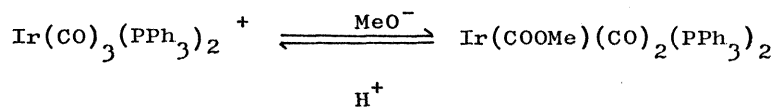
After oxidative addition has occurred, the complex now contains a substrate molecule which is in an activated condition ready for further reaction. For example, hydrogenation of olefins is favoured by initial formation of a hydride. This may be derived

from H_2 gas,¹²⁵ acids,¹²⁸ alcohols,¹²⁹ silanes¹³⁰ etc, but when an alcohol (ROH) is the source, true oxidative addition does not occur and only the hydrogen appears in the adduct, not the OR.

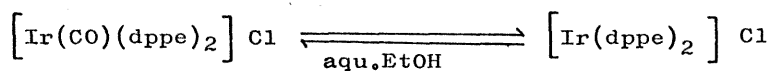
The addition of alcohols to $[\text{Ir}(\text{CO})(\text{dmpe})_2] \text{Cl}$ by a type 2 reaction is the first reported example¹³¹ where both H and OR become coordinated. This was discovered during research in the Petrochemical and Polymer Laboratory into the reactions of coordinated dmpe,¹³² since this ligand is known (see Chapter 2.2) to enhance the activity of metals to oxidative addition. The reaction is:-



This may be contrasted with the more usual reactions of iridium to form carboalkoxy compounds which do not yield hydrides, e.g.:-¹³³



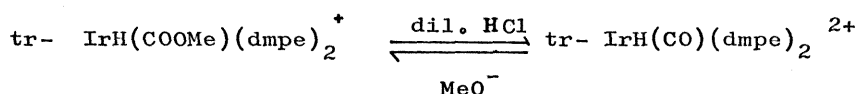
dmpe is the only phosphine known to cleave alcohols in this manner; with the dppe analogue the reaction is:-¹³²



and this difference may be due, as in the case of $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, to the increased electron density on the metal atom, which could be dispersed into ligand orbitals by increasing the oxidation state and coordination number.

Properties

The complex $[\text{IrH}(\text{COOMe})(\text{dmpe})_2] (\text{BPh}_4)$, mpt. 180° , is stable towards base, but reacts with acids:-



The origin of the hydridic hydrogen was confirmed by deuteration. The IR spectrum has strong bands, $\nu(\text{Ir-H})$ at 1960 cm^{-1} , and $\nu(>\text{C=O})$ at 1625 cm^{-1} .

The NMR shows the phosphine methyls at 8.2τ , methylenes at 7.8τ , ester protons at 6.8τ , and the BPh_4 protons at $2.7 - 3.2\tau$ with $J(\text{H-H})$ 7 cps.

The hydridic hydrogen appears as a quintet of bands at 25.5τ with $J(\text{P-H})$ 18 cps. which is characteristic of hydride cis to phosphorus. The proposed structure was therefore a trans carbomethoxy hydride. This has been confirmed by the structural analysis.

Preliminary Observations

White, platey crystals of $[\text{IrH}(\text{COOMe})(\text{dmpe})_2] \text{BPh}_4$ were prepared by S D Ibekwe. The analogous BF_4 or PF_6 complexes could not be obtained crystalline;

possibly a bulky anion is necessary for the formation of good crystals. The crystals were thin and brittle; they showed slight pleochroism even under ordinary light, and extinguished polarized light in two perpendicular directions. Preliminary photographs showed the symmetry to be orthorhombic, and that the space group absences were consistent with two space groups; $Pna2_1$ (No.33) and $Pnma$ (No.62) if the indices are suitably interchanged. $Pna2_1$ is noncentric, and in general has four molecules in the unit cell. The cell volume is $\sim 4000 \text{ \AA}^3$ and so one unit would occupy just less than 1000 \AA^3 . $Pnma$ is a centric space group with eight general positions. This did not seem to provide enough space per molecule. If the molecular unit had a mirror plane or centre, then $z = 4$, but this was known to be impossible. The space group $Pna2_1$ was therefore chosen.

Crystal Data

$C_{38}H_{56}IrP_4O_{12}B$, $M = 871.3$; orthorhombic, $a = 12.752 \pm 0.006$, $b = 31.852 \pm 0.012$, $c = 9.988 \pm 0.006 \text{ \AA}$,
 $U = 4057.0 \text{ \AA}^3$, $D_m = 1.45$ (floatation) $Z = 4$,
 $D_c = 1.43$, $F(000) = 1768$, Space Group $Pna2_1(C_2^9; \text{no.33})$,
 Mo-K α radiation (Nb filter), $\lambda = 0.71070 \text{ \AA}$,
 $\mu = 37.5 \text{ cm}^{-1}$.

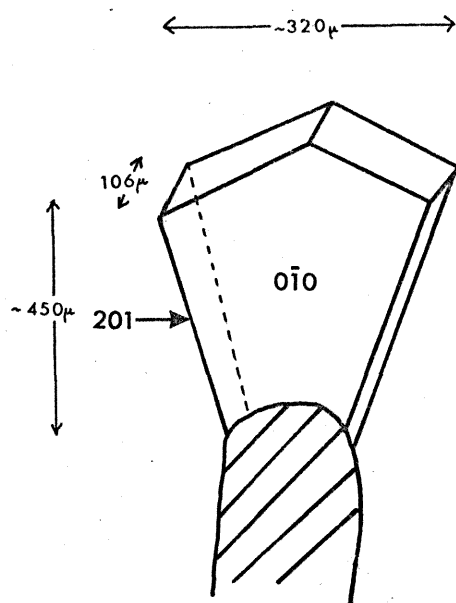


Figure 2.7.1a
 $\text{IrH}(\text{COOMe})(\text{dmpe})_2^+ \cdot \text{BPh}_4^-$ Crystal 1

The Equations of the Bounding Surfaces
of Crystal 1

	l	m	n	p	(hkl)
1	0.2283	0.0275	0.9732	224.90	
2	-0.4208	0.8895	0.1780	183.95	
3	-0.7585	0.4790	-0.4418	141.62	
4	0.7026	-0.6965	-0.1459	180.99	201
5	0.0084	-0.3308	-0.9437	264.58	
6	0.5923	0.8022	-0.0747	53.34	$0\bar{1}0$
7	-0.5922	-0.7981	0.1108	53.69	010

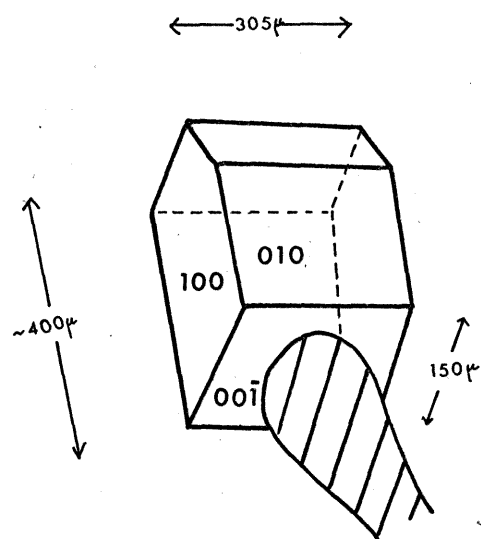


Figure 2.7.1b

 $\text{IrH}(\text{COOMe})(\text{dmpe})_2^+ \cdot \text{BPh}_4^-$ Crystal 2

 The Equations of the Bounding Surfaces
of Crystal 2

	l	m	n	p	(hkl)
1	-0.6507	0.3078	-0.6941	231.89	
2	0.4662	-0.1689	-0.8684	155.23	
3	-0.6124	-0.3331	0.7170	150.40	
4	0.8376	0.0113	0.5461	175.92	
5	0.1051	-0.9945	0.0030	103.65	
6	0.2652	0.9486	0.1726	83.45	$0\bar{1}0$
7	-0.2136	-0.9671	-0.1382	66.01	010

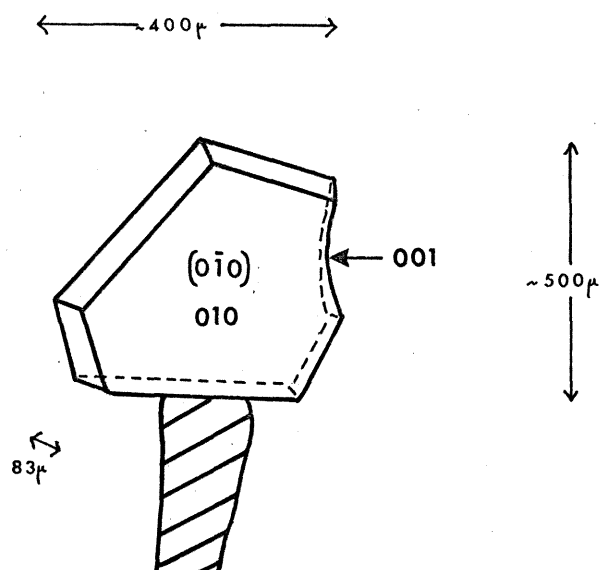


Figure 2.7.1c
 $\text{IrH}(\text{COOMe})(\text{dmpe})_2^+ \cdot \text{BPh}_4^-$ Crystal 3

The Equations of the Bounding Surfaces
of Crystal 3

	l	m	n	p	(hkl)
1	0.0204	-0.9728	-0.2308	202.11	001
2	-0.9140	-0.2090	-0.3476	41.59	010
3	0.9102	0.2563	0.3253	41.73	0 $\bar{1}$ 0
4	-0.2202	0.8539	0.4715	206.83	
5	-0.3548	0.3934	-0.8482	208.17	
6	-0.0566	-0.1470	-0.9875	207.15	
7	-0.1871	-0.4475	0.8745	288.00	

Data Collection

Temperature R.T; scan range -0.4° to $+0.5^{\circ}$;
 Scan speed $2^{\circ} 2\theta/\text{minute}$; fixed time 15 seconds;
 Standards (0 0 6) and (0 18 2); maximum $2\theta = 60^{\circ}$;
 cell dimensions from 7 reflections (28 measurements)
 giving angles $\alpha = 89.99(5)^{\circ}$, $\beta = 90.01(5)^{\circ}$,
 $\gamma = 90.09(4)^{\circ}$; total number of independent
 structure amplitudes obtained after data reduction
 and collation of equivalent reflections 4256.

Data collection was complicated by the fact that
 the crystals decomposed under molybdenum irradiation,
 and so three crystals were necessary. The first
 (X1) lasted for 24 hours, decomposing slowly at
 first, then very rapidly. It turned orange but
 remained transparent. The second crystal (X2)
 decomposed more gradually over $2\frac{1}{2}$ days. The third
 crystal (X3) survived till all the data had been
 collected (ten days); details of the size and shape
 of crystals are given in Figures 1a-c. Seven
 reflections from the first crystal were used to
 obtain the cell dimensions. The reflections (0 0 6)
 and (0 18 2) were used for scaling; their
 intensities fell by 11%, 11% and 25% during the
 respective periods of data collection.

Chirality of Crystals

As $\text{Pna}2_1$ is a polar space group I originally intended

preserving the distinction between hkl and $\bar{h}\bar{k}\bar{l}$ for each crystal, in order to allow for the effect of Δf on the structural parameters. However, this was clearly unrealistic since the results from three rather unhealthy crystals would certainly not be accurate enough to justify this. It was noted, however, that there were detectable differences, on photographs, between $\frac{1}{2}(0\ 5\ 5)$ $(0\ 2\ 2)$ $(0\ 5\ 3)$ $(0\ 3\ 7)$ and, by measuring these accurately in all four quadrants, that the original choice of axes for X2 was the inverse of those for X1, i.e. $hkl(2) = \bar{h}\bar{k}\bar{l}(1)$. The reasons for not preserving the handedness were:-

1. The decomposition was different for each crystal (worst for X3).
2. The awkward shape of the crystals (very platey) would result in an inaccurate absorption correction.
3. The three crystals may not all be of the same hand - it could be incorrect to assume that they are all the same.

Scaling of the Data

Friedel's Law was therefore assumed to hold. In order to scale the three sets of data, the measurements common to all three sets were corrected for L_p factors and absorption:-

<u>Crystal</u>	<u>Volume</u> (cm ³)	<u>Mesh</u> (cm)	<u>No. of Points</u>
X1	1.61×10^{-5}	0.004	208
X2	2.01×10^{-5}	0.003	491
X3	1.72×10^{-5}	0.004	216

The corrected amplitudes were next compared for the three crystals, and it was apparent that for the undecomposed crystals, if all values for X1 were multiplied by 1.08 and all for X3 by 1.07, they would be comparable to those for X2. Also, the ratios of totals, for 1:2, and for 2:3 checked, as did 3:1. (ratio = $1.01 \approx 1.08/1.07$). Comparison of the anomalous pairs measured at the end of each crystal's life showed that there was no need to correct for decomposition for X1 and X2, and that slightly more decomposition had occurred with X3, i.e. at the end of data collection the ratio 2:3 = 1.065. Scale factors were thus applied to the complete data (raw intensities) as follows:-

- (a) for X1 no correction;
- (b) for X2 all intensities multiplied by $1/1.08^2 = 0.876$;
- (c) for X3 all intensities multiplied by $1/1.01^2 = 0.980$;

and L_p and absorption corrections were applied to all measurements.

Solution and Refinement of Structure

Formfactors for Iridium and phosphorus were corrected for $\Delta f'$. The Patterson of $\text{Pna}2_1$, which has equivalent positions:-

$$\begin{array}{ccc} x & y & z \\ -x & -y & \frac{1}{2} + z \\ \frac{1}{2} - x & \frac{1}{2} + y & \frac{1}{2} + z \\ \frac{1}{2} + x & \frac{1}{2} - y & z \end{array}$$

contains Harker planes at:-

$$\begin{array}{ccc} \frac{1}{2} & \frac{1}{2} \pm 2y & 0 \\ \pm 2x & \pm 2y & \frac{1}{2} \\ \frac{1}{2} \pm 2x & \frac{1}{2} & \frac{1}{2} \end{array}$$

z is indeterminate, therefore all that need be calculated are the two sections at $z = 0, \frac{1}{2}$. Three peaks appeared, consistent with an Ir position at $(0.2115, 0.1398, 0)$, and so this position was refined, cycles 1 - 3 (see Table 1). The z coordinate was held constant throughout the analysis.

An $F(\text{obs})$ map computed over a cube of 5\AA edge, centred on the Ir position, contained a pseudo-mirror plane at $z = 0$, all peaks appearing at $+z$ and also $-z$. Weaker ghost peaks also appeared at symmetrical positions round the Ir atom, at $x = \text{Ir} - a_1$, $y = a_2$, $z = -a_3$, where a genuine peak is probably at $x = \text{Ir} + a_1$, $y = a_2$, $z = a_3$. There were several possible P atom positions, of which two

TABLE 2.7.1(a)
Refinement of the structure of $\text{IrH}(\text{COOMe})(\text{dmpe})_2 \cdot \text{BPh}_4$

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Ir	P	Matrix type	Alk.	BPh ₄	Ir	P	Vibrations	C(p)	Alk.	BPh ₄	Weighting used
1-3	449	min.amp.40 min.amp./ deviation 15	18.8	Ir	b	-	-	-	-	i	-	-	-	-	-	1
4-6	859	min.amp.30	15.5	Ir,P1,P2	b	b	-	-	-	i	i	-	-	-	-	1
7-9	2039	min.amp.15	14.2	Ir,P1-P4	b	b	-	-	-	i	i	-	-	-	-	1
10-12	2039	min.amp.15	11.3	Ir,P1-P4,B, 2 rings	pb(1)	pb(1)	-	-	b(1)	a	a	-	-	-	i	1
13	2039	min.amp.15	10.6		pb(1)	pb(1)	b(3)	-	b(1) b(2)	a tb(1)	a tb(1)	i	-	-	i	1
14	2039	min.amp.15	9.9	all atoms	pb(1)	pb(1)	b(1) b(2)	b(7)	b(3)- b(6)	a tb(1)	a tb(1)	i	i	i	i	1

Matrix types: b = full block
pb = positional block
tb = vibrational block
tbd} = block diagonals
pbd}
C(p) = C(phosphine)
Alk = COOMe group

Thermal parameters: a = anisotropic
i = isotropic

TABLE 2.7.1(b)
Refinement of the structure of $\text{IrH}(\text{COOMe})(\text{dmpe})_2 \cdot \text{BPh}_4$

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Matrix type				Vibrations				Weighting used	
					Ir	P	C(p)	Alk. BPh ₄	Ir	P	C(p)	Alk. BPh ₄		
15	2039	min.amp.15	6.4	all atoms, ring 4 altered	pb(1)	pb(1)	b(1) b(2)	b(7)	b(3)- b(6)	a tbd	i tbd	i i	i i	c ₁ = 147 c ₂ = 0 (2)
16	2039	min.amp.15	4.5	all atoms, ring 4 altered	pb(1)	pb(1)	b(1) b(2)	b(7)	b(3)- b(6)	a tbd	i tbd	i i	i i	2
17	3169	min.amp.8	6.2	all atoms	pb(1)	pb(1)	b(1) b(2)	b(7)	b(3)- b(6)	a tbd	i tbd	i i	i i	2

Matrix types: b = full block
pb = positional block
tbd} = block diagonals
pbd}

C(p) = C(phosphine)
Alk = COOMe group

Thermal parameters: a = anisotropic
i = isotropic
Final scale = 2.36 (cycle 17)

were chosen, both on $z \sim 0$. P1 was given a small negative z value, P3 a small positive z , and cycles 4 - 6, and an $F(\text{diff})$ map were calculated. The strong ghosts mirrored by $z = 0$ still came up, but not the weaker ones. P2 and P4 were assigned negative and positive z values respectively, by choosing the stronger of the two peaks in each case. On refining these positions, R was reduced to 14.2% after three cycles (7 - 9). An $F(\text{diff})$ map computed over the entire asymmetric unit still had pseudo mirror symmetry, but two rings and the P1 - P2 bridge appeared clearly. From this stage Ir and P atoms were refined anisotropically, and at $R = 10.6\%$ (cycle 13), an $F(\text{diff})$ map showed the carbomethoxy group and its ghost. Refinement was continued, including all atoms (see table), but the geometry of one of the borate rings remained irregular. This was attributed to insufficient data, (2039 out of a possible 4256 terms), and so one cycle (17) was calculated on 3169 terms. The distorted ring immediately refined to a reasonable configuration, at an R value of 6.2%. On the final $F(\text{diff})$ map, small peaks were observed, associated with carbon atom anisotropy, but none of these were higher than $2 \text{ e}/\text{\AA}^3$. One peak, of height $0.4 \text{ e}/\text{\AA}^3$ appeared 1.5\AA from Ir. Although this was near the expected position for the hydridic hydrogen, the

ratio of peak height to background was not significant. The unobserved reflections were calculated; none were greater than twice the minimum observed.

Results and Discussion

The final positional and vibrational parameters are shown in the Appendix in Tables 2 and 3; the molecular geometry is listed in Table 4. The only carbon-carbon inter-molecular contact less than 3.5\AA is that between C23 and C135 (3.42\AA). The final agreement analysis is listed in Table 5. Figure 2 shows the geometry of the cation, Figure 3 that of the anion (these also indicate the numbering system used), and Figure 4 shows the inter-molecular packing.

The ions in the complex are quite separate. The cation has the trans-hydride-carbomethoxy structure predicted from the trans addition of MeOH across $[\text{Ir}(\text{CO})(\text{dmpe})_2] \text{Cl}$. The stereochemistry round iridium is only slightly distorted from octahedral if one assumes the hydride position trans to the COOMe group, the slight deviations from 90° and 180° being associated with the usual effect of a small ligand, i.e. all four Ir-P bonds are bent towards the hydride position by 2° - 3° . The equation of the plane through the four P atoms is:-

$$7.88x + 16.21y - 5.99z - 3.75 = 0$$

the maximum deviation from this being 0.02\AA . (Ir lies 0.10\AA out of this plane.)

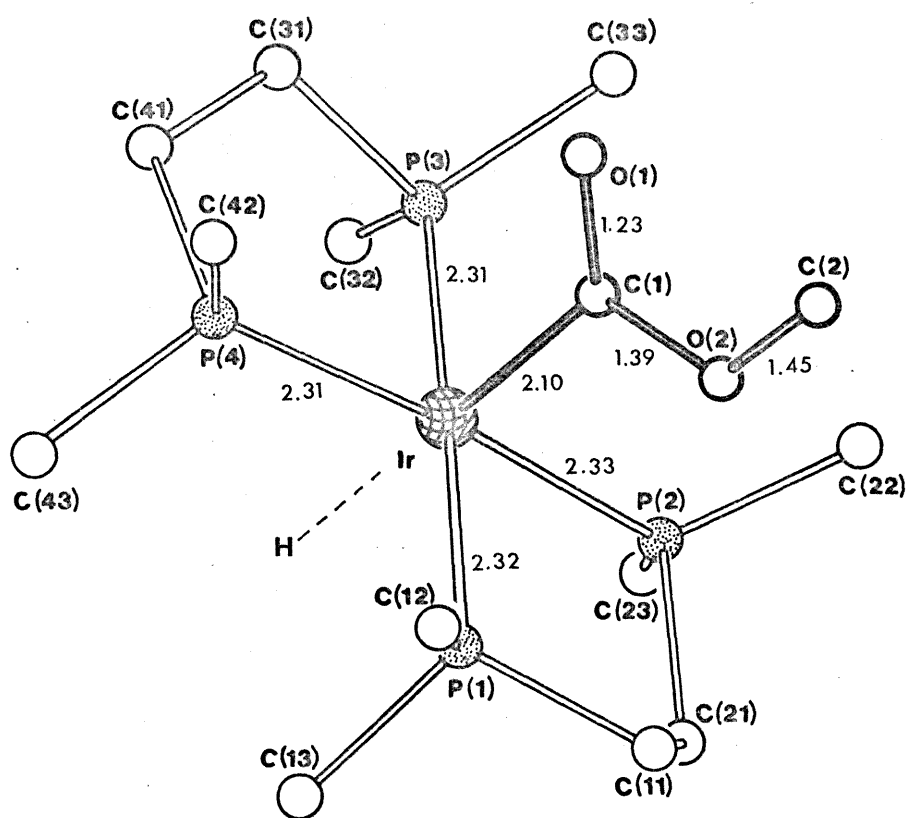


Figure 2.7.2

View of $\text{IrH}(\text{COOMe})(\text{dmpe})_2^+$, illustrating the numbering system and the geometry round iridium.

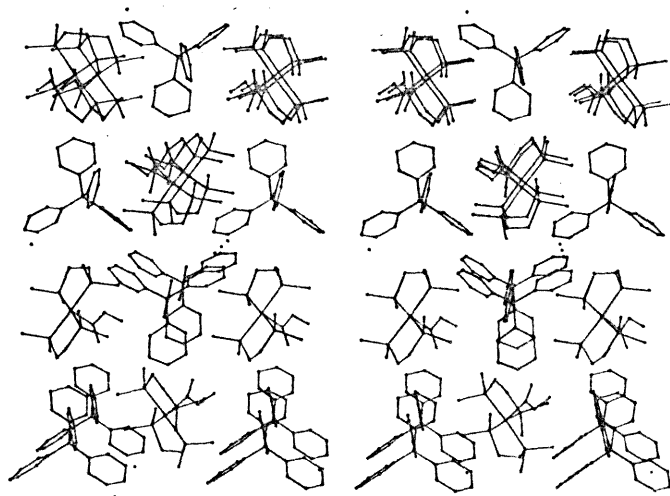


Figure 2.7.4

Stereo drawing of the packing viewed down z axis

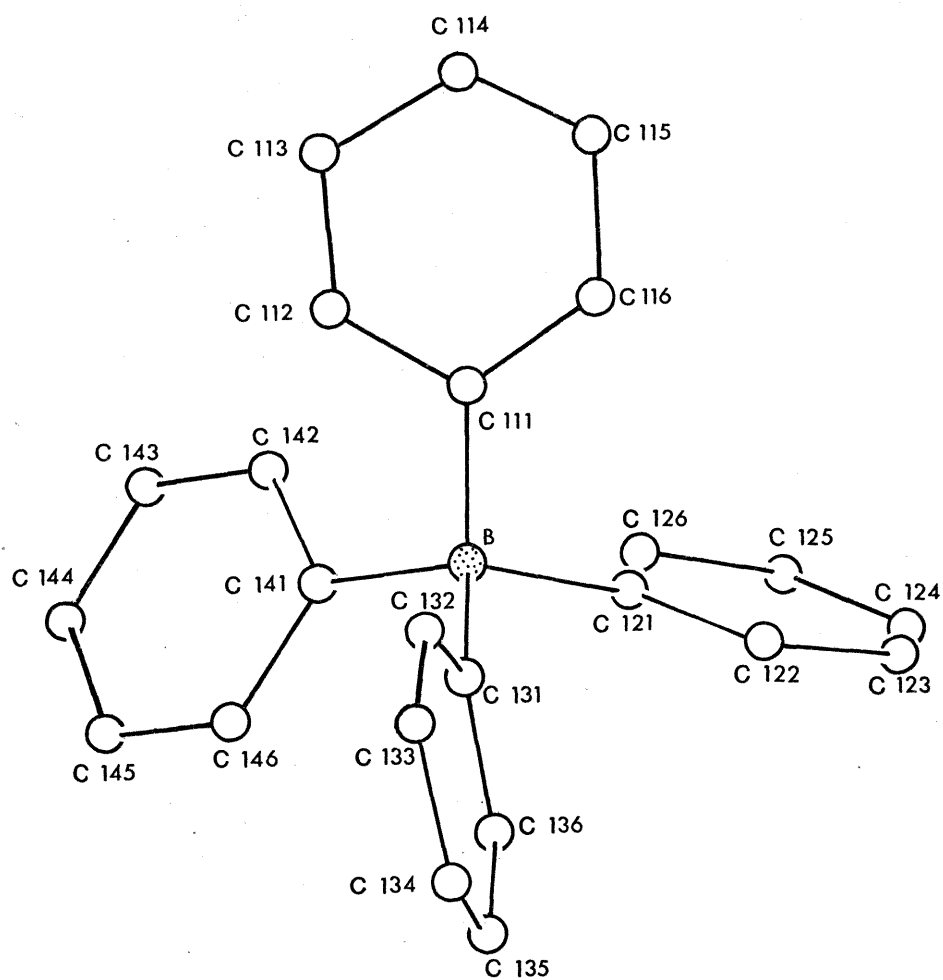
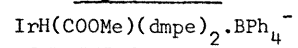


Figure 2.7.3



View of BPh_4^- , showing the numbering system used.

Table 2.7.4

Bond distances (\AA) and angles ($^\circ$), with their estimated standard deviations

Around Iridium

Ir-P(1)	2.318(4)	P(1)-Ir-P(2)	83.3(2)
Ir-P(2)	2.326(6)	P(1)-Ir-P(3)	176.1(2)
Ir-P(3)	2.308(5)	P(1)-Ir-P(4)	96.1(3)
Ir-P(4)	2.306(8)	P(1)-Ir-C(1)	91.9(6)
Ir-C(1)	2.098(22)	P(2)-Ir-P(3)	96.3(2)
		P(2)-Ir-P(4)	173.9(2)
		P(2)-Ir-C(1)	93.5(7)
		P(3)-Ir-P(4)	83.9(3)
		P(3)-Ir-C(1)	92.1(6)
		P(4)-Ir-C(1)	92.6(7)

Phosphine Groups

P(1)-C(11)	1.87(3)	Ir-P(1)-C(11)	108.2(8)
P(1)-C(12)	1.85(2)	Ir-P(1)-C(12)	119.4(7)
P(1)-C(13)	1.85(3)	Ir-P(1)-C(13)	115.5(9)
P(2)-C(21)	1.85(3)	Ir-P(2)-C(21)	107.6(11)
P(2)-C(22)	1.84(4)	Ir-P(2)-C(22)	119.1(11)
P(2)-C(23)	1.86(4)	Ir-P(2)-C(23)	118.3(13)
P(3)-C(31)	1.81(3)	Ir-P(3)-C(31)	108.9(10)
P(3)-C(32)	1.86(4)	Ir-P(3)-C(32)	117.3(11)
P(3)-C(33)	1.92(4)	Ir-P(3)-C(33)	116.7(12)
P(4)-C(41)	1.75(5)	Ir-P(4)-C(41)	109.4(17)
P(4)-C(42)	1.87(3)	Ir-P(4)-C(42)	121.8(11)
P(4)-C(43)	1.90(5)	Ir-P(4)-C(43)	115.6(15)
C(11)-P(1)-C(12)	108.1(16)	C(31)-P(3)-C(32)	104.3(15)
C(11)-P(1)-C(13)	105.4(13)	C(31)-P(3)-C(33)	102.9(14)
C(12)-P(1)-C(13)	99.3(14)	C(32)-P(3)-C(33)	105.2(16)
C(21)-P(2)-C(22)	107.3(15)	C(41)-P(4)-C(42)	102.9(18)
C(21)-P(2)-C(23)	103.1(15)	C(41)-P(4)-C(43)	106.4(22)
C(22)-P(2)-C(23)	99.9(17)	C(42)-P(4)-C(43)	99.1(18)
C(11)-C(21)	1.43(4)	P(1)-C(11)-C(21)	108.3(21)
C(31)-C(41)	1.48(5)	P(2)-C(21)-C(11)	111.9(22)
		P(3)-C(31)-C(41)	111.0(25)
		P(4)-C(41)-C(31)	116.5(32)

Carbomethoxy Group

C(1)-O(1)	1.23(3)	Ir-C(1)-O(1)	128.0(19)
C(1)-O(2)	1.39(3)	Ir-C(1)-O(2)	117.8(15)
C(2)-O(2)	1.45(3)	O(1)-C(1)-O(2)	113.8(21)
		C(1)-O(2)-C(2)	120.7(19)

Table 2.7.4 (contd.)

Bond distances (\AA) and angles ($^\circ$), with their estimated standard deviations

Tetraphenylboron Group

B-C(111)	1.68(4)	C(111)-B-C(121)	107.8(19)
B-C(121)	1.67(4)	C(111)-B-C(131)	107.3(19)
B-C(131)	1.66(4)	C(111)-B-C(141)	107.8(19)
B-C(141)	1.62(3)	C(121)-B-C(131)	109.9(19)
		C(121)-B-C(141)	111.2(19)
		C(131)-B-C(141)	112.6(18)
C(111)-C(112)	1.41(3)	C(121)-C(122)	1.43(3)
C(112)-C(113)	1.47(4)	C(122)-C(123)	1.39(4)
C(113)-C(114)	1.42(4)	C(123)-C(124)	1.40(4)
C(114)-C(115)	1.32(4)	C(124)-C(125)	1.33(3)
C(115)-C(116)	1.49(3)	C(125)-C(126)	1.42(3)
C(116)-C(111)	1.38(3)	C(126)-C(121)	1.45(4)
B-C(111)-C(112)	122.0(22)	B-C(121)-C(122)	119.9(22)
B-C(111)-C(116)	123.8(22)	B-C(121)-C(126)	121.3(21)
C(112)-C(111)-C(116)	114.2(22)	C(122)-C(121)-C(126)	118.7(22)
C(111)-C(112)-C(113)	125.4(24)	C(121)-C(122)-C(123)	118.0(26)
C(112)-C(113)-C(114)	114.7(26)	C(122)-C(123)-C(124)	122.7(29)
C(113)-C(114)-C(115)	123.8(33)	C(123)-C(124)-C(125)	120.2(28)
C(114)-C(115)-C(116)	118.2(29)	C(124)-C(125)-C(126)	121.7(27)
C(111)-C(116)-C(115)	123.3(24)	C(121)-C(126)-C(125)	118.5(26)
C(131)-C(132)	1.42(3)	C(141)-C(142)	1.41(3)
C(132)-C(133)	1.34(6)	C(142)-C(143)	1.39(4)
C(133)-C(134)	1.44(5)	C(143)-C(144)	1.37(4)
C(134)-C(135)	1.38(4)	C(144)-C(145)	1.39(5)
C(135)-C(136)	1.44(4)	C(145)-C(146)	1.40(4)
C(136)-C(131)	1.41(3)	C(146)-C(141)	1.44(3)
B-C(131)-C(132)	124.6(19)	B-C(141)-C(142)	122.8(22)
B-C(131)-C(136)	118.7(20)	B-C(141)-C(146)	121.7(20)
C(132)-C(131)-C(136)	116.6(23)	C(142)-C(141)-C(146)	115.4(22)
C(131)-C(132)-C(133)	123.8(22)	C(141)-C(142)-C(143)	123.9(26)
C(132)-C(133)-C(134)	120.4(27)	C(142)-C(143)-C(144)	120.2(29)
C(133)-C(134)-C(135)	117.9(32)	C(143)-C(144)-C(145)	118.3(31)
C(134)-C(135)-C(136)	121.4(28)	C(144)-C(145)-C(146)	122.8(29)
C(131)-C(136)-C(135)	119.8(27)	C(141)-C(146)-C(145)	119.3(23)

The Ir-P bonds (average 2.31\AA) are all significantly shorter than is generally found in Ir phosphine complexes (see Table 6). However, most reported Ir structures contain Ir(I), also there are no reports of Ir-P(alkyl) bonds, nor are there any rhodium alkyl phosphine complexes for comparison. With the exception of $[\text{Ir}(\text{O}_2)(\text{dppe})_2] \text{PF}_6^{134}$ and $\text{IrH}(\text{CO})(\text{PPh}_3)_2 - (\text{fumarodinitrile})^{21}$ both of which involve back bonding from Ir to a pi-bonded system, and in which the shortness of the Ir-P bonds may be attributed to a general flow of electron density into the $\text{M}-\text{C}\equiv\text{N}$ bond, the average Ir-P distance is about 2.36\AA . (However, a recent determination of Ir-P in a TCNE complex gives 2.40\AA).¹³⁵ In the present complex, the short distances may be related to the higher electron density maintained at the metal atom, by dmpe, and therefore available for back-bonding to phosphorus. In ligands such as dppe or PPh_3 , the excess electron density is delocalised among the phenyl groups.

The two phosphine systems have 'bites' of 83° and 84° and adopt the conformation often observed in complexes of bidentate phosphines, i.e. one C(methylene) atom - (C21 and C41) - of each phosphine lies almost in the equatorial plane, while the other - (C11 and C31) - lies further from the plane. This conformation has been calculated for ethylenediamine complexes,¹³⁶ to be as stable as the symmetrical arrangement with all C(methylene) atoms displaced equal amounts from the metal-nitrogen plane, and this is borne out by structural analyses (see Table 2 of reference 136). This same flexibility of the

TABLE 2.7.6(a)

Ir-P and Ir-C(carbonyl) Distances

	<u>Ir-P</u>	<u>Ir-C</u>	<u>Reference</u>
$\text{IrH}(\text{COOMe})(\text{dmpe})_2^+$	2.31	(2.10)	
$\text{IrCl}(\text{CO})(\text{O}_2)(\text{PPh}_3)_2$	2.36, 2.38	disordered	a
$\text{IrCl}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$	2.36, 2.33	1.96	b
$\text{IrCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2^+$	2.41	1.86	c
$\text{IrCl}(\text{CO})_2(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_6$	2.32, 2.34	2.04 (disordered)	d
$\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$	2.37, 2.38	1.83, 1.86	e
$\text{IrH}(\text{CO})(\text{CN} \cdot \text{CH} : \text{CH} \cdot \text{CN})(\text{PPh}_3)_2$	2.32	1.98	f
$\text{IrBr}(\text{CO})(\text{TCNE})(\text{PPh}_3)_2$	2.40	disordered	f
$\text{Ir}(\text{CO})(\text{TCNE})_2(\text{PPh}_3)_2$	2.40	1.79	g
$\text{IrI}(\text{CO})(\text{O}_2)(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$	2.39	disordered	h
$\text{IrI}(\text{CO})(\text{NO})(\text{PPh}_3)_2^+$	2.35, 2.37	1.70	i
$\text{Ir}(\text{NO})_2(\text{PPh}_3)_2^+$	2.34	-	j

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TABLE 2.7.6(b)

Ir-P and Ir-C(carbonyl) Distances

	<u>Ir-P</u>	<u>Ir-C</u>	<u>Reference</u>
$\text{Ir}(\text{dppe})_2^+$	2.27-2.33	-	k
$\text{Ir}(\text{O}_2)(\text{dppe})_2^+$	2.28-2.45	-	l
$\text{Ir}(\text{CO})(\text{dppe})_2^+$	2.35-2.39	1.82	m
$\text{Ir}(\text{CO})(\text{dppm})_2^+$	2.32-2.41	1.81	n
$(\text{NO})(\text{PPh}_3)\text{Ir}-\text{O}-\text{Ir}(\text{PPh}_3)(\text{NO})$	2.31	-	o
$\text{Ir}_2\text{Cl}_4\text{Me}_2(\text{CO})_4$	-	1.74, 1.76	p
$\text{IrI}_2(\text{CO})(\text{COOMe})(\text{bipy.})$	-	1.80	q

k. B T Kilbourn, unpublished data

l. J A McGinnety, N C Payne & J A Ibers, JACS, 1969, 91, 6301

m. J A J Jarvis et al., Chem.Comm., 1966, 906


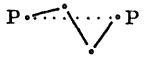
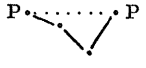
n. B T Kilbourn & A M Wood, unpublished data

o. P Carty et al., JCS(D), 1969, 1374

p. N A Bailey et al., Chem.Comm., 1967, 1051

q. V G Albano, P L Bellon & M Sansoni, Inorg.Chem., 1969, 8, 298

5-membered ring system is observed in complexes of chelating diphosphines; the exact equilibrium conformation appears to be governed by packing considerations, the only constant factor being the torsion angle $\tau(\text{C-C})$ about the central C-C bond. This is generally less than the ideal staggered 60° , ranging from 45° to 55° . $\tau(\text{M-P})$ and $\tau(\text{P-C})$ vary over a wide range. The only instance of the totally symmetrical arrangement $\tau(\text{M-P1}) = \tau(\text{P2-M})$ is in the complex $\text{ReH}_3(\text{PPh}_3)_2(\text{dppe})$ ¹¹⁵ where there is only one diphosphine and therefore presumably there are no steric reasons for a distortion. The various possible configurations are:-

1.  $\tau(\text{M-P1}) = \tau(\text{P2-M})$
both same sign e.g. $\text{ReH}_3(\text{PPh}_3)_2(\text{dppe})$ ¹¹⁵
2.  $\tau(\text{M-P1}) > \tau(\text{P2-M})$
both same sign e.g. $\text{IrH}(\text{COOMe})(\text{dmpe})_2$ ⁺
3.  $\tau(\text{M-P1}) > \tau(\text{P2-M})$
opposite signs e.g. $\text{RuCl}_2(\text{PhMeP} \cdot \text{C}_2\text{H}_4 \cdot \text{PMePh})_2$ ¹³⁷

The commonest arrangements are 2 and 3 (see Table 7 and Table 9 of Chapter 3.2). In the present complex, (Case 2), both $\tau(\text{C-C})$ have the same sign; this corresponds, other factors being constant, to the most favourable steric arrangement of two trans diphosphine ligands.

Angles round coordinated phosphorus tend to vary widely from tetrahedral, because of non-bonded interactions

Table 2.7.4

Selected Torsion Angles ($^{\circ}$), positive values
indicating clockwise rotation

P(1)-C(11)-C(21)-P(2)	+50
P(3)-C(31)-C(41)-P(4)	+36
Ir-C(1)-O(2)-C(2)	-173
O(1)-C(1)-O(2)-C(2)	+ 1
O(1)-C(1)-Ir-P(1)	-137
B-C(111)-C(112)-C(113)	-178
B-C(121)-C(122)-C(123)	-177
B-C(131)-C(132)-C(133)	-178
B-C(141)-C(142)-C(143)	-177

Table 2.7.7

Torsion Angles ($^{\circ}$) in dmpe Complexes

	$\tau(\text{M-P})$	$\tau(\text{P-C})$	$\tau(\text{C-C})$	$\tau(\text{C-P})$	$\tau(\text{P-M})$
$\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	+22	-43	+44	-28	- 1
	- 2	+22	-25	+17	- 9
$\text{OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	-25	+51	-52	+34	- 2
	- 7	+32	-40	+33	-11
$\text{IrH}(\text{COOMe})(\text{dmpe})_2^+$	+14	-41	+50	-38	+ 8
	+ 3	-31	+36	-25	+13

(+ corresponds to δ
 - corresponds to λ)

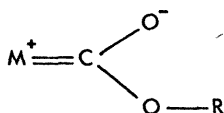
on the convention defined in: Inorg.Chem., 1970, 9, 1)

between the different substituents. In the present example these angles range from 99° to 122° , and there is also considerable variation in P-C bond lengths. The average, 1.865\AA , is long compared to most measured phosphine P-C(sp^3) bonds, but is close to the theoretical radius sum ($1.10 + 0.77\text{\AA}$). Usually these, and also P-C(sp^2) bonds, are about 1.83\AA . The C-C bonds in each ligand (1.43 and 1.48\AA) are shorter than in complexes of dppe. This seems to be a feature of dmpe - compare C-C bonds of 1.50 and 1.44\AA in $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$ with 1.58 and 1.60\AA in $[\text{Ir}(\text{dppe})_2]\text{Cl}$.

Pauling gives an Ir(III) octahedral radius of 1.32\AA .¹³⁸ However, studies on Ir-C(σ) bonds suggest that the true radius is longer than this.

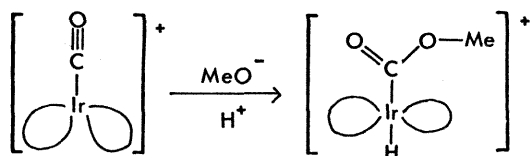
Complex	Ir-C	derived Ir radius		reference
$\text{Ir}(\text{CO})\text{I}_2(\text{COOMe})(\text{bipy})$	2.05(2)	1.31	sp^2	139
$\text{IrH}(\text{COOMe})(\text{dmpe})_2^+$	2.10(2)	1.36	sp^2	-
$\text{Ir}(\text{Me}_2\text{SO})_2\text{Cl}_2(\text{C}_{15}\text{H}_{13}\text{O})$	2.16(2)	1.39	sp^3	140
$\text{Ir}_2\text{Cl}_4\text{Me}_2(\text{CO})_4$	2.10	1.33	sp^3	141

The Ir-C bonds in the two carbomethoxy complexes are probably not pure sigma bonds, because of contributions from the form:-



(In $\text{IrH}(\text{COOMe})(\text{dmpe})_2^+$ the hydridic hydrogen may exert a trans weakening influence which would explain the longer bond length.) The most reasonable Ir(III) radius is therefore likely to be $1.36 - 1.39\text{\AA}$.

The Ir-C bond is $\sim 0.3\text{\AA}$ longer than an average Ir-C (carbonyl) bond (see Table 6). It is interesting to speculate on the mechanism of the reaction:-

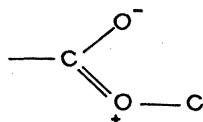


Since the structure of $\text{Ir}(\text{CO})(\text{dmpe})_2^+$ is unknown the closest analogues are $\text{Ir}(\text{CO})(\text{dppe})_2^+$ ⁷⁶ and $\text{Ir}(\text{CO})(\text{dppm})_2^+$ ¹⁴². In both these complexes, there is considerable distortion away from regular geometry. This may be necessary to accommodate phenyl groups.

$\text{Ir}(\text{CO})(\text{dmpe})_2^+$ would probably be quite stable in a square pyramidal form.

In fact a compromise might be achieved, with phosphine groups bent away from the CO position, but not so close that entry of hydrogen is prevented, as it is with dppe and dppm. (These will not even form dihydrides, whereas $\text{Rh}(\text{dmpe})_2^+$ adds H_2 to form $\text{cis-RhH}_2(\text{dmpe})_2$.)¹⁴³ Possibly $\text{Ir}(\text{CO})(\text{dmpe})_2^+$ has a geometry somewhat similar to $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$, with hydride removed and CO taking the place of C_{10}H_7 . In any case, the formation of $\text{IrH}(\text{COOMe})(\text{dmpe})_2^+$ should be easy sterically.

The geometry within the ester group is normal compared both to organic and complexed COOMe (see Table 8), the methyl group and ketonic oxygen O1 being cis to one another. There are no close contacts to force it out of the planar configuration which is generally adopted, since this allows a contribution from the form:-



The torsion angles Ir-C1-O2-C2 and O1-C1-O2-C2 are 173° and 0° respectively. The ester grouping in this complex is well separated from the phosphine methyls, and has a staggered relationship to the phosphine ligands, e.g. $(\text{O1-C1-Ir-P1}) = -137^\circ$. Since $\text{IrH}(\text{COOMe})(\text{dppe})_2^+$ cannot be isolated, this may also be partly a result of the steric limitations of dppe.

The vacant position trans to the carbomethoxy group is certainly occupied by the hydridic hydrogen; none of the methyl groups approaches close to this hole, so there is no reason to expect much distortion away from the expected position. From the only observed Ir-H bond, in $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ ¹⁴⁴, the distance is assumed to be in the range 1.65 to 1.7 \AA . The peak on the final F(diff) map tends to suggest a shorter bond length, but the evidence is not substantial.

TABLE 2.7.8

Ester Geometries

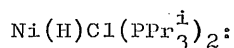
	<u>C₁=O</u>	<u>C₁-O</u>	<u>O-C₂</u>	<u>Reference</u>
IrH(COOMe)(dmpe) ₂ ⁺	1.23	1.39	1.45	
IrI ₂ (CO)(COOMe)(C ₁₀ N ₂ H ₈)	1.18	1.28	1.48	a
Co(CH ₂ COOMe)(C ₅ H ₅ N)(N ₂ C ₄ O ₂) ₂	1.22	1.34	1.46	b
(MeOOC) ₂ C-C(COOMe) ₂	1.19	1.32	1.45	c
MeOOC-COOMe	1.19	1.31	1.46	d
Me-COOMe	1.22	1.36	1.46	e

- a. V G Albano, P L Bellon & M Sansoni, Inorg.Chem., 1969, 8, 298
- b. P G Lenhert, Chem.Comm., 1967, 980
- c. J P Schaefer & C R Costin, J.Org.Chem., 1968, 33, 1677
- d. M W Dougill & G A Jeffrey, Acta Cryst., 1953, 6, 831
- e. J M O'Gorman, W Shand & V Schomaker, JACS, 1950, 72, 4222

As in $(\text{Ir}(\text{O}_2)(\text{dppe})_2)\text{PF}_6$ ¹³⁴ and $(\text{Ir}(\text{CO})\text{Cl}(\text{NO})(\text{PPh}_3)_2)\text{BF}_4$ ¹⁴⁵, the anion plays no part in the coordination about the metal; it is drawn in Figure 3. It has a regular geometry. The economical way in which BPh_4 completes the crystal packing may explain the lack of success in crystallizing the present complex with other, smaller anions, e.g. BF_4 , PF_6 . There is no evidence of disorder, as there sometimes is with smaller spherically symmetrical anions, e.g. in $\text{Fe}(\text{N}(\text{C}_2\text{H}_4\text{N}=\text{CHC}_5\text{H}_4\text{N})_3)(\text{BF}_4)_2$ ¹⁴⁶ and in $(\text{IrI}(\text{CO})(\text{NO})(\text{PPh}_3)_2)\text{BF}_4 \cdot \text{C}_6\text{H}_6$ ¹⁴⁷.

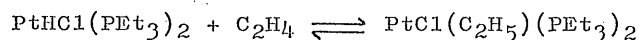
CHAPTER 2.8

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRANS-

CELL DATA FOR TRANS-Ni(Me)Cl(PPr₃ⁱ)₂

Although platinum hydrides are very stable and palladium hydrides moderately stable, their nickel analogues have proved difficult to isolate. For example, NiHCl(PPr₃ⁿ)₂ is unstable.¹⁴⁸ This instability was attributed to the general trend for first row complexes to be less stable than their second or third row analogues, until NiHCl(PPr₃ⁱ)₂¹⁴⁹ and NiHCl(P(cyclohexyl)₃)₂¹⁵⁰ were prepared. It then became evident that the reason for the instability of NiHCl(PPr₃ⁿ)₂ might be partly steric. In a complex containing bulky phosphines attack along the z axis (perpendicular to the molecular plane) is hindered, as is rearrangement to a tetrahedral configuration which would be more susceptible to attack. Other stable nickel hydrides have since been discovered, also containing bulky phosphines.¹⁵¹

Ni-H bonds, also Ni-C(σ) bonds, are almost certainly involved in nickel catalysed dimerisations of olefines,³⁵ and it is possible that a reaction analogous to:-



takes place.⁵⁴ Nickel complexes are also involved in hydrosilylation¹⁵² and dienylation¹⁵³ catalysts. There are

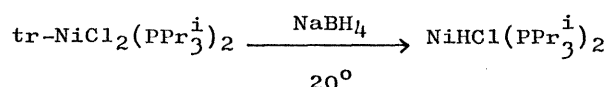
no reports of structural studies on nickel complex hydrides and so the effect of an Ni-H bond on other bonds in the molecule is unknown. Consequently it seemed that a structural analysis of one of these stable hydrides would be valuable. All published, reliable M-H bond lengths fall in a very narrow range, regardless of the metal involved; a slightly shorter Ni-H distance would be predicted from summing covalent radii, and so it was hoped that a crystal structure determination would show whether this constancy of M-H distances is fortuitous or not.

No M-H distances are known for any of the platinum group. However, Pd-H and Pt-H bonds are known to exert significant trans weakening influences on Pd-C1 and Pt-C1 bonds, and this influence probably extends to nickel. Workers in the Petrochemical and Polymer Laboratory have studied the crystal structures of two nickel isopropyl phosphine complexes ($\text{trans-NiCl}_2(\text{PPr}_3^i)_2$ and $\text{trans-Ni(SCN)}_2(\text{PPr}_3^i)_2$)¹⁵⁴ and so $\text{NiHCl}(\text{PPr}_3^i)_2$ was chosen for detailed study.

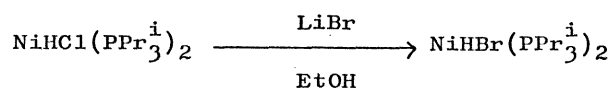
Crystals of the methide-chloride $\text{trans-Ni(Me)Cl}(\text{PPr}_3^i)_2$ were also examined and photographed. Unfortunately the complex is exceedingly unstable; the crystals decomposed rapidly, even in capillary tubes, so no detailed analysis was possible.

Preliminary Observations

Cherry red crystals of $\text{tr-NiHCl}(\text{PPr}_3^i)_2$ were kindly prepared by T Saito in Oxford, by the reaction (performed under argon):-



(The Br and I analogues can be easily prepared by displacement of Cl);



The crystals (m.pt. $65-67^\circ\text{C}$) show $\nu(\text{Ni-H})$ at 1937 cm^{-1} , $\delta(\text{Ni-H})$ 34.3τ , $J(\text{P-H})$ 77.8 cps . They were large hexagonal prisms up to 1 mm . across, and were mounted with silicone grease in argon filled capillary tubes. The crystal used for data collection is shown in Figure 1.

Crystal Data

$\text{C}_{18}\text{H}_{43}\text{NiP}_2\text{Cl}$, $M = 415.3$; monoclinic, $a = 16.350 \pm 0.007$, $b = 8.961 \pm 0.002$, $c = 15.904 \pm 0.003\text{ \AA}$, $\beta = 93.73 \pm 0.03^\circ$, $U = 2325.1\text{ \AA}^3$, $D_m \approx 1.13$ (difficult to measure because of decomposition in air), $Z = 4$, $D_c = 1.167$, $F(000) = 904$, Space Group $P2_1/c$, (C_{2h}^5 ; no. 14), Mo- $K\alpha$ radiation (Nb filter), $\lambda = 0.71070\text{ \AA}$, $\mu = 10.62\text{ cm}^{-1}$.

Data Collection

Temperature -70°C ; scan range -0.55° to $+0.55^\circ$;
Scan speed $2^\circ 2\theta/\text{minute}$; fixed time 20 seconds;
Standards (0 1 7) and (0 6 5) both falling to 94%
of initial intensity; reflections measured in

octants $\{hkl\}$ and $\{hk\bar{l}\}$, to a maximum

$$2\theta = 27.7^\circ;$$

total number of independent structure amplitudes obtained after data reduction and collation of equivalent reflections 5125.

The crystal was unfortunately lost in an explosion which occurred when the cold sphere was accidentally allowed to warm up, so it was not possible to measure the dimensions for absorption corrections. The cell dimensions are also approximate, as the accident occurred before they had been accurately measured.

Structure Solution and Refinement

Formfactors for Ni, P, Cl were corrected for $\Delta f'$.

The Patterson (calculated on 346 terms $>50\sigma$ on initial scaling) gave a nickel position of (0.25 0.0089 0.0052). After two cycles of refinement of this position (see Table 1), an $F(\text{obs})$ map was computed, and this produced four peaks of approximately the same height, in a square-planar arrangement around Ni. This was because of its special position in the cell ($y = z \sim 0$). Since it was impossible at this stage to decide which were genuine, two peaks in a cis configuration were chosen, and structure factors calculated. These were refined as phosphorus atoms (cycles 3 and 4), and at $R=34\%$ an $F(\text{obs})$ map showed which was a phosphorus and which a chlorine atom. The refinement was therefore continued

TABLE 2.8.1

Refinement of the structure of $\text{NiHCl}(\text{PPR}_3)_2$

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Ni	P	Cl	C	H(p)	Ni	P	Cl	C	H(p)	Vibrations	Weighting used
1,2	1026	min.amp.30	40.5	Ni	b	-	-	-	-	i	-	-	-	-	-	1
3,4	1026	min.amp.30	29.0	Ni,"P1,P2"	b	b	-	-	-	i	i	-	-	-	-	1
5,6	1946	min.amp.20 min.amp./ deviation 5	6.4	all atoms	pb(1)	pb(1)	pb(1)	b(1) b(2)	-	a	a	a	i	-	tb(1) tb(1) tb(1)	1
7,8	1946	min.amp.20 min.amp./ deviation 5	5.5	all atoms	pb(1)	pb(1)	pb(1)	b(1) b(2)	-	a	a	a	i	-	tb(1) tb(1) tb(1)	$c_1 = 40$ $c_2 = 0$ (2)
9	3243	min.amp./ deviation 10	7.0	all atoms + hydrogens	pb(1)	pb(1)	pb(1)	pb(1) pbd	c	a	a	a	i	i	tb(1) tb(1) tb(1) c	2

Matrix types:

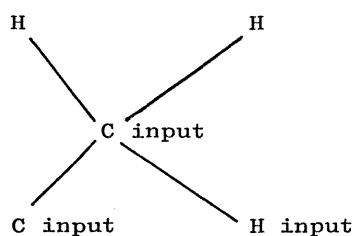
b = full block
 pb = positional block
 tb = vibrational block
 tbd} = block diagonals
 pbd}
 c = contribution only
 H(p) = H(propyl)

Thermal parameters:

a = anisotropic
 i = isotropic
 c = constant
 Final scale = 1.07 (cycle 8)
 Final convergence factor = 0.069 (cycle 8)

with the correct labelling of atoms, and two cycles (5 and 6) reduced R to 6.4%, on all atoms. A weighting scheme was now applied with constants $c_1 = 40$ and $c_2 = 0$, and after cycles 7 and 8 R was 5.5%.

The F(diff) map calculated on these planes showed the H(propyl) atoms clearly; in order to obtain the best geometry about each carbon, the position of the highest H peak was chosen in each case, and used to calculate the positions of the remaining two:-



The hydrogen on the α -carbon in each propyl group was similarly calculated. In all cases the calculated positions were at, or very near, the observed positions. Structure factors and one cycle of refinement (cycle 9), using the calculated H positions, were computed. This was a more approximate refinement, as block diagonals were used for all atoms except hydrogens, which were added as constant contributions. R was 7.0% and the corresponding F(diff) map showed areas of electron density near some of the carbon and H(propyl) peak positions of height $\sim 0.3 \text{ e/\AA}^3$. Apart from two peaks

of height $\sim 1 \text{ e}/\text{\AA}^3$ (one near H23 and one in an empty part of the cell), the highest peak (peak 1) was near the nickel (height $0.7 \text{ e}/\text{\AA}^3$, and 1.37\AA away) at $(0.256 \text{ } -0.085 \text{ } -0.050)$. This was almost trans to the chlorine position (Cl-Ni-Peak = 177°); another peak (peak 2), $\sim 2.56 \text{\AA}$ away from the Ni position, also appeared. This was height $0.5 \text{ e}/\text{\AA}^3$, and 1.2\AA away from peak 1. To ascertain whether these peaks were genuine or spurious, a series of $F(\text{diff})$ maps was calculated, in a similar manner to those computed for $\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$. For these maps the calculated planes at $R=7.0\%$ were used, i.e. structure factors were not calculated for each separate set of data. At the lowest resolution (maximum $\sin \theta / \lambda = 0.3$) the two peaks 1 and 2 merged together, but at all higher resolutions the nearer of the two remained consistently higher than the farther one, and constant in position:-

<u>Resolution</u>	<u>Height($\text{e}/\text{\AA}^3$)</u>		<u>Ni-H(\AA)</u>
	<u>Peak 1</u>	<u>Peak 2</u>	
all data	0.66	0.52	1.37
0.6	0.64	0.54	1.37
0.5	0.62	0.48	1.37
0.4	0.52	0.35	1.37
0.3	0.33		

Assuming that Peak 1 represents the hydride scattering, the derived Ni-H distance is 1.4\AA .

The unobserved reflections were calculated (those with amplitude $< 2\sigma$, and amplitude: deviation < 5); all were sensibly small.

Results and Discussion

Final positional and vibrational parameters are listed in the Appendix (Tables 2 and 3). The molecular geometry is given in Table 4, and Table 5 lists the agreement analysis at $R=5.5\%$. A drawing of one molecule is shown in Figure 2 with the numbering system used, and a stereo drawing of the crystal packing in Figure 3.

The structure consists of discrete molecules with the closest non-hydrogen contacts C1-C25 3.65; C16-C21 3.63; C22-C28 3.62 $\overset{\circ}{\text{A}}$. The nickel and coordinated atoms form a nearly regular square plane, the maximum deviation from the plane through Ni, C1, P1, P2:-

$$15.11x + 2.46y - 5.15z - 3.79 = 0$$

being 0.01 $\overset{\circ}{\text{A}}$. The Ni-P distances (average 2.193 $\overset{\circ}{\text{A}}$), are considerably shorter than in other square planar Ni(II) complexes - see Table 6. Though in other Ni(II) geometries, e.g. 5 coordinate and octahedral, a wide variety of Ni-P bond lengths is observed, in tetrahedral and square planar Ni these are generally in the range 2.25 - 2.28 $\overset{\circ}{\text{A}}$. (These are all trans

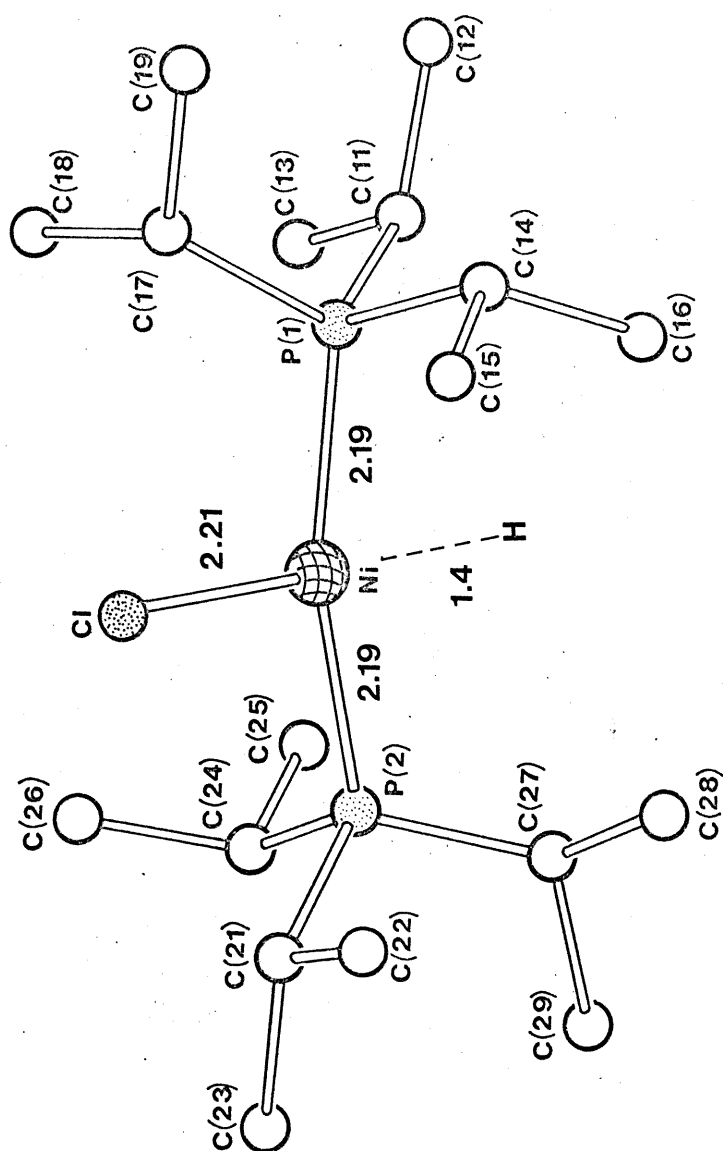


Figure 2.8.2
 $\text{NiHCl}(\text{PPR}_3)_2$

View of one molecule, illustrating the numbering system and the geometry round nickel.

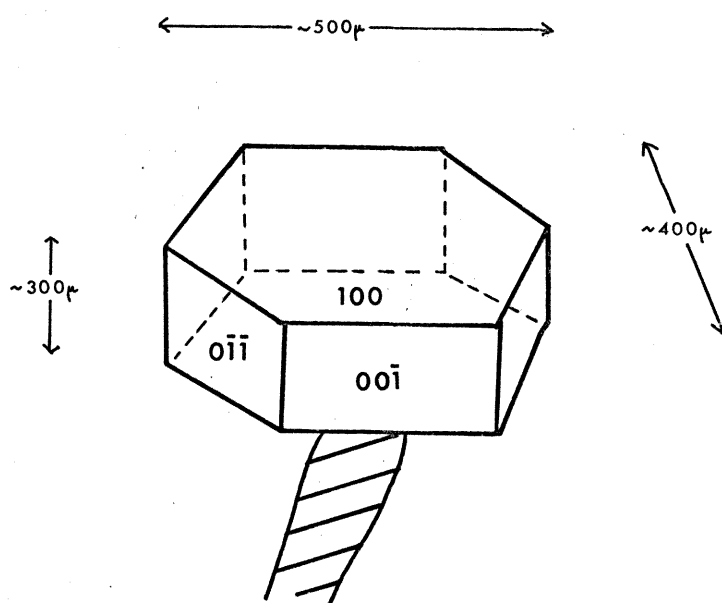


Figure 2.8.1
 $\text{NiHCl}(\text{PPr}_3^i)_2$ Crystal

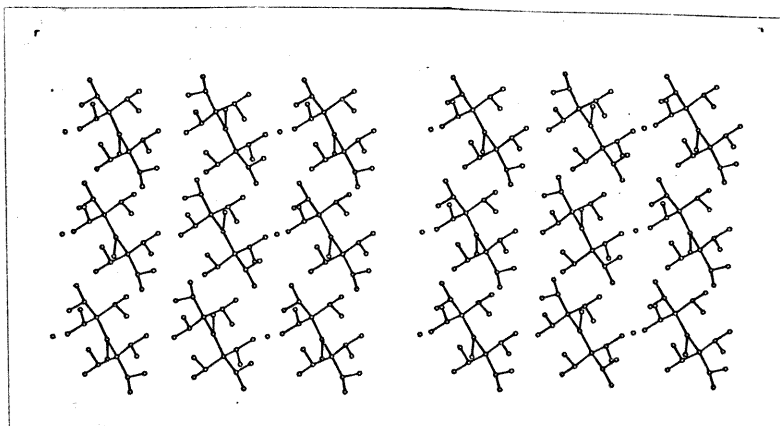


Figure 2.8.3
 $\text{NiHCl}(\text{PPr}_3^i)_2$

Stereo drawing of the packing viewed down y axis.

Bond distances (\AA) and angles ($^\circ$), with their
estimated standard deviations

Around Nickel

Ni-P(1)	2.193(2)	P(1)-Ni-P(2)	163.5(1)
Ni-P(2)	2.192(2)	P(1)-Ni-Cl	98.3(1)
Ni-Cl	2.207(2)	P(2)-Ni-Cl	98.2(1)

Phosphine Groups

P(1)-C(11)	1.86(1)	Ni-P(1)-C(11)	113.7(3)
P(1)-C(14)	1.85(1)	Ni-P(1)-C(14)	110.3(3)
P(1)-C(17)	1.87(1)	Ni-P(1)-C(17)	114.6(3)
C(11)-C(12)	1.56(1)	Ni-P(2)-C(21)	112.9(3)
C(11)-C(13)	1.54(1)	Ni-P(2)-C(24)	110.5(3)
C(14)-C(15)	1.56(1)	Ni-P(2)-C(27)	114.1(3)
C(14)-C(16)	1.56(1)	C(11)-P(1)-C(14)	103.3(4)
C(17)-C(18)	1.52(2)	C(11)-P(1)-C(17)	110.8(4)
C(17)-C(19)	1.55(1)	C(14)-P(1)-C(17)	102.9(4)
P(2)-C(21)	1.86(1)	C(21)-P(2)-C(24)	103.2(4)
P(2)-C(24)	1.86(1)	C(21)-P(2)-C(27)	111.6(4)
P(2)-C(27)	1.85(1)	C(24)-P(2)-C(27)	103.6(4)
C(21)-C(22)	1.54(2)	P(1)-C(11)-C(12)	116.1(6)
C(21)-C(23)	1.55(1)	P(1)-C(11)-C(13)	112.1(7)
C(24)-C(25)	1.53(1)	C(12)-C(11)-C(13)	111.4(8)
C(24)-C(26)	1.56(1)	P(1)-C(14)-C(15)	109.5(7)
C(27)-C(28)	1.57(1)	P(1)-C(14)-C(16)	111.8(6)
C(27)-C(29)	1.58(1)	C(15)-C(14)-C(16)	108.4(8)
		P(1)-C(17)-C(18)	110.9(7)
		P(1)-C(17)-C(19)	117.6(7)
		C(18)-C(17)-C(19)	110.6(8)
		P(2)-C(21)-C(22)	110.6(8)
		P(2)-C(21)-C(23)	116.4(7)
		C(22)-C(21)-C(23)	113.0(9)
		P(2)-C(24)-C(25)	111.5(6)
		P(2)-C(24)-C(26)	109.5(6)
		C(25)-C(24)-C(26)	109.3(8)
		P(2)-C(27)-C(28)	112.1(6)
		P(2)-C(27)-C(29)	116.7(7)
		C(28)-C(27)-C(29)	108.5(8)

complexes.) Values ranging from 1.10 to 1.26 $\overset{\circ}{\text{\AA}}$ have been suggested¹⁵⁵ as Ni(II) radii. However, if 2.28 $\overset{\circ}{\text{\AA}}$ is assumed to represent a pure Ni-P sigma bond length, then a covalent radius of 1.18 $\overset{\circ}{\text{\AA}}$ is derived. In trans-Ni(C \equiv C.Ph)₂(PEt₃)₂,¹⁵⁶ a complex with P cis to C(σ), Ni-P is 2.17 $\overset{\circ}{\text{\AA}}$, and this is analogous to the present case, in which P is cis to hydride. Both H and C(σ) are known to exert strong static trans weakening effects (see later), and it appears that they may also have considerable cis strengthening effects. This will also be discussed later.

The Ni-C1 bond, 2.207 $\overset{\circ}{\text{\AA}}$, is longer than the radius sum (2.18 $\overset{\circ}{\text{\AA}}$), and, like other platinum group hydrides, is longer than in the corresponding trans dihalide. (See Table 7) It is compared to other square planar Ni(II) halides in Table 8. Many hydride complexes of square planar or octahedral symmetry show this effect but it is not generally observed for other geometries, perhaps because of the strongly directional nature of such bond-weakening effects.

The two phosphine groups are related by a pseudocentre of symmetry (see Figure 2), indicating that replacement of C1 by H has very little effect on the ligand geometries. (NiCl₂(PPR₃¹)₂ is centrosymmetric.)

TABLE 2.8.6

Ni-P Distances in square planar complexes

	<u>Ni-P</u>	<u>Reference</u>
tr-NiHCl(PPr ⁱ ₃) ₂	2.19	
tr-NiCl ₂ (PPr ⁱ ₃) ₂	2.28	a
tr-Ni(SCN) ₂ (PPr ⁱ ₃) ₂	2.27	a
tr-NiCl ₂ (P(C ₁₀ H ₁₁) ₃) ₂	2.27	b
tr-NiBr ₂ (PEt ₃) ₂	2.28	c
tr-Ni(C≡CØ) ₂ (PEt ₃) ₂	2.17	d
tr-Ni(Se.o-C ₆ H ₄ .PPh ₂) ₂	2.17	e
tr-NiBr ₂ (PPh ₂ .C ₆ H ₅ CH ₂) ₂	2.26	f
tr-NiBr ₂ (PMe ₂ Ph) ₂	2.25	g
Ni(C ₂ H ₄)(PPh ₃) ₂	2.18, 2.20	h

- a. M C Hall, B T Kilbourn & R H B Mais, unpublished data
- b. P L Bellon et al., Ric.Sci., 1963, 33, 1213
- c. V Scatturin & A Turco, J.Inorg.Nucl.Chem., 1958, 8, 447
- d. G R Davies, R H B Mais & P G Owston, JCS(A), 1967, 1750
- e. R Curran, J A Cunningham & R Eisenberg, Inorg.Chem., 1970, 9, 2749
- f. B T Kilbourn & H M Powell, JCS(A), 1970, 1688
- g. D W Meek et al., JACS, 1969, 91, 4920
- h. C D Cook et al., Chem.Comm., 1967, 426

TABLE 2.8.7

Comparison of trans dihalides with
trans hydride halides

	M-X	Reference
tr-NiHCl(PPr ₃ ⁱ) ₂	2.21	
tr-NiCl ₂ (PPr ₃ ⁱ) ₂	2.16	a
tr-PdHCl(PPr ₃ ⁱ) ₂	2.39	b
tr-PdCl ₂ (DMSO) ₂	2.29	c
tr-PtHBr(PEt ₃) ₂	2.56	d
tr-PtBr ₂ (PEt ₃) ₂	2.43	e

TABLE 2.8.8

Ni-Cl Distances in square planar complexes

	Ni-Cl	Reference
tr-NiHCl(PPr ₃ ⁱ) ₂	2.21	
tr-NiCl ₂ (PPr ₃ ⁱ) ₂	2.16	a
tr-NiCl ₂ (P(C ₁₀ H ₁₁) ₃) ₂	2.18	f

- a. M C Hall, B T Kilbourn & R H B Mais, unpublished data
- b. See Chapter 2.9
- c. M J Bennett et al., Acta.Cryst., 1967, 23, 788
- d. P G Owston, J M Partridge & J M Rowe, Acta.Cryst., 1960, 13, 246
- e. G G Messmer & E L Amma, Inorg.Chem., 1966, 5, 1755
- f. P L Bellon et al., Ric.Sci., 1963, 33, 1213

Within each PPr_3^1 group, the distances appear normal, with an average P-C bond of 1.86\AA , and C-C bonds of 1.52 to 1.58\AA . These values are all slightly longer than in the other two nickel isopropyl phosphine complexes (P-C all 1.85\AA , C-C average 1.52\AA in $\text{NiCl}_2(\text{PPr}_3^1)_2$, P-C average 1.83\AA , C-C average 1.52\AA in $\text{Ni}(\text{SCN})_2(\text{PPr}_3^1)_2$.)

The Ni-H distance of 1.4\AA is among the shortest observed using X-rays; it is consistent with the radius sum ($1.18 + 0.26\text{\AA}$). This is the first reported platinum group M-H bond length, and its significance will be discussed further in Chapter 2.10.

The cis and trans effects of the hydridic hydrogen

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The trans influence has been defined as the static weakening effect of one ligand on the bond trans to it, as distinct from the trans effect which is principally a factor in influencing the rates of substitution reactions, mainly of Pt(II) complexes. Various theories have been advanced to explain the order of ligands in a trans-(effect or influence-) series; (the order is very similar for both series).

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1. the electrostatic polarisation theory,
2. the π -bonding theory,^{159, 160}
3. the σ -bonding theory.^{161, 162}

There is general agreement nowadays that the main factor is the degree of sigma bond strength of the labilizing bond, since it is otherwise impossible to explain why H^- and Me^- have such large trans influences (see e.g. Table 7), which illustrates that a trans influence is generally reflected in bond distances. An alternative view would be that static trans influences are recognised by their effects on bond lengths. Following from calculations on ligand-metal p orbital overlap integrals, (Gray and Langford,¹⁶³ and extended by Mason)^{155a} it has been shown that the degree of p orbital overlap in the M-L bond is directly correlated with the trans influence of L.

It is thought that good π -acceptor ligands, e.g. CO, CN^- , which exert a large trans influence, do so mainly because of a high σ -trans influence which is actually reduced by their π -trans influence, and that ligands such as ethylene have no static trans influence, their trans effects operating entirely through stabilisation of a transition state.

In the case of nickel the overlap integral for $\text{Ni}(4p\sigma)$ with $\text{H}(1s)$ was shown^{155a} to be 0.56, higher than for any other Ni-L(sp hybrid) bond. While the $\text{H}(1s)$ orbital also has good overlap with Pd and Pt p orbitals, the integral is lower than for Ni; this

may be a factor contributing to the stability of the Ni-H bond in $\text{NiHCl}(\text{PPr}_3^i)_2$. This seems intuitively reasonable, in view of the polarisability of the hydrogen atom, and the small, compact nature of its 1s orbital, which can form a very strong, highly directed sigma M-H bond.

According to Syrkin,¹⁶¹ the trans influence of a ligand L is due, not to favourable p orbital overlap, but to an increase in the s character of the bond M-L i.e. there is a re-hybridisation of the metal orbitals to give a predominantly sd orbital for this bond. This results in the trans bond having more p character, and in a simultaneous strengthening of the cis bond, which can also use an orbital of greater sd character. This suggestion that a large trans weakening influence is accompanied by a cis strengthening influence, is supported by the bond lengths in $\text{NiHCl}(\text{PPr}_3^i)_2$.

(Cis weakening effects are less easy to explain, except on a straightforward polarisation theory. The effects of trans directing properties can be measured using physical properties such as IR force constants and NMR coupling constants and shifts, which are sensitive to trans ligands, but cis influences, being usually smaller, are more difficult to detect. One property which has recently been shown to be affected by cis ligands is the ³⁵Cl NQR frequency. Recent

studies by Fryer¹⁶⁴ on Ni(II), Pd(II), and Pt(II) complexes only considered ligands cis to chlorines. P was shown to have a very small effect and therefore in $\text{NiHCl}(\text{PPr}_3^i)_2$ the trans effect of hydride is more important than the cis effect of P.)

In the present complex the cis bonds are each shortened by 0.087\AA whereas the trans bond is only lengthened by 0.027\AA , so that the cis strengthening is the more important result of replacing chloride by hydride. Since one would expect a cis weakening by hydride, Syркин rehybridisation is presumed to be the factor that reverses this lengthening effect. However, this cannot account for the entire shortening observed, as one would still expect the cis influence to be less noticeable than the trans influence. In this case the most likely reason for the additional shortening of Ni-P is the possibility of π -bonding into P(d) orbitals. In this way the excess charge concentrated on Ni by the hydrogen can be dissipated by back bonding rather than remaining on the Ni atom and thus enhancing the polarity of the cis bond, as is the case with Fryer's complexes.

Summarising, in the present complex, the hydridic hydrogen probably forms a very strong, highly concentrated bond to nickel, which weakens the trans Ni-Cl bond, and also the cis Ni-P bonds. The

resultant concentration of electron density on the nickel atom is dispersed by back bonding into the phosphorus d orbitals, which shortens the Ni-P bonds. The cis effect of hydride appears to be larger than the trans influence, and is in fact quite significant.

The Stability of $\text{NiHCl}(\text{PPr}_3^i)_2$

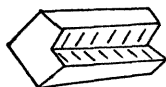
In the absence of structural information the stability of the Ni-H bond was assumed to be partly steric, as PPr_3^i is a very bulky ligand, which could hinder rearrangement of the square planar complex to a tetrahedral configuration, and also hinder attack of reagents along the z axis, by folding in around the Ni-H region.

$\text{NiHCl}(\text{P.cyclohexyl})_2$ is also stable, for the same reason. ¹⁵⁰ $\text{NiHCl}(\text{PPr}_3^n)_2$ is unstable; molecular models show that this can just exist in the tetrahedral form, whereas the isopropyl complex cannot. $\text{NiHCl}(\text{PEt}_3)_2$ can easily exist in a tetrahedral form. These are undoubtedly important contributing factors, but the structure analysis reveals that the hydride ligand has a very pronounced effect on the electron density round the nickel atom, and hence on the ligand orbitals, so that this is seen to be a factor contributing to the stability of this complex.

Trans- Ni(Me)Cl(PPr₃ⁱ)₂

The compound tr- Ni(Me)Cl(PPr₃ⁱ)₂ contains the trans chloride-methyl grouping, in which the trans influence of a methyl should be observable in the Ni-Cl bond length. Methyl is known to exert a weakening effect comparable to hydride.

The crystals were transparent khaki coloured needles up to 2 mm. in length, which turned gradually red in the dry box, under nitrogen. They were mounted with silicone grease in tubes, but the majority had decomposed before photographs could be taken. From photographs of those that had not decomposed, the symmetry appeared to be triclinic, with no evidence of the twinning suggested by the crystal shape (long clefts down the middle).



From photographs of an a axis mounted crystal:-

$$\begin{array}{ll} a = 8.7 \text{ \AA} & \\ b = 8.3 \text{ \AA} & \alpha^* \approx 108^\circ. \\ c = 15.2 \text{ \AA} & \end{array}$$

Further photography indicated the occurrence of a

monoclinic modification (twinned?) whose c axis, only, was consistent with that of the triclinic crystals:-

$$\begin{array}{ll} a = 5.6 \text{ \AA} & \\ b = 13.2 \text{ \AA} & \beta^* \approx 106^\circ. \\ c = 15.2 \text{ \AA} & \end{array}$$

No more pictures could be obtained from the sample, so it was decided to wait until a better sample could be prepared, to resolve this ambiguity.

CHAPTER 2.9

THE CRYSTAL AND MOLECULAR STRUCTURE OF

TRANS-PdHCl(PPrⁱ₃)₂

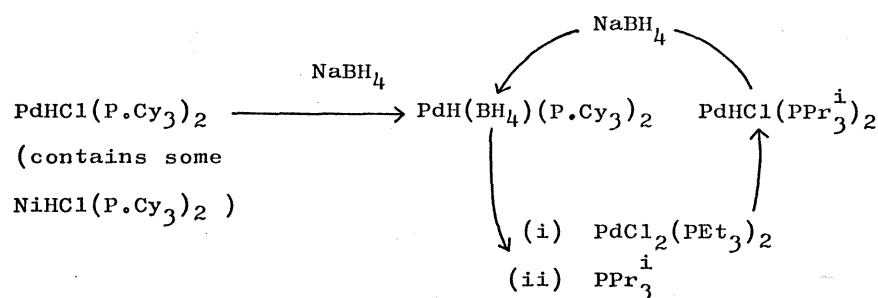
Palladium is involved in several industrially important catalytic reactions but there is less structural information about its complexes than about either nickel or platinum complexes. This has probably arisen because the palladium and platinum analogues tend to behave similarly, and are expected to be isostructural in many cases. However, palladium is relatively less likely to obscure the observation of very small electron densities such as hydride ligands. The crystal structure of the stable hydride PdHCl(PPrⁱ₃)₂ was studied for this reason. It was hoped to locate the hydridic hydrogen in order to provide more evidence on the length of an M-H bond, and particularly to confirm whether the short Ni-H bond is part of a general trend to contraction at the end of the transition series.

Furthermore, the structural influence of the hydride ligand on stereochemistry and on neighbouring metal-ligand bonds, could be observed and compared with nickel and platinum structures.

Preparation

PdHCl(PPrⁱ₃)₂ cannot be prepared in the same way as NiHCl(PPrⁱ₃)₂; it has to be reached via the cyclohexyl

phosphine derivative, and purified by a cyclic
 procedure:-¹⁶⁵



Cy = Cyclohexyl

The colourless crystals were prepared by H Munakata in Oxford, as large hexagonal prisms, almost perfectly shaped. These were fairly stable under nitrogen, but were mildly photosensitive. The crystal used is shown in Figure 1.

Crystal Data

$\text{C}_{18}\text{H}_{43}\text{PdP}_2\text{Cl}$, $M = 463.0$; monoclinic, $a = 16.335 \pm 0.007$,
 $b = 8.944 \pm 0.004$, $c = 16.343 \pm 0.011 \text{ \AA}$, $\beta = 93.41 \pm 0.05^\circ$;
 $V = 2383.5 \text{ \AA}^3$, $D_m = 1.29$ (flotation), $Z = 4$, $D_c = 1.30$,
 $F(000) = 976$;
 Space Group $P2_1/c$, (C_{2h}^5 ; no.14), Mo- $K\alpha$ radiation
 (Nb filter), $\lambda = 0.71070 \text{ \AA}$, $\mu = 10.13 \text{ cm}^{-1}$

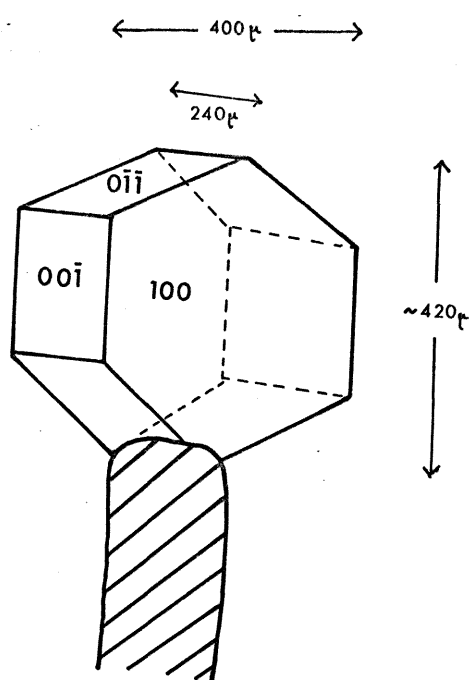


Figure 2.9.1

 $\text{PdHCl}(\text{PPri}_3)_2$ Crystal

The Equations of the Bounding Surfaces
of the Crystal

	l	m	n	p	(hkl)
1	-.6415	.5795	-.5026	123.56	$\bar{1}00$
2	.5887	-.6171	.5221	122.92	100
3	-.5807	-.7486	-.3201	201.00	$00\bar{1}$
4	-.7539	-.2386	.6122	222.65	$0\bar{1}\bar{1}$
5	-.1783	.4359	.8821	225.35	$0\bar{1}1$
6	.5531	.7927	.2563	199.17	001
7	.5758	.3937	-.7166	214.73	011
8	.0962	-.3398	-.9356	218.89	$01\bar{1}$

Data Collection

Temperature -70° ; scan range -0.5° to $+0.5^{\circ}$;
 Scan speed $2^{\circ} 2\theta/\text{minute}$; fixed time 10 seconds;
 Standards $(0\ 0\ \bar{1}2)$, $(\bar{1}0\ 0\ 0)$ and $(0\ 6\ 0)$ falling
 to 78%, 94% and 95% of initial intensity;
 reflections measured in octants $\{hkl\}$ and $\{\bar{h}\bar{k}\bar{l}\}$,
 to a maximum $2\theta = 27^{\circ}$; cell dimensions from 5
 reflections (20 measurements) giving angles
 $\alpha = 89.99(4)^{\circ}$, $\gamma = 90.06(4)^{\circ}$; total number of
 independent structure amplitudes obtained after
 data reduction and collation of equivalent
 reflections 4325.

Solution and Refinement of Structure

Preliminary photography had indicated that $\text{PdHCl}(\text{PPr}_3^i)_2$
 would be isostructural with the nickel analogue, and
 so the final parameters for the nickel hydride were
 input and refined; Pd, Cl, P were corrected for $\Delta f'$,
 and were given anisotropic U_{ij} s, while the carbon atoms
 were given isotropic U values. Hydrogen atoms were
 not included.

Cycles 1 - 3 (see Table 1) reduced R to 8.8%, at which
 point an improved weighting scheme was introduced. The
 final refinement (Cycles 4,5) used the 1936 terms with
 $\text{observed amplitude} > 3\sigma$ and ratio of amplitude to
 $\text{deviation} > 8$, so that the number of planes refined was

TABLE 2.9.1

Refinement of the structure of $\text{PdHCl}(\text{PPr}^i)_2$

Cycle Number of terms	Criteria	R Value	Atoms included	Pd	P	Cl	Matrix type	H(p)	Pd	P	Cl	C	H(p)	Weighting used
1	2332 min.amp./ min.amp./ deviation 5	21.7	all atoms	pb(1)	pb(1)	pb(1)	b(1) b(2)	-	a	a	a	i	-	1
2,3	1576 min.amp./ min.amp./ deviation 8	8.8	all atoms	pb(1)	pb(1)	pb(1)	b(1) b(2)	-	a	a	a	i	-	1
4,5	1936 min.amp./ min.amp./ deviation 8	6.1	all atoms	pb(1)	pb(1)	pb(1)	b(1) b(2)	-	a	a	a	i	-	$c_1 = 90$ $c_2 = 0$ (2)
6	4025 min.amp./ deviation 10	7.9	all atoms + hydrogens	pb(1)	pb(1)	pb(1)	pb(1)	c	a	a	a	i	i	2

Matrix types:

pb = positional block
 tb = vibrational block
 tbd} = block diagonals
 pbd}
 c = contribution only
 H(p) = H(propyl)

Thermal parameters:

a = anisotropic
 i = isotropic
 c = constant

Final scale = 0.82 (cycle 5)
 Final convergence factor = 0.18 (cycle 5)

comparable for the palladium and nickel complexes. This refinement proceeded smoothly to convergence at $R = 6.1\%$, when an $F(\text{diff})$ map was computed. There was considerable residual electron density round the metal, but all the H(propyl) atoms could be seen. The programme HCOORD was again used to check the positions, and these were then included, as constant contributions, in a final cycle. This was based on 4025 terms $> 10\sigma$, and used the same block diagonal approximation as had been used for $\text{NiHCl}(\text{PPr}_3^i)_2$. The corresponding $F(\text{diff})$ map again showed evidence of unaccounted-for anisotropy around Pd (maximum peak height $1.5e$), and so it was not possible to locate the hydridic hydrogen. A small peak was visible, 1.88\AA from Pd and almost trans to chlorine, but it was surrounded by residual density. As with the Ni structure a neutron study would be very worthwhile. Unobserved reflections were calculated; none were greater than $1.3\times$ the minimum observed.

Results and Discussion

Final positional and vibrational parameters are listed in the Appendix in Tables 2 and 3; the molecular geometry is shown in Table 4. The agreement analysis at $R = 6.1\%$ is listed in Table 5. The molecule, which has an almost identical shape to $\text{NiHCl}(\text{PPr}_3^i)_2$, is shown in Figure 2. The packing of molecules is also

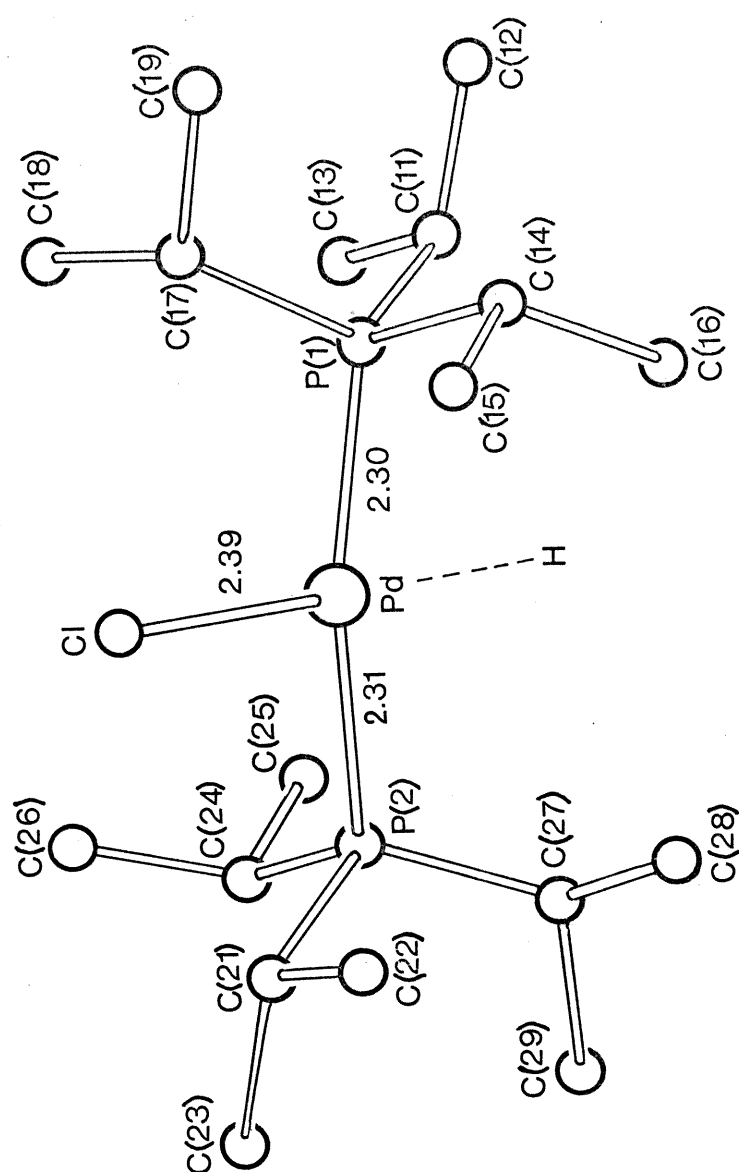


Figure 2.9.2
 $\text{PdHCl}(\text{PPR}_3^i)_2$

View of one molecule, illustrating the numbering system and the geometry round palladium.

Table 2.9.4

Bond distances (\AA) and angles ($^\circ$), with their estimated standard deviations

Around Palladium

Pd-P(1)	2.299(3)	P(1)-Pd-P(2)	167.4(1)
Pd-P(2)	2.312(3)	P(1)-Pd-C1	95.9(1)
Pd-C1	2.390(4)	P(2)-Pd-C1	96.7(1)

Phosphine Groups

P(1)-C(11)	1.87(2)	Pd-P(1)-C(11)	112.7(5)
P(1)-C(14)	1.84(2)	Pd-P(1)-C(14)	111.1(6)
P(1)-C(17)	1.85(2)	Pd-P(1)-C(17)	112.6(5)
C(11)-C(12)	1.55(2)	Pd-P(2)-C(21)	111.4(5)
C(11)-C(13)	1.53(2)	Pd-P(2)-C(24)	110.4(4)
C(14)-C(15)	1.59(3)	Pd-P(2)-C(27)	113.4(5)
C(14)-C(16)	1.55(3)	C(11)-P(1)-C(14)	103.9(7)
C(17)-C(18)	1.56(3)	C(11)-P(1)-C(17)	112.0(7)
C(17)-C(19)	1.59(3)	C(14)-P(1)-C(17)	103.8(7)
P(2)-C(21)	1.85(2)	C(21)-P(2)-C(24)	104.4(7)
P(2)-C(24)	1.89(1)	C(21)-P(2)-C(27)	112.7(7)
P(2)-C(27)	1.85(1)	C(24)-P(2)-C(27)	103.9(6)
C(21)-C(22)	1.57(3)	P(1)-C(11)-C(12)	116.2(11)
C(21)-C(23)	1.54(3)	P(1)-C(11)-C(13)	113.3(12)
C(24)-C(25)	1.52(2)	C(12)-C(11)-C(13)	110.1(14)
C(24)-C(26)	1.55(2)	P(1)-C(14)-C(15)	110.0(13)
C(27)-C(28)	1.56(2)	P(1)-C(14)-C(16)	110.7(12)
C(27)-C(29)	1.59(2)	C(15)-C(14)-C(16)	108.0(16)
		P(1)-C(17)-C(18)	111.6(12)
		P(1)-C(17)-C(19)	115.9(13)
		C(18)-C(17)-C(19)	111.5(16)
		P(2)-C(21)-C(22)	109.5(12)
		P(2)-C(21)-C(23)	116.8(11)
		C(22)-C(21)-C(23)	111.1(15)
		P(2)-C(24)-C(25)	112.3(10)
		P(2)-C(24)-C(26)	108.4(9)
		C(25)-C(24)-C(26)	110.1(12)
		P(2)-C(27)-C(28)	113.0(10)
		P(2)-C(27)-C(29)	114.6(11)
		C(28)-C(27)-C(29)	108.7(13)

very similar and is not given as a separate drawing.

The complex is isostructural with $\text{NiHCl}(\text{PPr}_3^i)_2$, consisting of well-separated molecules. No intermolecular contacts are less than 3.5\AA , except some involving hydrogens. The best plane through Pd, P, Cl atoms is:-

$$15.10x + 2.52y - 5.09z - 3.77 = 0$$

and Pd lies only 0.009\AA from this plane. The structure may be compared chiefly with the similar $\text{PdHCl}(\text{PEt}_3)_2^{166}$ and the analogous Ni and Pt hydrides ($\text{NiHCl}(\text{PPr}_3^i)_2$, $\text{PtHBr}(\text{PEt}_3)_2^{167}$, $\text{PtHCl}(\text{PEtPh}_2)_2^{168}$); also with analogous Pd-C(σ) complexes ($\text{PdBr}(\text{pyridine})_2(\text{C}_7\text{H}_8\text{OMe})^{169}$ and $\text{PdCl}(\text{C}_{12}\text{H}_9\text{N}_2)(\text{PEt}_3)_2^{170}$).

Pt- and Pd-P distances tend to be very similar, and these bonds are always shorter than the theoretical radius sum $^{138}(2.42\text{\AA})$. In the present case, $\text{Pd-P} = 2.30\text{\AA}$, and so the shortening is not exceptional (see Table 6). This length is identical to that in $\text{PdHCl}(\text{PEt}_3)_2$, and, by analogy with the nickel hydride, this may be attributed to a cis strengthening effect of hydride. However, in the two Pt hydrides the same effect is observed to a significantly greater extent (2.26\AA in $\text{PtHBr}(\text{PEt}_3)_2$, 2.27\AA in $\text{PtHCl}(\text{PEtPh}_2)_2$).

Pt- and Pd-Cl distances are usually in the range 2.30 to 2.38\AA (radius sum 2.30\AA), and so the Pd-Cl bond of

TABLE 2.9.6

Pd-P Distances

	<u>Pd-P</u>	<u>Reference</u>
tr-PdHCl(PPr_3) ₂ ⁱ	2.30	
tr-PdHCl(PEt_3) ₂	2.31	a
tr-PdCl($\text{C}_{12}\text{H}_9\text{N}_2$)(PEt_3) ₂	2.30-2.32	b
cis-PdCl ₂ ($\text{Ph}_2\text{P.NEt.PPh}_2$)	2.22	c
cis-Pd(NCS)(SCN)(dppe)	2.26, 2.25	d
cis-Pd(NCS)(SCN)($\text{Ph}_2\text{P.C}_3\text{H}_6\text{.NMe}_2$)	2.24	e
Pd($\pi\text{-C}_3\text{H}_5$)(SnCl_3)(PPh_3)	2.32	f
PdCl($\text{Me-C}_3\text{H}_4$)(PPh_3)	2.31	g
Pd(CS_2)(PPh_3) ₂	2.32, 2.42	h
tr-PdI ₂ (PMe_2Ph) ₂	2.34	i

- a. H M M Shearer, personal communication
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TABLE 2.9.7

Pd-Cl Distances in square planar complexes

	<u>Pd-Cl</u>	<u>Reference</u>
tr-PdHCl(PPr ₃ ⁱ) ₂	2.39	
tr-PdHCl(PEt ₃) ₂	2.43	a
tr-PdCl(C ₁₂ H ₉ N ₂)(PEt ₃) ₂	2.38	b
tr-PdCl ₂ (DMSO) ₂	2.29	c
tr-PdCl ₂ (C ₆ H ₁₀ NOH) ₂	2.24	d
cis-PdCl ₂ (Ph ₂ P.NEt.PPh ₂)	2.37	e
cis-PdCl ₂ (norbornadiene)	2.31	f
PdCl ₂ (benzonitrile) ₂	2.32	g
PdCl(π-CH ₃ C ₃ H ₄)(PPh ₃)	2.38	h
PdCl ₄ ²⁻	2.30	i

- a. H M M Shearer, personal communication
- b. D L Weaver, Inorg.Chem., 1970, 9, 2250
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- h. R Mason & D R Russell, Chem.Comm., 1966, 26
- i. R H B Mais, P G Owston & A M Wood, unpublished data

2.39⁰Å in the present complex is not lengthened so much as in the comparable Pd and Pt complexes (2.43⁰Å in PdHCl(PEt₃)₂, 2.42⁰Å in PtHCl(PEtPh₂)₂). This suggests that the trans weakening influence is not so strong in PdHCl(PPrⁱ₃)₂, and this fits in well with an order of increasing trans and cis effects of hydride in this series; it may also provide some insight into the effectiveness of palladium complexes as catalysts. Platinum hydrides are generally very stable, whereas nickel hydrides are often unstable. It appears that palladium complexes may lie in the middle range of reactivity and the particular balance between the strengths of the different bonds could be favourable for catalytic activity.

	M-P	Radius Sum	Δ	M-Cl	Radius Sum	Δ
NiHCl(PPr ⁱ ₃) ₂	2.19	2.28	-0.09	2.21	2.18	+0.03
PdHCl(PPr ⁱ ₃) ₂	2.30	2.42	-0.12	2.39	2.30	+0.09
PtHCl(PEtPh ₂) ₂	2.27	2.42	-0.15	2.42	2.30	+0.12

Similar trans effects are noted in Pd-C(σ) complexes, e.g. Pd-Cl 2.38⁰Å in PdCl(C₁₂H₉N₂)(PEt₃)₂, Pd-Br 2.58⁰Å in PdBr(Pyridine)₂(C₇H₈OMe); Pd-halide distances are listed in Table 7.

The angles at the metal are distorted from 90° and 180° , as is always observed with transition metal hydrides. The size of the distortion is, as expected, in proportion to the size of the central atom, and is greatest for the smallest metal.

	<u>P-M-P</u>	<u>P-M-X</u>
$\text{NiHCl}(\text{PPr}_3^i)_2$	163°	$98, 98^\circ$
$\text{PdHCl}(\text{PPr}_3^i)_2$	168	96, 97
$\text{PdHCl}(\text{PEt}_3)_2$	169	95, 95
$\text{PtHCl}(\text{PEtPh}_2)_2$	171	93, 95
$\text{PtHBr}(\text{PEt}_3)_2$	172	94, 94

However, the slight increase in distortion in P-M-P from Pt to Pd is unexpected, since the sizes of these two metals are almost the same. (cf. in the ruthenium and osmium naphthyl complexes the angles are nearly identical.) This again suggests that apparently similar palladium and platinum complexes may show slight structural differences which are just large enough to influence catalytic behaviour.

The configurations of the two phosphine groups are very close to those in the nickel analogue. Again, there is very nearly a centre of symmetry. Within each group the geometries are unexceptional: the average P-C bond (1.865\AA), is longer than in $\text{PdHCl}(\text{PEt}_3)_2$ (1.844\AA), as is

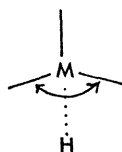
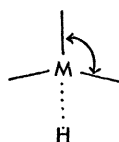
the average C-C of 1.55\AA compared with 1.50\AA . The values are similar to those in $\text{NiHCl}(\text{PPr}_3)_2$,

The hydridic hydrogen was not observed, and in view of the residual density round Pd, no attempt was made to locate the hydrogen by successive $F(\text{diff})$ maps. It is assumed to lie about 1.7\AA from the metal, in the vacant site trans to chlorine.

CHAPTER 2.10SUMMARY OF RESULTS ON HYDRIDE COMPLEXES:COMPARISON WITH OTHER WORK

Within the last few years there has been a proliferation in crystallographic studies on transition metal hydrides. The complexes studied for this thesis illustrate some of the problems encountered in obtaining accurate results. The known crystal structures are listed in Table 1, and these show that in almost all cases the hydridic hydrogen occupies a normal coordination position. The only reported exceptions to this generalisation are $\text{RhH}(\text{PPh}_3)_4$ (and its mixed arsine analogue),¹¹⁴ in which the hydrogen appears to be mobile, and $\text{CoH}(\text{PF}_3)_4$.¹⁷¹ There are some gaps in the coverage of each transition series, and in particular a general scarcity of data on first row complexes. This is because, although there is a greater chance of locating the hydrogen, first row hydride complexes are less stable than their heavier analogues. The hydrogen atom is very small and so a distortion is often observed in the surrounding angles, leading to a reduction in crowding in other parts of the molecule, for example:-

$\text{PtHBr}(\text{PEt}_3)_2$ ¹⁶⁷	Br-Pt-P	94°
$\text{NiHCl}(\text{PPr}^i_3)_2$	Cl-Ni-P1	98°
$\text{IrH}(\text{COOMe})(\text{dmpe})_2^+$	P2-Ir-Cl	94°
$\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$ ⁸⁵	P1-Os-P2	158°
$\text{NiHCl}(\text{PPr}^i_3)_2$	P1-Ni-P2	163°
$\text{PdHCl}(\text{PPr}^i_3)_2$	P1-Pd-P2	167°
$\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	Cl-Ru-P4	162°



All known M-H distances are consistent with covalent radius sums (assuming $0.26 - 0.3\text{\AA}$ ⁰ as the covalent radius of H^-), if one bears in mind the very wide variation in covalent radii assigned to transition metals. An 'average' radius, derived from M-M distances in metal-metal bonded compounds, is $1.1 - 1.3\text{\AA}$ ⁰, and this leads to prediction of a 'normal' M-H distance of $1.4 - 1.7\text{\AA}$ ⁰; this range does indeed cover all reported distances. Spectral information for diatomic hydrides also predicts distances in this range.¹⁷²

There has been much controversy over the question of whether a hydride ligand is buried in the electron cloud of the metal atom, because of some early calculations and claims of very short distances.^{51a, 64b, 173} The argument over $\text{MnH}(\text{CO})_5$, in particular, has only recently been resolved by accurate X-ray and neutron analyses, which

Table 2.10.1
Transition Metal Complex Hydride
Structure Determinations

<u>Complex</u>	<u>Reference</u>	<u>M-H</u>	
$\text{Cr}(\text{B}_3\text{H}_8)(\text{CO})_4^-$	a	1.75	observed
$\text{Cr}_2\text{H}(\text{CO})_{10}^-$	b	1.70	inferred
$\text{Mo}_2\text{H}(\pi\text{Cp})_2(\text{PMe}_2)(\text{CO})_4$	c	(1.80)	inferred
$\text{MoH}_2(\pi\text{Cp})_2$	d	-	-
$\text{WH}(\text{CO})_3$	e	-	-
$\text{MnH}(\text{CO})_5$	f	1.6	observed
$\text{Mn}_2\text{H}(\text{CO})_8(\text{PPh}_2)$	g	(1.86)	observed
$\text{Mn}_3\text{H}(\text{CO})_{10}(\text{BH}_3)_2$	h	(1.65)	inferred
$\text{MnHRe}_2(\text{CO})_{14}$	i	1.7	inferred
ReH_9^{2-}	j	1.6-7	observed
$\text{ReH}_3(\text{PPh}_3)_2(\text{dppe})$	k	-	-
$\text{Re}_3\text{H}(\text{CO})_{12}^{2-}$	l	1.7	inferred
$\text{Re}_3\text{H}_2(\text{CO})_{12}^-$	m	1.6	inferred
$\text{Re}_4\text{H}_6(\text{CO})_{12}^{2-}$	n	1.6	inferred
$\text{cis-FeH}_2(\text{PPh}(\text{OEt})_2)_4$	o	1.5	?
$\text{FeH}(\text{SiCl}_3)_2(\pi\text{Cp})(\text{CO})$	p	-	-
$\text{Fe}_3\text{H}(\text{CO})_{11}^-$	q	-	-
$\text{FeRu}_3\text{H}_2(\text{CO})_{13}$	r	-	-
$\text{RuHCl}(\text{PPh}_3)_3$	s	1.7	observed
$\text{RuH}(\text{COOMe})(\text{PPh}_3)_3$	t	1.7	observed
$\text{cis-RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	u	1.7	observed
$\text{Ru}_6\text{H}_2(\text{CO})_{18}$	v	-	-
$\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$	x	-	-
$\text{cis-OsH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	y	-	-
$\text{OsH}_4(\text{PEt}_3\text{Ph})_3$	z	-	-

Complex	Reference	M-H	
tr-CoH(N ₂)(PPh ₃) ₃	aa	1.65	observed
CoH(PF ₃) ₄	bb	-	-
RhH(CO)(PPh ₃) ₃	cc	1.60	observed
RhHCl(SiCl ₃)(PPh ₃) ₂	dd	(1.5)	observed
RhH(NH ₃) ₅ ²⁺	ee	-	-
RhH(PPh ₃) ₄	ff	-	-
RhH(PPh ₃) ₃ (AsPh ₃)	gg	-	-
Rh ₃ H(πCp) ₄	hh	(1.57)	inferred
IrH(CO) ₂ (PPh ₃) ₂	ii	1.7	observed
tr-IrH(COOMe)(dmpe) ₂ ⁺	jj	-	-
IrH(CO)(PPh ₃) ₂ (C ₄ H ₂ N ₂)	kk	-	-
IrH ₂ (CO)(PPh ₃) ₂ (GeMe ₃)	ll	-	-
IrHCl ₂ (Me ₂ SO) ₃	mm	-	-
IrH(NO)(PPh ₃) ₃ ⁺	nn	-	-
tr-NiHCl(PPr ₃) ₂	oo	1.4	observed
tr-PdHCl(PPr ₃) ₂	oo	-	-
tr-PdHCl(PET ₃) ₂	pp	-	-
tr-PtHBr(PET ₃) ₂	qq	-	-
tr-PtHCl(PETPh ₂) ₂	rr	-	-
Zn ₂ H ₂ (MeN.C ₂ H ₄ .NMe ₂) ₂	ss	1.6	observed

Table 2.10.2

Transition Metal Hydrogen Distances

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
		1.7 (b)	1.6 (f)	1.5 (o)	1.6 (aa)	1.4 (oo)		1.6 (ss)
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
				1.7 (s,t,u)	1.5-6 (cc,dd)			
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
			1.6-7 (i,j)		1.7 (ii)			

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U A Gregory et al., JCS(A), in press (paper O/573).
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showed that the Mn-H distance is $1.6\overset{\circ}{\text{\AA}}$, in the same range as all the others. (See references 51b, 174, 175) The evidence is thus wholly in support of a normal covalent bond.

Almost all the most reliable M-H distances are from 1.6 to $1.7\overset{\circ}{\text{\AA}}$, and there seems to be a remarkable constancy, extending from chromium to zinc, for metals in their normal oxidation states. The only exceptions are Fe-H ($1.5\overset{\circ}{\text{\AA}}$), and Ni-H ($1.4\overset{\circ}{\text{\AA}}$). These metals are both in the first row, and there is a tendency for M-H to lengthen from first to second row, and then to remain constant from second to third. This is probably a size effect rather than an indication that stronger bonds are formed with first row metals. The Fe-H distance may be anomalous in that it occurs in the only example of a cis dihydride (excluding the rhenium hydrides) and there may in this case be some cis effect operating to shorten both bonds. There is no discernible trend along each series, or paralleling the number of d electrons. Neutron studies on $\text{NiHCl}(\text{PPr}_3^i)_2$ and $\text{PdHCl}(\text{PPr}_3^i)_2$ would be worthwhile, to verify the short Ni-H distance, and to establish whether Pd-H is also short. If the short distance were confirmed this would suggest that there is a trend to contraction of M-H at the completion of a 'd' shell. This could arise if a stronger bond is formed at the end of a series, using predominantly s and p orbitals, after the d orbitals have

sunk into the core.

The only metal for which there are reliable M-H

distances in two common oxidation states, is rhodium.

Rh(I)-H is $1.6 - 1.7 \overset{\text{O}}{\text{Å}}$,⁸⁴ while Rh(III)-H is $1.5 \overset{\text{O}}{\text{Å}}$ ⁷⁸

(though this is not such an accurate determination).

The M-H bond seems to be exceptionally strong, because

of the very polarisable 1s orbital. This highly

directed bond is very sensitive to its environment

(e.g. the influence of trans ligands on $\nu(\text{M-H})$), and

also apparently strongly perturbs the metal orbitals,

as judged by changes in the rest of the molecule. The

most obvious effect is that of polarisation which weakens

all the other bonds. This is most noticeable in the

trans bond and an additional explanation is provided in

terms of rehybridisation.¹⁶¹ (See Chapter 2.8) The effect

is most noticeable in regular geometries.

Square planar complexes:-

$\text{NiHCl}(\text{PPr}_3^1)_2$	Ni-Cl	2.21	(2.16 in $\text{NiCl}_2(\text{PPr}_3^1)_2$)
$\text{PdHCl}(\text{PPr}_3^1)_2$	Pd-Cl	2.39	(2.30 in PdCl_4^{2-})
$\text{PdHCl}(\text{PEt}_3)^{166}_2$	Pd-Cl	2.43	
$\text{PtHCl}(\text{PEtPh}_2)^{168}_2$	Pt-Cl	2.42	(radius sum 2.30)
$\text{PtHBr}(\text{PEt}_3)^{167}_2$	Pt-Br	2.56	(radius sum 2.43)

It can be seen that the trans lengthening increases

markedly from Ni to Pd.

Octahedral complexes:-

$\text{RuH}(\text{C}_{10}\text{H}_7)(\text{dmpe})_2$	Ru-P	2.33	(2.28-2.30 in cis positions)
$\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$	Os-P	2.56	(2.34 " " ")
$[\text{IrH}(\text{COOMe})(\text{dmpe})_2]^+$	Ir-C	2.10	(2.05 in $\text{IrI}_2(\text{CO})(\text{COOMe})$ (bipy) ¹³⁹)
$\text{IrHCl}_2(\text{Me}_2\text{SO})_3$ ¹⁴⁰	Ir-S	2.39	(2.25 in cis positions)
$\text{RuH}(\text{acetate})(\text{PPh}_3)_2$ ⁸⁷	Ru-O	2.26	(2.21 " " ")

BUT

$\text{MnH}(\text{CO})_5$ ¹⁷⁵	Mn-C	1.82	(1.85 in cis positions)
--	------	------	-------------------------

In the bonds cis to hydrogen the polarisation effect is cancelled by formation of a very strong bond, in agreement with Syrkin's theory.

$\text{NiHCl}(\text{PPr}_3)_2$	Ni-P	2.19	(2.28 in $\text{NiCl}_2(\text{PPr}_3)_2$ ¹⁵⁴)
$\text{RhHCl}(\text{SiCl}_3)(\text{PPh}_3)$ ⁷⁸	Rh-Si	2.20	(radius sum 2.49)
$\text{PtHBr}(\text{PEt}_3)_2$	Pt-P	2.26	(radius sum 2.42)

In each case the cis ligand contains suitable orbitals for back donation, and this may explain the marked strengthening effect of cis hydrogen.

In a more general way, hydrogen may perturb the electron clouds round other atoms because of the build-up of electron density at the metal, and it is possible that

the energies of the bonding orbitals in, say, a C-C system may be altered by the presence of a hydride, so that a reaction can take place. It is thought that in catalytic hydrogenations the substrate must be cis to the hydrogen and this suggests that some direct interaction occurs between substrate orbitals and the hydrogen 1s orbital. However, the cis bond seems to be strengthened, which could inhibit reaction. The trans bond, while weakened, is less favourably placed for further reaction.

All these effects appear to be more pronounced at the ends of each series. Possibly the d shell is more susceptible to such influences when it is nearly full. This suggests that metals at the end of each series are most affected by the formation of M-H, and the observation that the trans effect increases from Ni to Pt suggests that the heavier metals are more affected. Possibly this could be correlated with a stronger M-H bond at the lower right hand side of the d block caused by greater orbital overlap. The catalytically important metals lie in this region; presumably a strong M-H bond is necessary in order for hydrogen to remain on the complex long enough for reaction. Also, since these metals are most susceptible to changes in their electronic environment, they should be most effective catalytically.

CHAPTER 3.1

ACTIVATION OF SMALL MOLECULES BY TRANSITION METALS:

THE ATTEMPTED STRUCTURE DETERMINATION OF A MOLYBDENUM DINITROGENYL COMPLEX

Transition metal intermediates are probably important in biological reactions, particularly those involving small molecules, e.g. O_2 , N_2 . These may be taken up by metallo-proteins and utilised in biochemical processes; an example is the uptake of oxygen by the iron-containing protein haemoglobin. Simple analogues of these systems may be found among certain transition metal complexes, and Vaska's compound, $IrCl(CO)(PPh_3)_2$,¹²⁴ in particular, reacts with small gaseous molecules in several ways:-

1. The small molecule is dissociated, and the atoms bond separately to the metal atom, e.g. addition of H_2 to give a cis dihydride $Ir(H)_2Cl(CO)(PPh_3)_2$.¹²⁵
2. Both atoms bond to the metal but the molecule remains associated, e.g. $Ir(O_2)Cl(CO)(PPh_3)_2$;¹²⁶
 $Pt(O_2)(PPh_3)_2$.¹⁷⁶ These may be compared to olefine and acetylene adducts, e.g. $Ir(TCNE)Br(CO)(PPh_3)_2$.²¹
 (Case 1 is really the extreme of Case 2; the strength of

the complexed O=O bond depends on the electron density at the metal.)

3. One atom bonds to the metal, e.g. in addition of CO, SO₂, N₂, NO. In some of these adducts, the small molecule retains the same shape as in its uncomplexed form (e.g. Ir(SO₂)Cl(CO)(PPh₃)₂¹⁷⁷), whereas in others a distortion in geometry occurs e.g. [Ru(SO₂)Cl(NH₃)₄]¹⁷⁸Cl. Also, some diatomic molecules bond linearly (e.g. Ir(CO)Cl(CO)(PPh₃)₂¹¹⁸, Fe(NO)(S₂CNMe₂)₂³⁶), others at an angle (e.g. Ir(NO)Cl(CO)(PPh₃)₂¹⁴⁵). It has been suggested¹⁷⁹ from these and related observations that the electronic effect of bonding to a metal can be equivalent to raising the molecule to an excited state. There is some support for this from the geometries of, e.g. Pt(CS₂)(PPh₃)₂¹⁸⁰, (NMe₃Et)₂ [(PtCl₃)₂(butadiene)]¹⁸¹.
4. The small molecule is linearly coordinated to two metal atoms, e.g. [Co(NH₃)₅]₂(O₂)⁴⁺¹⁸², [Ru(NH₃)₅]₂(N₂)¹⁸³. Bridging dinitrogenyl complexes will be discussed in the following section as the two molybdenum structures to be described arose out of work on Mo-(N₂) complexes.

Transition Metal Dinitrogenyl Complexes

Nitrogen is classically described as an inert gas; however, biological systems can convert atmospheric nitrogen at normal temperatures and pressures into ammonia and thence into useful nitrogen-containing compounds. The equivalent industrial process, (Haber-Bosch), though economic, requires extreme conditions.¹⁸⁴ The nitrogen-fixing enzyme is now known to contain iron and molybdenum fractions, and so it is possible that an inorganic compound might exist which would perform the same function. Attempts to achieve fixation using transition metal catalysts have been widely reviewed.¹⁸⁵⁻¹⁸⁸

The existence of $M-(N_2)$ complexes was predicted in 1960,¹⁸⁹ although it was thought that they would be less stable than complexes of the isoelectronic $C\equiv O$. It was also suggested that the sideways mode of bonding would be relatively more stable than $M-\overset{C}{\underset{O}{\parallel}}$, but this argument did not take into account the fact that the orbitals are less favourably disposed for sideways bonding to a metal.

The first $M-(N_2)$ complex was not isolated until 1965 - $Ru(NH_3)_5(N_2)^{2+}$ ¹⁹⁰, but probably many had been unwittingly prepared before. Examples are now known for many Group VIII metals,¹⁹¹ also Mo,¹⁹² Re,¹⁹³ and W,¹⁹⁴ as well as bridging dinuclear¹⁹⁵, and bis- (N_2) ¹⁹⁶ complexes, and many of these

have been prepared directly from atmospheric nitrogen.

Electronic factors influence the stabilities of such compounds; good donor ligands help to stabilize a $M-(N_2)$ bond, and the complexes, once formed, are usually very stable indeed. This is particularly true of the heavier metals where the larger d orbitals provide better overlap, and the most stable complexes lie on the Ni-W line.

In free nitrogen, the stretching vibration is only Raman-active, at 2331 cm^{-1} , but all $M-(N_2)$ complexes have a band in the IR, usually $200\text{--}300\text{ cm}^{-1}$ lower than this. This corresponds to a slightly weaker $N\equiv N$ bond, still much stronger than $N=N$ in eg. Ph-N=N-Ph ($\nu(N=N)$ 1510 cm^{-1}). The lowest $\nu(N\equiv N)$ yet observed for a mononuclear complex is 1922 cm^{-1} for $\text{ReCl}(N_2)(\text{PMe}_2\text{Ph})_4$ ¹⁹⁷, but significant lowering of $\nu(N\equiv N)$ occurs in the dinuclear compounds which are consequently thought to be more readily reducible, given the appropriate conditions.

So far no $M-(N_2)$ complexes have been reduced to ammonia, and it has been suggested that the end-on structure is too stable. (All known nitrogenyl complexes contain end-on bonded nitrogen.) There is no evidence, however, that reducible species need contain sideways-bonded nitrogen, except by analogy with catalytic hydrogenations of olefines. It is hoped that the $N\equiv N$ bond will be weakened and activated by complexes. Structural studies have been reported for

four complexes:-

	<u>M-N</u>	<u>N≡N</u>	<u>M-N-N</u>	<u>Reference</u>
$\left[\text{Ru}(\text{NH}_3)_5(\text{N}_2) \right] \text{Cl}_2$	2.10(1)	1.12(8)	$\sim 180^\circ$ (disordered)	198
$\left[\text{Ru}(\text{NH}_3)_5 \right]_2(\text{N}_2)$	1.93(1)	1.21(1)	178°	183
$\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$	1.81(2)	1.11(1)	178°	199
$\left[\text{Ru}(\text{N}_3)(\text{N}_2)(\text{en})_2 \right] \text{PF}_6$	no data available			200

These results show that the bond length is almost the same as in free gaseous N_2 (1.1\AA),²⁰¹ i.e. still essentially a triple bond.

Although there were some early claims²⁰² that complexed nitrogen had been successfully reduced to NH_3 , there is no authenticated example of this happening. Various Ziegler-Natta type systems have been found to generate ammonia, but always in strongly reducing, non-aqueous conditions. Some of these are catalytic reactions,²⁰³ and there is some evidence (ESR)^{188b} for hydride intermediates. This correlates with the observation that all nitrogen-fixing bacteria contain hydrogenases, and it is possible that cis coordinated H and N_2 would be in the most favourable orientation for reduction. The recently discovered heterodinuclear complexes may be the closest,¹⁹⁷ so far, to a nitrogenase model; it has been suggested that the $\text{Re(I)}-(\text{N}_2)-\text{Mo}$ system in $(\text{PMe}_2\text{Ph})_4\text{ClRe}-(\text{N}_2)-\text{MoCl}_4$ (PEtPh_2) is analogous to $\text{Fe(II)}-(\text{N}_2)-\text{Mo}$. A bonding scheme has been postulated in which the Mo acts as an

electron sink to polarise the $N\equiv N$ bond. In the extreme case this would give $Re\equiv N-N\equiv Mo$, which could then break up giving NH_3 .

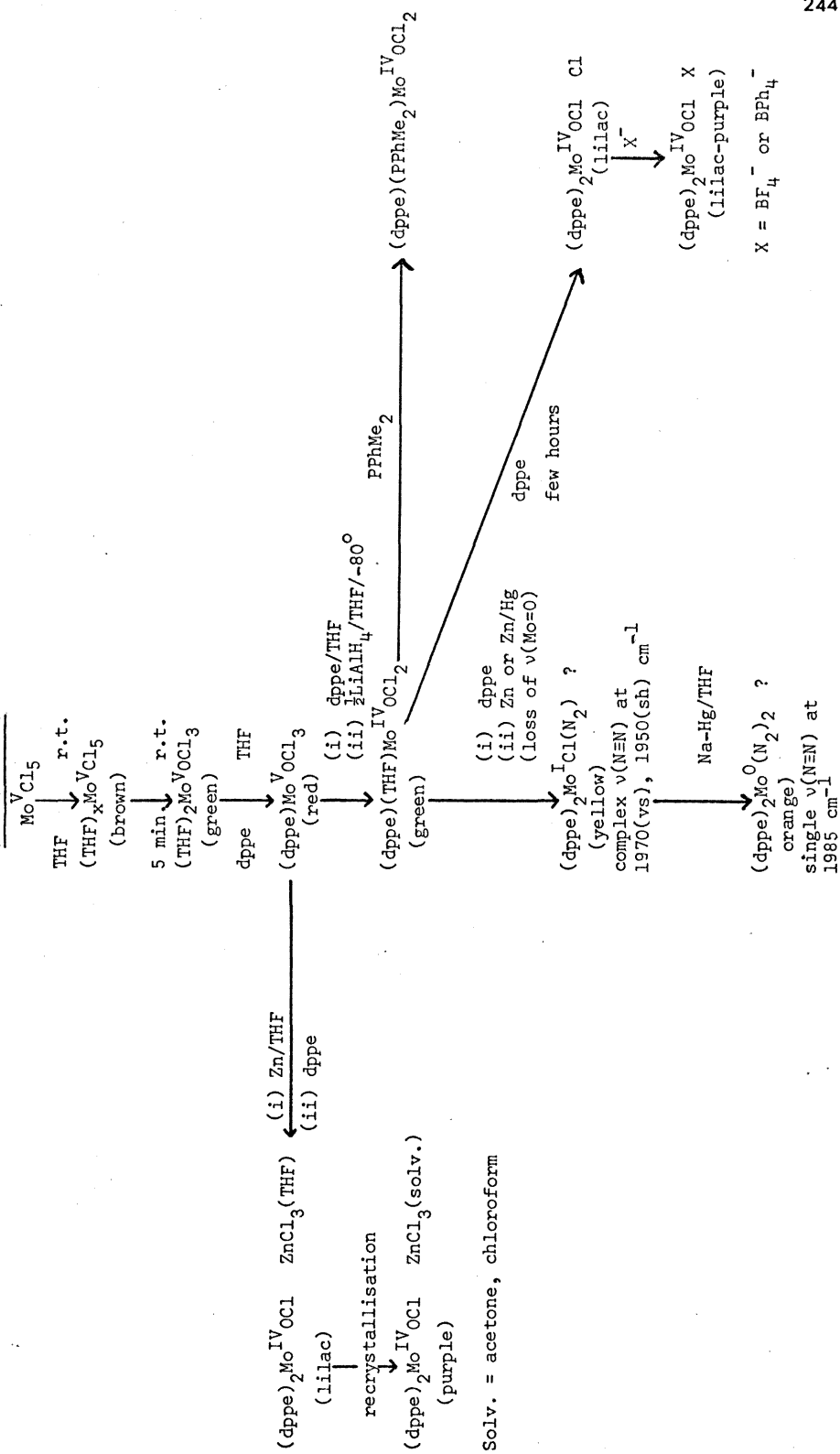
There have also been studies on nitrogen fixation on metal surfaces, e.g. with nickel a strong band at 2202 cm^{-1} in the IR indicates that the bonding is probably end-on, and that chemisorption has occurred.²⁰⁴

Molybdenum-Nitrogen System

D C Smith and co-workers in Petrochemical and Polymer Laboratory have been studying routes to molybdenum dinitrogenyl complexes, starting from $Mo(V)$.²⁰⁵ The precise course of the reduction to $Mo(I)$ and $Mo(0)$ was, however, unclear because of difficulties in characterising the intermediates. The reaction scheme, as finally elucidated, is shown in Figure 1. The yellow, air-stable $Mo(I)$ complex gave variable analyses, the nearest formula being $MoCl(N_2)(dppe)_2$. (The analysis was complicated by the presence of co-product $Mo(N_2)_2(dppe)_2$.) Different samples always had one, sometimes two, bands at 1970 and 1950 cm^{-1} , which were assigned to $\nu(N\equiv N)$. Far IR (single $\nu(Mo-Cl)$ at 313 cm^{-1}) and $\mu_{eff}(2.1\text{ BM})$ were also in agreement with this structure. The complex reacts with $MoCl_4(THF)_2$ to give a blue product with $\nu(N\equiv N)$ at 1770 , 1720 cm^{-1} , and this probably contains the $Mo-(N_2)-Mo$ grouping, by analogy with Chatt's Re-Mo nitrogen complex.¹⁹⁷

Crystals were prepared by D C Smith, and recrystallised

FIGURE 3.1.1.1



Solv. = acetone, chloroform

by Mrs V C Adam from 98% acetone/2% pentane. They were very thin, brittle yellow flakes of irregular shape. The crystal used for collecting data was one of the largest obtainable, and is shown in Figure 2.

Crystal Data

$C_{52}H_{48}MoP_4Cl_2$, $M = 963$, monoclinic; $a = 49.161 \pm 0.076$,
 $b = 10.958 \pm 0.012$, $c = 18.171 \pm 0.019$ Å, $\beta = 99.1 \pm 0.1^\circ$,
 $V = 9666$ Å³, $Z = 8$, $D_c = 1.33$, $F(000) = 3968$,
 Space Group $C2/c$ (C_{2h}^6 ; no. 15), $MoK\alpha$ (Nb filter),
 $\lambda = 0.7107$ Å, $\mu = 5.5$ cm⁻¹.

Data Collection

Temperature -70° ; scan range -0.8° to $+0.5^\circ$;
 Scan speed 2° 2 θ /minute; fixed time 20 seconds;
 Standards (0 0 2) and (12 0 0) falling to 97% and
 100% of initial intensity; reflections measured in
 octants $\{hkl\}$ and $\{h\bar{k}l\}$, to a maximum
 $2\theta = 39^\circ$; cell dimensions from 4 reflections
 (16 measurements) giving angles $\alpha = 90.00(10)$,
 $\gamma = 89.97(12)$; total number of independent structure
 amplitudes obtained after data reduction and collation
 of equivalent reflections 3260.

Solution of Structure

Form factors for Mo, Cl, P atoms were corrected for $\Delta f'$.
 After averaging equivalent reflections, only 270 terms
 had observed amplitudes $>10\sigma$. All terms $>8\sigma$ were used in

TABLE 3.1.1

Refinement of the structure of $\text{MoCl}_2(\text{dppe})_2$

Cycle Number.	Number of terms	Criteria	R Value	Atoms included	Matrix type			Vibrations			Weighting used	
					Mo	P	Cl	Mo	P	Cl	C(B)	C(R)
1-3	455	min.amp.8	34.5	Mo	b	-	-	i	-	-	-	-
4-5	455	min.amp.8	31.1	Mo,Pl-P3	b	b	-	i	i	-	-	-
6	455	min.amp.8	32.5	Mo,Pl-P3 Cl 1, 6 C(ring)	bd	bd	bd	i	i	i	-	i
7	455	min.amp.8	30.3	Mo,Pl-P4, Cl 1, C(bridging) Some C(ring) (see text)	bd	bd	bd	bd	i	i	i	i
8,9	455	min.amp.8	14.5	all atoms	b(1)	b(1)	b(1)	rbg	i	i	i	i

Matrix types:

b = full block
 bd = block diagonal
 rbg = rigid bodies
 C(B) = C(bridging)
 C(R) = C(ring)

Thermal parameters: i = isotropic

Final scale = 21.5 (cycle 9)

Final convergence factor = 0.37 (cycle 9)

the analysis, giving a total of 455. The Patterson map of C2/c has Harker vectors at:-

$$\begin{array}{ccc} 2x & 2y & 2z \\ 0 & 2y & \frac{1}{2} \\ \frac{1}{2}-2x & \frac{1}{2} & \frac{1}{2}-2z \end{array}$$

corresponding to the equivalent positions at:-

$$\begin{array}{ccccc} x & y & z & -x & -y & -z \\ x & -y & \frac{1}{2}+z & -x & y & \frac{1}{2}-z \\ \frac{1}{2}+x & \frac{1}{2}+y & z & \frac{1}{2}-x & \frac{1}{2}-y & -z \\ \frac{1}{2}+x & \frac{1}{2}-y & \frac{1}{2}+z & \frac{1}{2}-x & \frac{1}{2}+y & \frac{1}{2}-z \end{array}$$

A consistent solution was found for Mo at (0.134 0.180 0.0505), and after three cycles (see Table 1) the R value for this position was 34.5%, though the U value had decreased to 0.014. The F(obs) map on these planes showed the positions of three possible P atoms, but after two more cycles R had only decreased to 31.1%. The corresponding F(diff) map showed that one P atom (P3) had been wrongly identified; it also indicated a Cl atom and the positions of the phosphine links. There was a blur of electron density in the area of the wrongly placed P atom, but it was not possible to identify this as a nitrogen molecule. Further calculations are shown in the table (Cycles 6 and 7), during which more carbon atoms were added.

It appeared from the maps computed that P3 was in fact a second chlorine atom. Accordingly, the rigid body parameters for the phenyl rings were calculated, and two cycles (8 and 9) of refinement assuming the formula $\text{MoCl}_2(\text{dppe})_2$ were computed. The $F(\text{obs})$ map at $R=14.5\%$ showed quite conclusively that there is no space to accommodate a nitrogen molecule so that N_2 must have been lost during recrystallisation. The geometry of the molecule was not very clearly defined, although the positions of the two chlorine atoms and the phosphine groups could be seen. Since the nitrogen had been lost, and the data was so weak, further refinement did not seem to be justifiable, and so was halted at $R=14.5\%$.

Results

The molecular geometry is listed in Table 4. (This is, however, not very accurate, because of lack of data. No standard deviations are given.) The final positional and vibrational parameters are given in Tables 2 and 3 in the Appendix. A drawing of one molecule is shown in Figure 3.

It is not possible to comment usefully on the coordination around Mo: the bond lengths vary considerably, but this is probably due to the low resolution. Mo-P distances vary from 2.38 to $2.76\overset{\text{O}}{\text{\AA}}$; the average being close to that in $\text{MoOCl}(\text{dppe})_2^+$, ($2.55\overset{\text{O}}{\text{\AA}}$). The two Mo-Cl bonds are

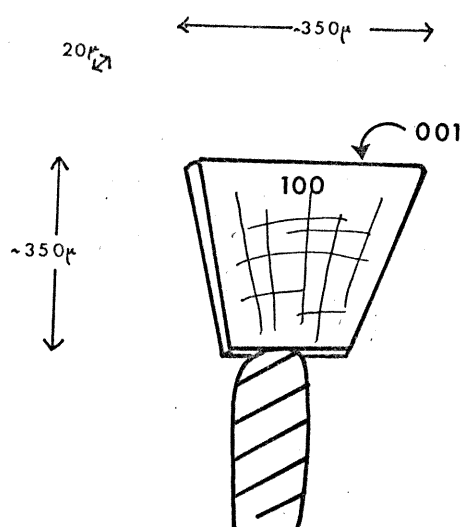


Figure 3.1.2

$\text{MoCl}_2(\text{dppe})_2$ Crystal

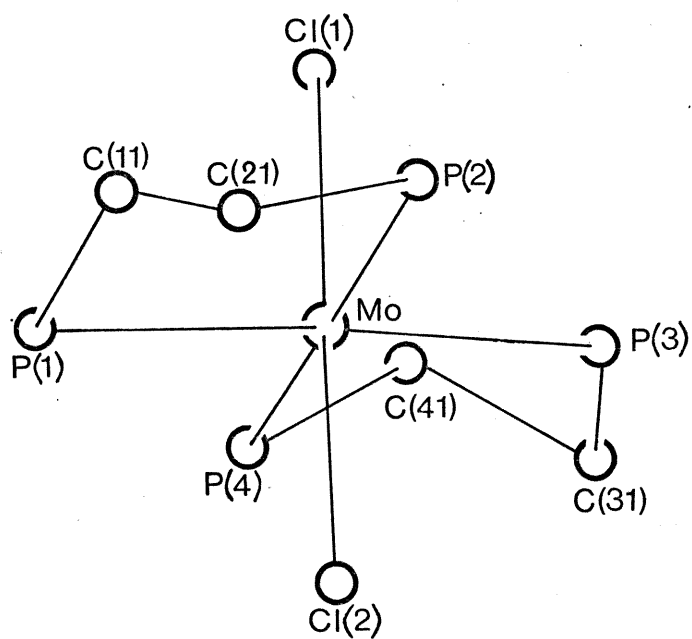


Figure 3.1.3

View of Molybdenum and ligand skeleton, with the numbering system used.

Table 3.1.4

Bond distances (\AA) and angles ($^\circ$).

Mo-Cl(1)	2.42	P(1)-Mo-P(2)	73
Mo-Cl(2)	2.48	P(1)-Mo-P(3)	172
Mo-P(1)	2.60	P(1)-Mo-P(4)	101
Mo-P(2)	2.76	P(1)-Mo-Cl(1)	104
Mo-P(3)	2.38	P(1)-Mo-Cl(2)	78
Mo-P(4)	2.49	P(2)-Mo-P(3)	107
		P(2)-Mo-P(4)	174
P(1)-C(11)	2.14	P(2)-Mo-Cl(1)	92
P(2)-C(21)	1.58	P(2)-Mo-Cl(2)	83
C(11)-C(21)	1.85	P(3)-Mo-P(4)	78
		P(3)-Mo-Cl(1)	84
P(3)-C(31)	2.30	P(3)-Mo-Cl(2)	94
P(4)-C(41)	1.53	P(4)-Mo-Cl(1)	87
C(31)-C(41)	2.16	P(4)-Mo-Cl(2)	98
P(1)-C(111)	1.79	P(3)-C(311)	2.04
P(1)-C(121)	1.90	P(3)-C(321)	1.75
P(2)-C(211)	1.79	P(4)-C(411)	1.98
P(2)-C(221)	1.81	P(4)-C(421)	1.96

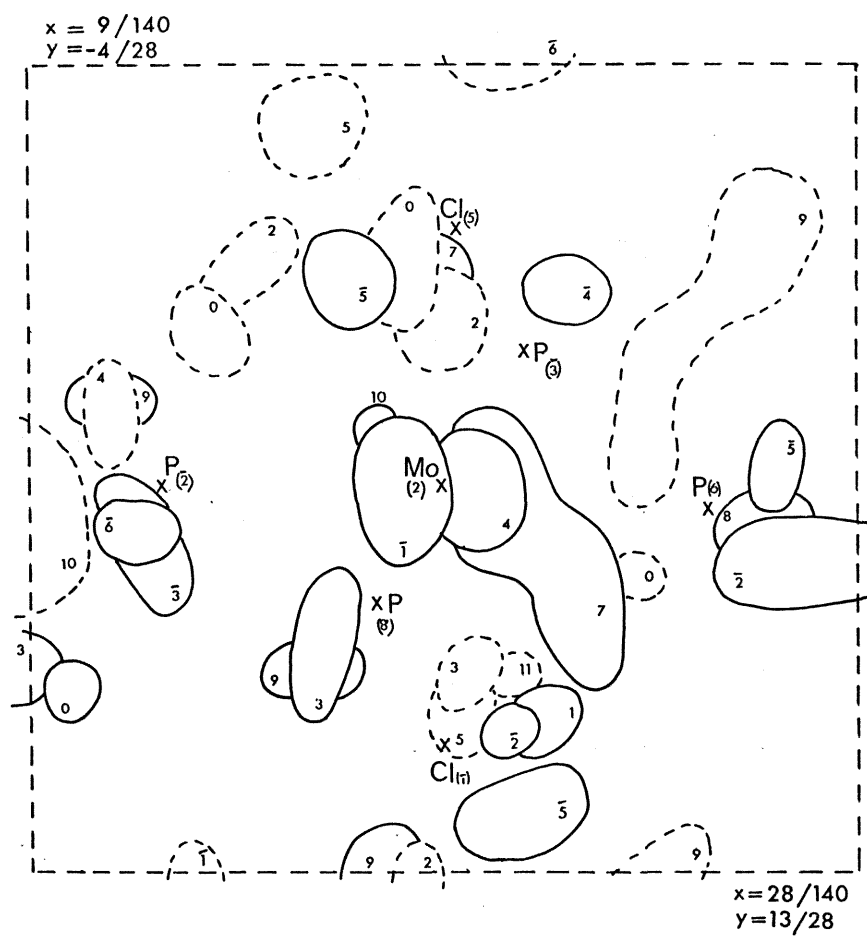


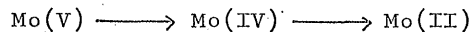
Figure 3.1.4
 $\text{MoCl}_2(\text{dppe})_2$

Projection down z of $F(\text{diff})$ map at cycle 9. Contours at intervals of $0.5 \text{ e}/\text{\AA}^3$; z heights (48ths) shown in small type.

similar to that in $\text{MoOCl}(\text{dppe})_2^+$, (2.46Å). All the angles round Mo are approximately 90° , the largest being P1-Mo-P4, 101° ; P1-Mo-Cl1, 104° ; P2-Mo-P3, 107° . None of these gaps is large enough to accommodate an extra ligand, nor is there any suggestion of electron density in any of the gaps. (See Figure 4) It is therefore impossible to decide where the nitrogen molecule was situated before it was lost from the complex. The geometry of the phosphine ligands is very approximate; the linking C(methylene) atoms, and some of the phenyl rings appear as smears of density.

Postscript

This structure analysis and that of $\text{MoOCl}(\text{dppe})_2^+$ (described in the following chapter), show that the reduction of Mo(V) species follows a complicated route, of which the main stages are:-



and that the intermediate stage probably involves a delicate equilibrium between several different complexes. The analysis of $\text{MoCl}_2(\text{dppe})_2$ has shown that the nitrogen-containing complex is a 7-coordinate Mo(II) species, since it probably has the formula $\text{Mo}^{\text{II}}\text{Cl}_2(\text{N}_2)(\text{dppe})_2$ rather than $\text{Mo}^{\text{I}}\text{Cl}(\text{N}_2)(\text{dppe})_2$. The nitrogen is readily

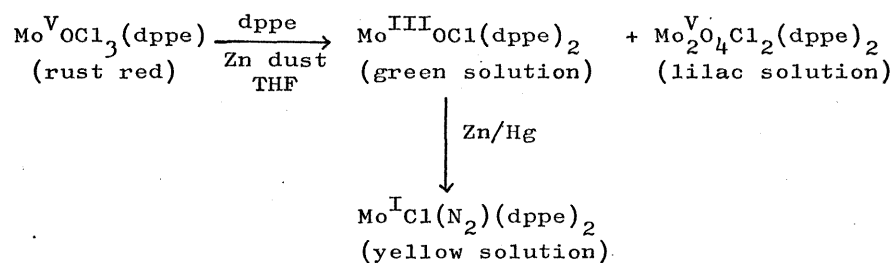
lost to give $\text{Mo}^{\text{II}}\text{Cl}_2(\text{dppe})_2$ as the stable product.

A sample of $\text{MoCl}_2(\text{dppe})_2$, prepared independently by D C Smith, was photographed, and shown to be identical with the crystals analysed. This confirms the composition of the sample studied.

CHAPTER 3.2

THE CRYSTAL AND MOLECULAR STRUCTURE OF
TRANS-[Mo(O)Cl(dppe)₂] [ZnCl₃(acetone)] .acetone

The route to molybdenum nitrogenyl complexes involving reduction of Mo(V) oxychloro complexes has been described in the preceding Chapter. Starting from MoCl₅, addition of tetrahydrofuran and then a phosphine, e.g. dppe, gives MoOCl₃(dppe). If a reducing agent is now added, many different low-valent complexes can be formed, depending on the agent used. At an early stage in these investigations, the postulated reaction scheme was:-



(dppe is the bidentate phosphine Ph₂P.C₂H₄.PPh₂)

The lilac compound was thought to be a dimer of Mo(V) formed by a disproportionation of Mo(IV) to Mo(V) and Mo(III). (The oxidation state and composition of the yellow complex were also uncertain at this time.)

Crystals could not be isolated from the green solution, but purple crystals could be obtained from either the lilac or the yellow solutions. However, these could not be satisfactorily characterised, and so the crystal structure of the purple compound was studied.

The structure analysis revealed the unexpected reason for poor analytical figures. The compound is not a dimer, but is a solvated ionic Mo(IV) complex - $\left[\text{MoOCl}(\text{dppe})_2 \right]^+ \left[\text{ZnCl}_3(\text{acetone}) \right]^-$. The presence of zinc was later confirmed by elemental analysis; conductivity measurements showed the compound to be a 1:1 electrolyte. Chemical analysis gave good agreement with the calculated values for crystals after allowing for the acetone molecule of solvation.

	<u>Observed</u>	<u>Calc. for</u> $\left[\text{MoOCl}(\text{dppe})_2 \right]^+ \left[\text{ZnCl}_3(\text{acetone}) \right]^- \cdot \text{acetone}$
Mo	-	7.8
Zn	-	5.3
Cl	11.68	11.53
P	10.32	10.07
O	-	3.9
C	55.8	56.5
H	5.14	4.88

By hindsight, this structure is also interesting because of the rarity of simple Mo(IV) oxo species; the only

other crystal structure is that of $\text{NaK}_3 \left[\text{MoO}_2(\text{CN})_4 \right] \cdot 6\text{H}_2\text{O}$.²⁰⁶ It is also an example of chemical analysis by crystallography!

The reaction scheme finally elucidated, is shown in Figure 1 of the preceding chapter (Chapter 3.1).²⁰⁷

This scheme also gives the method of preparation of the crystals used in the structure analysis.

Preliminary Observations

Two forms of the crystals were examined:-

- (a) triclinic needles from the lilac or green solution; and
- (b) orthorhombic prisms from the yellow solution.

The orthorhombic crystals were much better formed and were therefore chosen for detailed study. (Chemical analysis confirmed that both forms were the same compound.) The crystal used is shown in Figure 1.

Crystal Data

$\text{C}_{58}\text{H}_{60}\text{MoZnP}_4\text{Cl}_4\text{O}_3$, $M = 1231.3$; orthorhombic,
 $a = 25.377 \pm 0.030$, $b = 18.337 \pm 0.014$, $c = 24.558 \pm 0.011$ Å,
 $V = 11428$ Å³, $D_m = 1.40$ (floatation), $Z = 8$, $D_c = 1.43$,
 $F(000) = 7456$, Space Group Pbca (D_{2h}^{15} ; no. 61), $\text{MoK}\alpha$
 radiation (Nb filter), $\lambda = 0.7107$ Å, $\mu = 9.9$ cm⁻¹.

Data Collection

Temperature -70° ; scan range -0.8° to $+0.5^{\circ}$;
 Scan speed 2° 2θ /minute; fixed time 20 seconds;
 Standards (0 0 12) and (0 8 0) falling to 87%
 and 89% of initial intensity; reflections measured
 in the octant $\{hkl\}$ to a maximum $2\theta = 46^{\circ}$;
 cell dimensions from 5 reflections (20 measurements)
 giving angles $\alpha = 89.96(5)$, $\beta = 89.99(6)$, $\gamma = 90.07(8)$;
 total number of independent structure amplitudes
 obtained after data reduction and collation of
 equivalent reflections 3822.

Solution and Refinement of Structure

Formfactors for Mo, P, Cl were corrected for $\Delta f'$;
 also those for Zn, when the presence of zinc was
 discovered.

A modified planes list, containing only those terms
 with observed amplitude $> 3\sigma$ on initial scaling, was
 generated for the Patterson, which was solved for a
 Mo atom in the general position (0.158 0.1385 0.222).
 This corresponds to a Mo-Mo distance of $\sim 14\text{\AA}$, so that
 a binuclear structure was ruled out. Cycles 1-4 (see
 Table 1) gave $R=49.1\%$. The subsequent $F(\text{obs})$ map
 clearly revealed the positions of six atoms round the
 metal atom, but when refinement was attempted on Mo,
 and the five highest peaks, it diverged at 38.8%. The
 temperature factor of the atom labelled chlorine

TABLE 3.2.1(a)
Refinement of the structure of $\text{MoOCl}(\text{dppe})_2 \cdot \text{ZnCl}_3(\text{acetone}) \cdot \text{acetone}$

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Mo	Cl	O	P	C(B)	C(R)	Zn	Cl	acetone	free acetone	Weighting used
1-4	2931	min.amp./ deviation 10	49.1	Mo	b i	-	-	-	-	-	-	-	-	-	1
5,6	413	min.amp./ deviation 20	38.8	Mo, Cl Pl-P4	b i	b i	- i	b i	-	-	-	-	-	-	1
7-9	1799	min.amp./ deviation 18	39.6	Mo, Pl-P4	b i	-	-	b i	-	-	-	-	-	-	1
10,11	1799	min.amp./ deviation 18	33.0	Mo, O, Cl Pl-P4 Some carbons Zn Cl2 Cl3	pbd tbd i i	pbd tbd i i	pbd tbd i i	pbd tbd i i	pbd tbd i i	pbd tbd i i	pbd tbd i i	pbd tbd i i	-	-	
12	1799	min.amp./ deviation 18	20.2	(Mo) ⁺ Zn, Cl2-4	bd i	bd i	bd i	bd i	bd i	rbg i	bd i	bd i	-	-	1
13	1799	min.amp./ deviation 18	12.5	(Mo) ⁺ (Zn) ⁻	bd i	bd i	bd i	bd i	bd i	rbg i	bd i	bd i	bd i	-	1

Matrix types: b = full block
pbd} = block diagonals
tbd} = rigid bodies
bd} = C(bridging)
rbg = C(ring)

Thermal parameters: i = isotropic

TABLE 3.2.1(b)
Refinement of the structure of $\text{MoOCl(dppe)}_2 \cdot \text{ZnCl}_3(\text{acetone}) \cdot \text{acetone}$

Cycle Number	Number of terms	Criteria	R Value	Atoms included	Mo	Cl	O	P	C(B)	C(R)	Zn	Cl	acetone	free acetone	Weighting used
14	1799	min.amp./ deviation 18	13.0	$(\text{Mo})^+(\text{Zn})^-$	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(2) tbd	pb(2) tbd	pb(2) tbd	-	$c_1 = 120$ $c_2 = 120$ $c_2(2)$
15	1799	min.amp./ deviation 18	16.8	$(\text{Mo})^+(\text{Zn})^-$	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(1) tbd	pb(2) tbd	pb(2) tbd	pb(2) tbd	-	2
16-18	1799	min.amp./ deviation 18	8.3	$(\text{Mo})^+(\text{Zn})^-$	b(1) i	b(1) i	b(1) i	b(1) i	b(1) i	b(1) i	b(2) i	b(2) i	b(2) i	-	2
19,20	1799	min.amp./ deviation 18	6.6	all atoms	b(1) i	b(1) i	b(1) i	b(1) i	b(1) i	b(1) i	b(2) i	b(2) i	b(2) i	b(5) i	2

Matrix types:

b = full block
pb = positional block
tb = vibrational block
tbd = block diagonal
rbg = rigid bodies
C(B) = C(bridging)
C(R) = C(ring)

Thermal parameters: a = anisotropic
i = isotropic
Final scale = 6.14 (cycle 20)
Final convergence factor = 0.66 (cycle 20)

increased to 0.16 - (this was later seen to be a P atom) - and so three cycles omitting this atom were computed (Cycles 7-9), and an F(obs) map. All the vibrations were low, but not unreasonable. This map revealed a large peak a long way from the Mo coordination sphere, surrounded by three peaks. At the time, I did not know that zinc dust had been used in the reduction, and thought possibly that this extra atom (which was too high to be Al, Li, or C), might be another Mo, possibly part of a complex anion. When it was discovered that zinc had been in the reaction mixture, it seemed most likely that the anion was $(\text{ZnCl}_3\text{X})^-$, with X as yet unknown. The peak heights on this map were:-

Mo	99*	Zn	37
P1	24*	Cl2	19
P2	32*	Cl3	15
P3	27	Cl4	13
P4	28*		
Cl	26*		
O	9		

* input atoms

From some possible phenyl carbon positions, and bridging carbons, all the coordinated atoms were now identified and renumbered. Two further cycles (10, 11) were calculated using the block diagonal approximation, and an F(obs) map. As well as showing all the ring atoms, this suggested that the zinc was tetrahedrally coordinated, to three chlorine atoms, and to a trigonal planar molecule, possibly acetone.

At this stage, the phenyl rings were constrained to rigid bodies, and their group parameters were calculated. All atoms except the possible coordinated acetone were included in the first cycle (12) of rigid body refinement (as described in Chapter 1.2), and an $F(\text{obs})$ map was computed, over the area occupied by the acetone. This confirmed that it was a coordinated acetone, and it was included in the next cycle (13), which reduced R to 12.5%. A better weighting scheme was next introduced, and anisotropic refinement of the heavy atoms (Mo, P, Cl, Zn atoms), was attempted. However, after the first cycle (14), R was 13.0%, but all the shifts in U_{ii} were large and negative; the new U_{11} values were:-

Mo	.01	Zn	.03
P1	.01	Cl2	.02
P2	-.00	Cl3	.02
P3	.01	Cl4	.03
P4	.01		
Cl1	.02		

After Cycle 15, R increased to 16.8%, and all the anisotropic vibrations had regained their original values:-

Mo	.03	Zn	.05
P1	.04	Cl2	.06
P2	.04	Cl3	.05
P3	.05	Cl4	.08
P4	.05		
Cl1	.06		

The cause of this behaviour is not clear, but a contributing factor could be that the block diagonal

refinement used did not allow sufficiently for the correlations between chemically interdependent atoms; the shifts in Cycles 14 and 15 were in each case as large as the expected U values, and the parameters showed signs of oscillating. Accordingly, it was decided not to refine anisotropically, to use larger blocks, and to apply fractional shifts to all parameters. i.e. the atoms Mo, O1, P1-4, C11; Zn, C12-4; acetone; and bridging carbons, were put into four separate blocks in which positions and vibrations were refined together, and 0.8 of the calculated shifts were applied. After three cycles (16-18) of refinement, R was 8.3%, and the shifts were small compared to the standard deviations. The agreement analysis seemed reasonable, and so an F(diff) map was computed. This showed small variations of electron density at or near most of the atoms, corresponding to unaccounted-for anisotropy of vibration, and also several peaks due to hydrogen atoms. However, there was a very pronounced group of four peaks in an otherwise empty part of the cell, and this is presumed to be an acetone molecule of solvation. (The atoms appeared at heights of $\sim 2e$.) Refinement of the whole structure gave $R=6.6\%$ after two further cycles (19 and 20), and was not continued any further.

Table 3.2.4

Bond distances (\AA) and angles ($^\circ$), with their estimated standard deviations.

MoOC1(dppe)₂⁺

Mo-Cl(1)	2.462(6)	Cl(1)-Mo-P(1)	85.3(2)
Mo-P(1)	2.554(7)	Cl(1)-Mo-P(2)	86.1(2)
Mo-P(2)	2.569(7)	Cl(1)-Mo-P(3)	89.1(2)
Mo-P(3)	2.575(6)	Cl(1)-Mo-P(4)	86.2(2)
Mo-P(4)	2.574(7)	P(1)-Mo-P(2)	78.7(2)
Mo-O(1)	1.687(16)	P(1)-Mo-P(3)	100.0(3)
		P(1)-Mo-P(4)	171.4(2)
P(1)-C(11)	1.81(3)	P(2)-Mo-P(3)	175.1(3)
P(1)-C(111)	1.85(2)	P(2)-Mo-P(4)	101.6(2)
P(1)-C(121)	1.85(2)	P(3)-Mo-P(4)	79.0(2)
P(2)-C(21)	1.87(2)	O(1)-Mo-Cl(1)	176.8(6)
P(2)-C(211)	1.84(2)	O(1)-Mo-P(1)	97.2(6)
P(2)-C(221)	1.83(2)	O(1)-Mo-P(2)	96.4(6)
P(3)-C(31)	1.82(3)	O(1)-Mo-P(3)	88.5(6)
P(3)-C(311)	1.85(2)	O(1)-Mo-P(4)	91.4(6)
P(3)-C(321)	1.83(2)		
P(4)-C(41)	1.88(2)	P(1)-C(11)-C(21)	112.6(18)
P(4)-C(411)	1.85(2)	P(2)-C(21)-C(11)	111.8(17)
P(4)-C(421)	1.84(2)	P(3)-C(31)-C(41)	109.9(15)
C(11)-C(21)	1.51(4)	P(4)-C(41)-C(31)	105.2(14)
C(31)-C(41)	1.62(3)		
Mo-P(1)-C(11)	105.8(10)	Mo-P(2)-C(21)	108.6(7)
Mo-P(1)-C(111)	125.6(7)	Mo-P(2)-C(211)	119.1(8)
Mo-P(1)-C(121)	112.8(7)	Mo-P(2)-C(221)	117.6(7)
C(11)-P(1)-C(111)	101.9(12)	C(21)-P(2)-C(211)	98.7(11)
C(11)-P(1)-C(121)	105.3(12)	C(21)-P(2)-C(221)	104.8(10)
C(111)-P(1)-C(121)	103.5(9)	C(211)-P(2)-C(221)	105.6(10)
Mo-P(3)-C(31)	105.6(9)	Mo-P(4)-C(41)	108.8(7)
Mo-P(3)-C(311)	113.3(7)	Mo-P(4)-C(411)	128.1(7)
Mo-P(3)-C(321)	121.8(7)	Mo-P(4)-C(421)	110.7(8)
C(31)-P(3)-C(311)	101.4(11)	C(41)-P(4)-C(411)	99.8(9)
C(31)-P(3)-C(321)	106.2(11)	C(41)-P(4)-C(421)	104.1(11)
C(311)-P(3)-C(321)	106.4(10)	C(411)-P(4)-C(421)	102.7(11)

Table 3.2.4 (contd.)

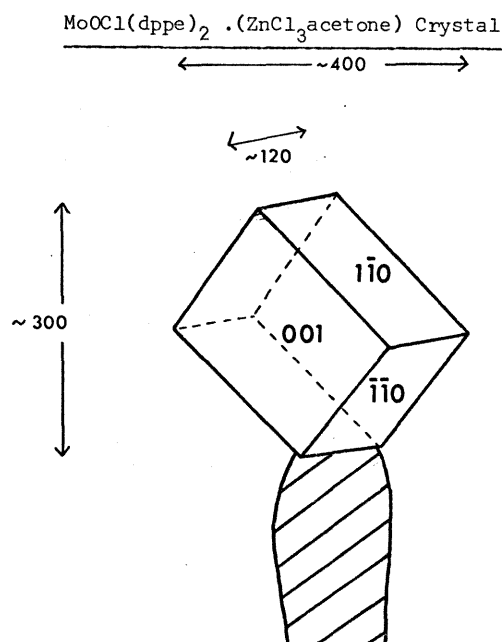
ZnCl₃.acetone⁻

Zn-Cl(2)	2.235(8)	Cl(2)-Zn-Cl(3)	117.6(3)
Zn-Cl(3)	2.221(8)	Cl(2)-Zn-Cl(4)	113.2(3)
Zn-Cl(4)	2.233(8)	Cl(2)-Zn-O(2)	99.1(6)
Zn-O(2)	2.121(20)	Cl(3)-Zn-Cl(4)	116.6(3)
		Cl(3)-Zn-O(2)	100.6(6)
		Cl(4)-Zn-O(2)	106.2(6)
O(2)-C(1)	1.24(4)	Zn-O(2)-C(1)	131.2(18)
C(1)-C(2)	1.52(5)	O(2)-C(1)-C(2)	118.4(26)
C(1)-C(3)	1.48(4)	O(2)-C(1)-C(3)	125.5(26)
		C(2)-C(1)-C(3)	115.8(26)

Free Acetone

O(3)-C(4)	1.21(4)	O(3)-C(4)-C(5)	123.1(31)
C(4)-C(5)	1.51(5)	O(3)-C(4)-C(6)	120.9(31)
C(4)-C(6)	1.47(5)	C(5)-C(4)-C(6)	115.9(28)

Figure 3.2.1



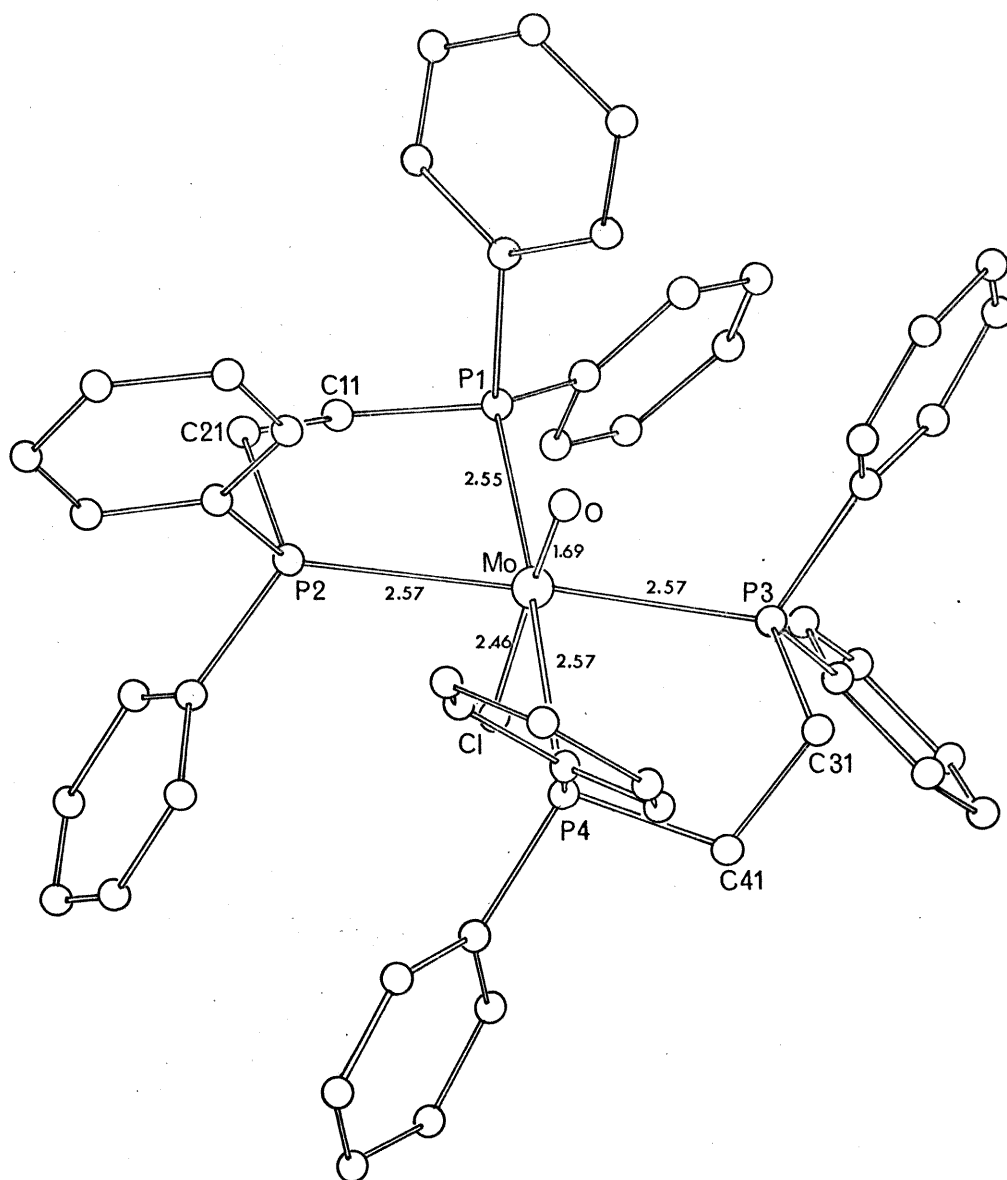


Figure 3.2.2
 $\text{Mo}(\text{O})\text{Cl}(\text{dppe})_2^+$

View of the cation, showing the geometry round molybdenum.

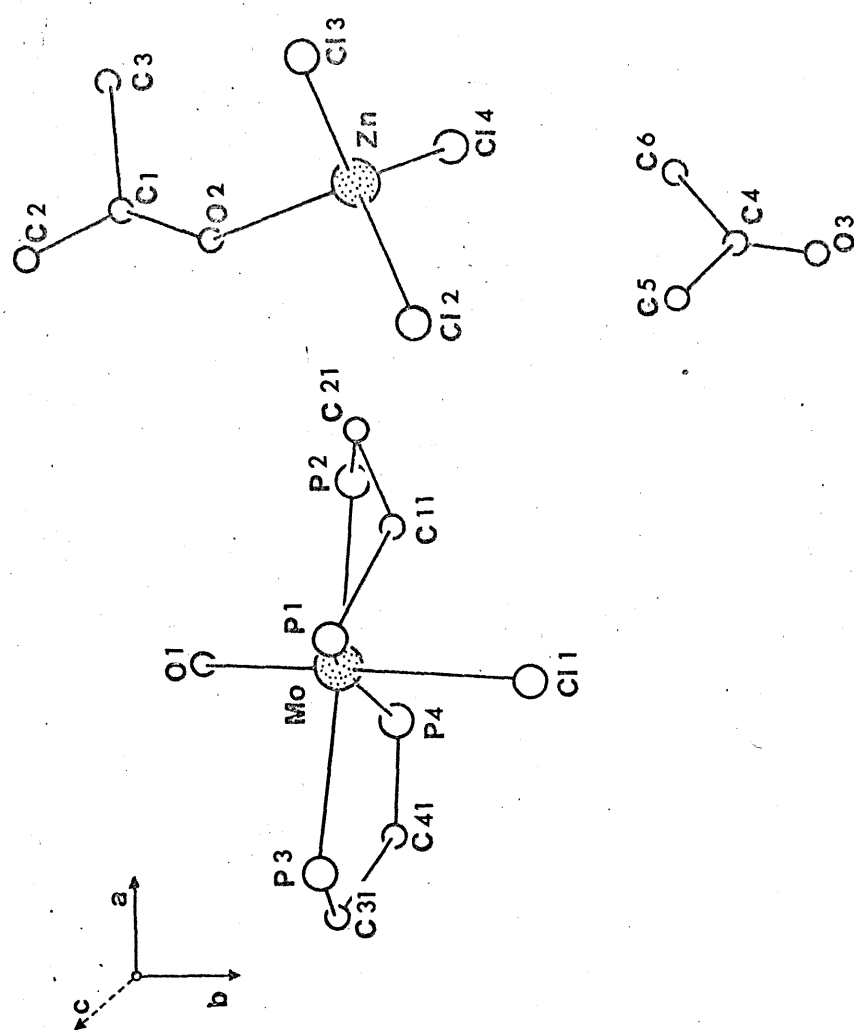


Figure 3.2.3

$\text{Mo(O)Cl(dppe)}_2 \cdot \text{ZnCl}_3(\text{acetone}) \cdot \text{acetone}$

One asymmetric unit viewed down the z axis.

Results and Discussion

The final positional and vibrational parameters are listed in Tables 2 and 3 in the Appendix, and the geometry of the complex in Table 4. The agreement analysis is shown in Table 5. Figure 2 shows the cation; Figure 3 shows one asymmetric unit of the structure, projected down the c axis. (This figure also shows the numbering scheme used.)

The cation has a nearly regular octahedral geometry, while the anion is distorted tetrahedral. The free acetone molecule of solvation plays no part in the coordination.

Considering first the Mo(IV) cation, the Mo=O bond (1.69\AA) is very comparable to other non-bridging Mo=O bonds, in which there is some double bonding. Similar M=O distances are observed with other heavy metals, e.g. 1.75\AA in $\text{OsCl}_4\text{O}_2^{2-}$ ²⁰⁸, 1.76\AA in ReClO_3 ²⁰⁹ and 1.89\AA in WOCl_4 (diars)²¹⁰. Bridging Mo-O bonds are longer, and terminal Mo-O single bonds (as in $\text{Mo}_2\text{O}_2(\text{oxalate})_2(\text{H}_2\text{O})_2$)²¹¹ are $\sim 2.1\text{\AA}$. Molybdenum is a metal for which there is extensive bond length data in all its oxidation states, and it can be seen that the Mo=O distance is not very sensitive to changes in the Mo oxidation state:-
(See also Table 6)

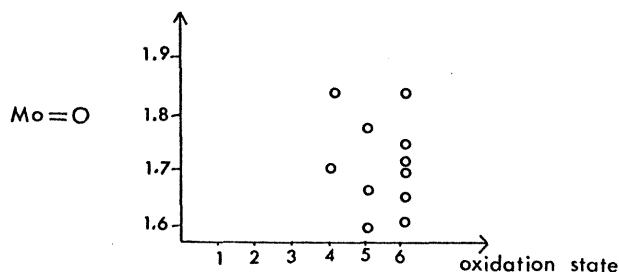


TABLE 3.2.6

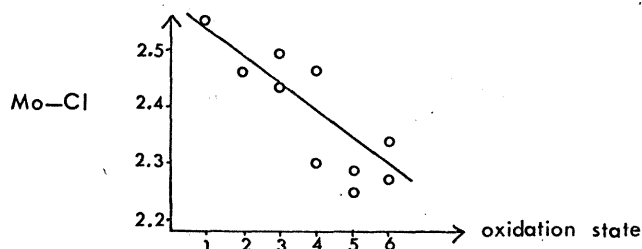
Mo-O Distances in mononuclear complexes

	Mo-O	Reference
$\text{Mo}^{\text{VI}}\text{OF}_4$	1.65	a
$\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}_2$ (gas)	1.75	b
$\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}_2(\text{NN-DMF})_2$	1.68	c
$\text{Mo}^{\text{VI}}\text{O}_3(\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2)$	1.74	d
$\text{Mo}^{\text{VI}}\text{O}_2(\text{C}_9\text{H}_6\text{NO})_2$	1.71	e
$\text{Mo}^{\text{VI}}\text{O}_2(\text{Et}_2\text{NCS}_2)$	1.63	f
$\text{Mo}^{\text{VI}}\text{O}_2(\text{C}_{10}\text{H}_8\text{N}_2)\text{Br}_2$	1.64, 1.83	g
$\text{Mo}^{\text{V}}\text{OBr}_4(\text{H}_2\text{O})^-$	1.78	h
$\text{Mo}^{\text{V}}\text{OCl}_3$	1.60	i
$\text{Mo}^{\text{V}}\text{OF}_5^{2-}$	1.66	j
$\text{Mo}^{\text{IV}}\text{O}_2(\text{CN})_4^{4-}$	1.83	k
$\text{Mo}^{\text{IV}}\text{OCl}(\text{dppe})_2^+$	1.69	l

- a. A J Edwards & B R Steventon, JCS(A), 1968, 2503
- b. A F Wells, "Structural Inorganic Chemistry", p.387
- c. L R Florian & E R Corey, Inorg.Chem., 1968, 7, 722
- d. F A Cotton & R C Elder, Inorg.Chem., 1964, 3, 397
- e. L O Atovmyan & Y A Sokolova, JCS(D), 1969, 649
- f. A Kopwillen & P Kierkegaard, Acta.Chem.Scand., 1969, 23, 2184
- g. R H Fenn, JCS(A), 1969, 1764
- h. J G Scane, Acta.Cryst., 1967, 23, 85
- i. G Ferguson, M Mercer & D W A Sharp, JCS(A), 1969, 2415
- j. D Grandjean & R Weiss, Compt.Rend., 1966, 263(C), 58
- k. V W Day & J L Hoard, JACS, 1968, 90, 3374
- l. V C Adam, U A Gregory & B T Kilbourn, JCS(D), 1970, 1400

An octahedral radius of $1.6\overset{\circ}{\text{\AA}}$ has been derived for Mo(0), from Mo-C sigma bonds but is probably not applicable to Mo(IV). Nevertheless, the correct radius for Mo(IV) is presumably greater than the Pauling ionic value of $1.3\overset{\circ}{\text{\AA}}$.¹³⁸

The oxygen and chlorine are almost exactly trans to each other ($\text{O-Mo-Cl} = 177^\circ$), with Mo-Cl $2.462\overset{\circ}{\text{\AA}}$. This fits in well with the trend of Mo-Cl distances for different oxidation states. It is not possible to say that the short Mo=O bond has a weakening effect on the bond trans to it, but there is a slight lengthening of Mo-Cl relative to Mo(III)-Cl of $2.45\overset{\circ}{\text{\AA}}$. If the interpolation is reliable:-



Mo(IV)-Cl should be about $2.40\overset{\circ}{\text{\AA}}$. (See also Table 7)

The Mo-P bonds (average $2.57\overset{\circ}{\text{\AA}}$) are all very similar and longer than in other Mo phosphine complexes (see Table 8);

TABLE 3.2.7

Mo-Cl Distances

	<u>Mo-Cl</u>	<u>Reference</u>
Mo ^{VI} O ₂ Cl ₂ (gas)	2.28	a
Mo ^{VI} O ₂ Cl ₂ (NN-DMF) ₂	2.34	b
Mo ^V Cl ₅	2.24, 2.25	c
Mo ^V OCl ₃	2.28	d
Mo ^{IV} OCl(dppe) ₂ ⁺	2.46	
Mo ^{IV} Cl ₆ ²⁻	2.31	e
Mo ^{III} Cl ₆ ³⁻	2.43-2.49	f
Mo ^{II} Cl ₈ ⁴⁻	2.44-2.46	g
Mo ₂ ^I Cl ₈ ³⁻	2.38	h
Mo ^I (CO) ₃ (π Cp)Cl	2.54	i
Mo ^I (CO)(π Cp)Cl(dppe)	2.55	j

- a. A F Wells, "Structural Inorganic Chemistry", p.387
- b. L R Florian & E R Corey, Inorg.Chem., 1968, 7, 722
- c. D E Sands & A Zalkin, Acta.Cryst., 1959, 12, 723
- d. G Ferguson, M Mercer & D W A Sharp, JCS(A), 1969, 2415
- e. A G Edwards, R D Peacock & A Said, JCS, 1962, 4643
- f. Z Amilius, B van Laar & H M Rietveld, Acta.Cryst., 1969, B25, 400
- g. J V Brencic & F A Cotton, Inorg.Chem., 1969, 8, 7
J V Brencic & F A Cotton, Inorg.Chem., 1969, 8, 2698
- h. M J Bennett, J V Brencic & F A Cotton, Inorg.Chem., 1969, 8, 1060
- i. S Chiawasie & R H Fenn, Acta.Cryst., 1968, B24, 525
- j. J H Cross & R H Fenn, JCS(A), 1970, 3019

TABLE 3.2.8
Mo-P Distances

	<u>Mo-P</u>	<u>Reference</u>
MoOCl(dppe) ₂ ⁺		
Mo(CO) ₄ (PEt) ₅	2.51, 2.53	a
Mo(CO) ₄ (Ph ₂ P.C ₆ H ₄ .CH:CHMe)	2.52	b
Mo(CO) ₄ (Ph ₂ P.NEt.PPh ₂)	2.51	c
Mo(CO) ₂ (πCp)(COCH ₃)(PPh ₃)	2.47	d
Mo ₂ (πCp) ₂ H(PMe ₂)(CO) ₄	2.43 (bridging)	e
Mo(CO) ₃ (Ph ₂ P.NEt.PPh.NEt.PPh ₂)	2.43-2.53	f
Mo(CO)Cl(πCp)(dppe)	2.44, 2.50	g

- a. M A Bush & P Woodward, JCS(A), 1968, 1221
- b. H Luth, M R Truter & A Robson, JCS(A), 1969, 28
- c. D S Payne, J A A Mokuolu & J C Speakman, Chem.Comm., 1965, 599
- d. M R Churchill & J P Fennessey, Inorg.Chem., 1968, 7, 953
- e. R J Doedens & L F Dahl, JACS, 1965, 87, 2576
- f. K K Cheung, T F Lai & S Y Lam, JCS(A), 1970, 3345
- g. J H Cross & R H Fenn, JCS(A), 1970, 3019

these other complexes contain the metal in a very low oxidation state which is not really comparable.

If there is no pi-bonding in the present example, a radius of 1.47\AA is derived for Mo (P 1.10\AA).

Since there will probably be some double bonding contribution, a radius of $\sim 1.5\text{\AA}$ would be a reasonable value for Mo(IV).

The four P atoms and the metal are almost co-planar, Mo lying 0.15\AA out of the plane;

$$-2.99x + 17.99y - 3.75z + 1.3 = 0$$

In the phosphine groups, each ligand has one short (1.81\AA) and one long (1.87\AA) P-C(bridging) bond. The average of the P-C(phenyl) bonds is 1.843\AA . The angles round P range from 99° to 125° . The 'bites' of both ligands are 79° , and within each ligand the torsion angles are comparable to those in other dppe complexes (see Table 9). It is noticeable that this is the only structure in which both ligands have the same ($\lambda\lambda$) conformation, i.e. the most favourable sterically for trans diphosphine groupings.

The phenyl groups were refined as rigid bodies, so no comment can be made on their geometries. The dihedral angles between rings are 83° , 82° , 75° , 79° . This

TABLE 3.2.9

Torsion angles ($^{\circ}$) in dppe complexes

	$\tau(\text{M-P})$	$\tau(\text{P-C})$	$\tau(\text{C-C})$	$\tau(\text{C-P})$	$\tau(\text{P-M})$	Reference
$\text{MoOCl}(\text{dppe})_2^+$	-24 -19	+51 +52	-51 -62	+26 +42	+2 -10	
$\text{ReH}_3(\text{PPh}_3)_2(\text{dppe})$	+14	-45	+55	-46	+14	a
$\text{Rh}(\text{dppe})_2 \text{ClO}_4$	-32 +26	+52 -51	-43 +51	+18 -31	+10 0	b
$\text{Ir}(\text{dppe})_2 \text{Cl}$	+30 -26	-49 +50	+42 -48	-18 +25	-9 +3	c
$\text{IrCO}(\text{dppe})_2 \text{Cl}$	-17 +31	+45 -47	-54 +38	+38 -13	-8 -12	d
$\text{Rh}(\text{O}_2)(\text{dppe})_2 \text{PF}_6$	-29 +27	+52 -46	-49 +43	+24 -21	+6 -6	e
$\text{Ir}(\text{O}_2)(\text{dppe})_2 \text{PF}_6$	-26 +24	+49 -50	-50 +53	+28 -30	+3 0	e
$\text{NiBr}(\text{dppe})(\text{CH}_2\text{CMeCH}_2)$	+31	-54	+48	-22	-8	f

- a. V Albano, P Bellon & V Scatturin, 1st Lombardo (Rend.Sci.)A, 1966, 100, 989
- b. M C Hall, B T Kilbourn & K A Taylor, JCS(A), 1970, 2539
- c. M C Hall & B T Kilbourn, unpublished data
- d. J A J Jarvis et al., Chem.Comm., 1966, 906
- e. J A McGinnety, N C Payne & J A Ibers, JACS, 1969, 91, 6301
- f. M R Churchill & T A O'Brien, JCS(A), 1970, 206

again fits in with other dppe geometries, e.g. in $\text{Rh}(\text{dppe})_2^+$ these angles are 54° , 59° , 63° , 88° .²¹³

The anion in this complex is derived from ZnCl_4^{2-} by replacement of one chlorine by a neutral molecule. In the crystals examined, this is acetone, though analogous compounds containing $\text{ZnCl}_3(\text{THF})^-$ and $\text{ZnCl}_3(\text{CHCl}_3)^-$ have also been prepared. This is thought to be the first reported structure of a ZnCl_3X^- ion, although ZnBr_3X^- and ZnI_3X^- have been described. (See Table 10). Zinc readily forms anions with neutral ligands, and the geometries are usually distorted tetrahedral, as in ZnCl_4^{2-} itself.²¹⁴ The zinc and acetone lie in a plane and the acetone forms a donor bond through its lone pair, at an angle of 131° and a distance of 2.12\AA . This is longer than other reported Zn-O distances which range from 2.03\AA in $\text{Zn}(\text{NH}_2\text{NHCO}_2)_2$ ²¹⁵ to 2.09\AA in $(\text{MeZnOMe})_4$,²¹⁶ and this may be related to the ease of replacement of acetone by other solvent molecules.

The acetone geometry is regular; the best plane being:-

$$5.08x - 5.63y - 22.84z + 0.3 = 0$$

The distances are C=O 1.24 , C-C 1.48 , 1.52\AA , and these are very similar to those in the free molecule of solvation (C=O 1.21 , C-C 1.47 , 1.51\AA). The best plane through the free acetone is:-

$$16.15x - 2.40y - 18.67z + 2.4 = 0$$

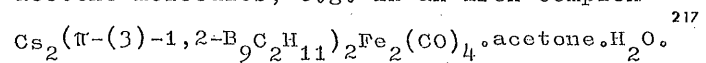
TABLE 3.2.10

 ZnCl_4^{2-} and related entities

	<u>Zn-X</u>	<u>Reference</u>
$(\text{ZnCl}_3 \cdot \text{acetone})^-$	2.23	
$(\text{ZnCl}_4)(\text{NMe}_4)_2$	2.27-2.30	a
$(\text{ZnCl}_4)(\text{N}_2\text{-pC}_6\text{H}_4\text{-N}_2)$	2.28	b
$(\text{ZnCl}_4)(\text{Co}(\text{NH}_3)_6)\text{Cl}$	2.22-2.36	c
$(\text{ZnBr}_3 \cdot \text{H}_2\text{O})^-$	2.36-2.39	d
$(\text{ZnI}_3 \cdot ((\text{C}_5\text{H}_{11})_2\text{SCH}_2)((\text{C}_5\text{H}_{11})_2\text{SMe}))$	2.62-2.68	e
$\text{ZnCl}_2(\text{terpyridyl})$	2.25-2.27	f
$\text{ZnCl}_2(\text{SC}(\text{NH}_2)\text{NHNH}_2)$	2.24	g
$\text{ZnCl}_2(1,10\text{-phenanthroline})$	2.20, 2.21	h
$\text{ZnCl}_2(\text{C}_7\text{H}_9\text{NO})_2$	2.25	i

- a. J R Wiesner et al., *Acta Cryst.*, 1967, 23, 565
- b. A Mostad & C Rømming, *Acta.Chem.Scand.*, 1968, 22, 1259
- c. D W Meek & J A Ibers, *Inorg.Chem.*, 1970, 9, 465
- d. H Follner & B Brehler, *Acta.Cryst.*, 1968, B24, 1339
- e. B T Kilbourn & D Felix, *JCS(A)*, 1969, 163
- f. F W B Einstein & B R Penfold, *Acta.Cryst.*, 1966, 20, 924
- g. L Cavalca, M Nardelli & G Branchi, *Acta.Cryst.*, 1960, 13, 688
- h. C W Reimann, S Block & A Perloff, *Inorg.Chem.*, 1966, 5, 1185
- i. R S Sager & W H Watson, *Inorg.Chem.*, 1968, 7, 1358

and the geometry is comparable with other solvated acetone molecules, e.g. in an iron complex



There are no abnormally close contacts and so the intermolecular contacts are not listed.

APPENDIX I

Programs used routinely in structural analyses

Program Name	Language	Author	Description
Gonioset	Fortran	R H B Mais	Generates control cards punched; $hkl\omega 2\theta_1 2\theta_2$, and blank data cards, for automatic data collection on Picker diffractometer.
Data check	Fortran	R H B Mais	Checks measurements during course of data collection, for crystal movement, uneven backgrounds.
Crystal geometry	K-code	A Wood	Converts readings of x and y coordinates of the corners of a crystal, to surface equations for use in Cosmos absorption routine.
Cosmos	K-code	R H B Mais	Master Crystal Structure Analysis program containing routines for:- data reduction absorption collating and sorting SF calculation LS refinement analysis of SF tables planes tabulation Fourier calculations molecular geometries
Edit planes	K-code	J A J Jarvis	Produces a modified planes list for use in Cosmos.
Moleg	Fortran	E T H (Zurich)	Calculates molecular geometries, esds., best planes, dihedral angles between planes.
Hcoord	Fortran	B T Kilbourn/ E T H	Calculates atomic positions from known geometries, e.g. aromatic hydrogens.
Ortep	Fortran	C Johnson Oak Ridge	Calculates molecular geometries, and plots any of a large variety of structural drawings, with vibrational ellipsoids if desired.
Refsys	Fortran	R H B Mais	Retrieves crystal structure references using a keyword system.

APPENDIX II

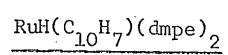
The final positional and thermal parameters are tabulated, for each completed structure analysis.

The tables of observed and calculated structure factors are arranged in the form:

- 1) centric structures: F_o F_c (sign of $\cos\alpha$)
- 2) acentric structures: F_o F_c α

l is the running index, and all the values are on the absolute scale.

Tables of the agreement between F_o and F_c , follow the structure factor tables.



CHAPTER 2.2

Table 2.2.2

Final Positional Parameters (fractional coordinates, $\times 10^5$ for the ruthenium and phosphorus atoms, $\times 10^4$ for the remainder) with estimated standard deviations, and mean square atomic vibrations ($\text{\AA}^2, \times 10^3$) for carbon atoms, with estimated standard deviations.

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
Ru	29769(5)	21965(8)	11775(4)	
P(1)	22779(25)	41342(35)	05189(19)	
P(2)	42400(22)	28765(33)	08915(18)	
P(3)	17669(23)	12651(35)	14247(20)	
P(4)	35209(23)	29860(33)	24363(15)	
*C(11)	2918(25)	4610(38)	-0144(21)	253(14)
*C(12)	1864(18)	5470(29)	0933(17)	189(9)
*C(13)	1272(21)	4361(34)	-0471(18)	217(12)
C(21)	3968(12)	4408(17)	0340(10)	114(5)
C(22)	4665(11)	1821(15)	0311(9)	102(4)
C(23)	5411(12)	3275(18)	1671(10)	120(5)
C(31)	1992(14)	1398(21)	2456(12)	137(6)
C(32)	1561(13)	-0485(20)	1264(11)	133(6)
C(33)	0574(16)	1898(23)	0907(13)	155(7)
*C(41)	2651(19)	2445(26)	2848(16)	175(9)
*C(42)	3632(13)	4680(20)	2810(11)	131(6)
*C(43)	4596(13)	2298(18)	3171(11)	121(5)
C(1)	1310(7)	1076(10)	-0524(6)	64(2)
C(2)	2553(7)	0863(10)	0195(6)	64(2)
C(3)	3058(10)	-0351(15)	0279(8)	96(4)
C(4)	2786(11)	-1263(16)	-0375(9)	105(4)
C(5)	1791(13)	-1977(18)	-1731(11)	121(5)
C(6)	1093(13)	-1590(19)	-2371(10)	121(5)
C(7)	0590(13)	-0480(20)	-2475(11)	129(6)
C(8)	0804(9)	0487(14)	-1890(8)	90(3)
C(9)	1568(8)	0148(12)	-1155(7)	79(3)
C(10)	2087(9)	-1027(14)	-1029(7)	85(3)

* atomic positions affected by disorder

Table 2.2.3

Mean square atomic vibrations (\AA^2 , $\times 10^4$) for ruthenium
and phosphorus atoms, with estimated standard deviations

Atom	U_{11}	$2U_{12}$	$2U_{13}$	U_{22}	$2U_{23}$	U_{33}
Ru	543(3)	032(7)	436(5)	611(4)	016(7)	403(3)
P(1)	898(21)	353(33)	609(31)	830(20)	231(30)	673(17)
P(2)	703(16)	-037(30)	869(28)	906(21)	096(31)	748(17)
P(3)	779(18)	-416(32)	960(32)	915(22)	-145(33)	847(19)
P(4)	854(19)	138(30)	371(26)	863(21)	-157(26)	470(13)

[illegible]

[illegible]

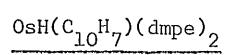
Table 2.2.6

Analysis of Agreement between Observed and Calculated
Structure Factors at R=8.0%

Range $ F_o $	No.	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta F $	Av.w $ \Delta F ^2$	R
0-11	611	5946	5925	865	2.78	0.145
11-23	1318	21121	20780	2092	2.71	0.099
23-34	632	17455	17323	1465	4.05	0.084
34-45	350	13564	13300	968	3.27	0.071
45-56	221	11001	10969	718	3.10	0.065
56-68	131	8047	7931	575	4.41	0.071
68-79	77	5634	5573	344	3.33	0.061
79-90	51	4336	4259	270	3.47	0.062
90-101	39	3732	3693	163	1.59	0.044
101-113	27	2881	2770	148	2.70	0.051
113-135	28	3429	3344	187	2.99	0.054
135-338	28	5021	4782	329	3.49	0.064
all data	3513	102167	100649	8124	-	0.080

Sin θ/λ

0.0-0.1	17	2498	2340	195	6.33	0.078
0.1-0.2	140	9270	8852	1018	12.86	0.110
0.2-0.3	384	21010	21159	1575	5.98	0.075
0.3-0.4	671	23982	23646	1914	4.02	0.080
0.4-0.5	986	24526	23670	1926	2.54	0.079
0.5-0.6	1046	17595	17605	1242	1.27	0.071
0.6-0.7	269	3284	3378	253	0.91	0.077



CHAPTER 2.4

Table 2.4.2

Final Positional Parameters (fractional coordinates, $\times 10^5$ for the osmium and phosphorus atoms, $\times 10^4$ for the remainder) with estimated standard deviations, and mean square atomic vibrations (\AA^2 , $\times 10^3$) for carbon atoms, with estimated standard deviations.

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
Os	29665(5)	22557(7)	11772(3)	
P(1)	22682(44)	41844(63)	05201(33)	
P(2)	42202(41)	29570(61)	09026(32)	
P(3)	17588(45)	13370(64)	14256(34)	
P(4)	34936(44)	30599(61)	24346(28)	
*C(11)	3230(29)	5380(41)	0599(23)	211(15)
*C(12)	1710(25)	5447(38)	0879(22)	185(13)
*C(13)	1385(25)	4363(38)	-0459(21)	185(13)
C(21)	3916(20)	4514(29)	0320(17)	138(9)
C(22)	4666(20)	1856(29)	0301(17)	138(9)
C(23)	5404(18)	3462(28)	1711(15)	129(8)
C(31)	1970(24)	1431(35)	2508(20)	166(11)
C(32)	1536(23)	-0429(34)	1290(19)	162(11)
C(33)	0562(22)	1952(31)	0952(18)	148(10)
*C(41)	2508(28)	2638(35)	2788(24)	179(13)
*C(42)	3733(21)	4771(30)	2779(18)	151(10)
*C(43)	4589(21)	2372(25)	3190(18)	130(9)
C(1)	1799(13)	1091(18)	-0496(11)	84(5)
C(2)	2571(12)	0941(17)	0205(10)	78(4)
C(3)	3087(18)	-0322(25)	0316(15)	119(7)
C(4)	2845(20)	-1193(28)	-0385(17)	135(9)
C(5)	1864(22)	-2027(29)	-1682(19)	138(9)
C(6)	1088(22)	-1580(33)	-2339(18)	143(9)
C(7)	0592(22)	-0536(34)	-2477(19)	152(10)
C(8)	0776(18)	0441(25)	-1878(15)	118(7)
C(9)	1566(14)	0131(19)	-1148(11)	89(5)
C(10)	2082(15)	-0985(23)	-1046(13)	102(6)

* atomic positions affected by disorder

Table 2.4.3

Mean square atomic vibrations (\AA^2 , $\times 10^4$) for osmium
and phosphorus atoms, with estimated standard deviations

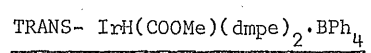
Atom	U_{11}	$2U_{12}$	$2U_{13}$	U_{22}	$2U_{23}$	U_{33}
Os	723(4)	059(7)	595(5)	763(4)	042(6)	490(3)
P(1)	1041(41)	354(64)	568(60)	1086(41)	328(58)	786(33)
P(2)	925(34)	-020(60)	983(56)	1158(42)	186(57)	808(31)
P(3)	1071(40)	-503(68)	1164(65)	1190(45)	-196(62)	878(35)
P(4)	1088(40)	270(64)	587(53)	1133(42)	099(52)	595(26)

L FC EC			L FC EC			L FC EC			L FC EC			L FC EC			L FC EC			L FC EC																																																																																	
L FC EC			L FC EC			L FC EC			L FC EC			L FC EC			L FC EC			L FC EC																																																																																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100

Table 2.4.6

Analysis of Agreement between Observed and Calculated
Structure Factors at R=7.2%

Range $ F_o $	No.	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta F $	Av.w $ \Delta F ^2$	R
0-17	226	3431	2520	1087	31.68	0.317
17-34	1172	28409	27022	3154	12.87	0.111
34-51	649	27003	27121	1568	9.03	0.058
51-68	371	21547	21605	1175	12.10	0.055
68-84	222	16679	16755	766	8.30	0.046
84-101	110	10105	10166	456	9.03	0.045
101-118	94	10330	10172	581	12.89	0.056
118-152	92	12213	12124	607	9.63	0.050
152-203	71	12163	11831	743	12.80	0.060
203-507	37	9782	9155	837	19.93	0.073
all data	3044	151662	148471	10974	-	0.072
Sin θ/λ						
0.0-0.1	18	3939	3513	480	36.38	0.122
0.1-0.2	154	16273	15554	1397	29.30	0.086
0.2-0.3	398	33761	33649	2136	15.78	0.063
0.3-0.4	698	39039	38609	2246	9.81	0.058
0.4-0.5	1036	38168	37614	2648	10.39	0.069
0.5-0.6	740	20481	19532	2067	13.66	0.101



CHAPTER 2.7

Table 2.7.2

Final positional parameters (fractional co-ordinates, $\times 10^5$
for Iridium and phosphorus atoms, $\times 10^4$ for the remainder)
with corresponding standard deviations and mean square atomic
vibrations ($\text{\AA}^3 \times 10^3$) for carbon atoms, with estimated
standard deviations

Atom	x	y	z	U
Ir	21143(4)	14042(2)	00000(0)	
P(1)	31448(31)	08061(14)	-01299(74)	
P(2)	12363(45)	10958(19)	-17887(70)	
P(3)	10081(43)	19736(17)	02168(82)	
P(4)	28747(65)	16670(23)	19192(78)	
C(11)	2865(20)	0541(8)	-1761(27)	68(6)
C(12)	4583(15)	0853(6)	0050(48)	66(5)
C(13)	2892(20)	0404(8)	1168(28)	65(6)
C(21)	1761(25)	0558(10)	-1997(34)	89(9)
C(22)	1282(28)	1351(10)	-3436(36)	100(10)
C(23)	4800(27)	3992(11)	-1635(40)	95(11)
C(31)	1557(25)	2333(9)	1434(32)	98(8)
C(32)	4655(27)	3130(10)	0836(36)	110(10)
C(33)	0832(31)	2321(12)	-1335(40)	103(12)
C(41)	2166(37)	2103(15)	2466(51)	174(17)
C(42)	4261(24)	1860(9)	1943(34)	100(9)
C(43)	2936(36)	1290(15)	3392(53)	145(17)
C(1)	3141(17)	1740(7)	-1244(24)	51(5)
C(2)	4437(20)	1724(8)	-3068(29)	72(7)
O(1)	3452(16)	2105(6)	1109(22)	91(6)
O(2)	3633(15)	1524(5)	-2271(19)	74(5)
B	2468(20)	4003(8)	3494(29)	50(6)
C(111)	2576(21)	3528(8)	4204(28)	64(7)
C(112)	1695(20)	3278(8)	4481(25)	75(7)
C(113)	1717(21)	2867(8)	5141(41)	97(8)
C(114)	2715(29)	2742(11)	5615(37)	111(12)
C(115)	3591(24)	2951(9)	5368(32)	95(10)
C(116)	3516(19)	3356(7)	4623(25)	70(7)
C(121)	3556(19)	4271(7)	3842(25)	63(6)
C(122)	4441(21)	4245(8)	2964(29)	72(7)
C(123)	5356(23)	4453(9)	3334(31)	88(8)
C(124)	5422(24)	4703(9)	4479(30)	85(9)
C(125)	4620(18)	4724(7)	5328(25)	73(7)
C(126)	3658(16)	4510(6)	5075(44)	60(5)
C(131)	2371(15)	3931(6)	1856(23)	46(5)
C(132)	2119(18)	3542(7)	1237(23)	65(5)
C(133)	2007(18)	3492(7)	-0085(56)	81(7)
C(134)	2145(22)	3842(9)	-0977(31)	82(7)
C(135)	2364(22)	4228(9)	-0423(28)	75(8)
C(136)	2478(22)	4281(9)	1002(30)	78(7)
C(141)	1445(17)	4231(7)	4123(22)	49(5)
C(142)	1172(20)	4199(8)	-4515(24)	72(7)
C(143)	0326(24)	4407(10)	-3940(33)	74(8)
C(144)	-0301(23)	4661(9)	-4708(31)	113(9)
C(145)	-0095(23)	4688(9)	3926(30)	84(7)
C(146)	0765(16)	4489(7)	3321(23)	53(5)

Table 2.7.3

Mean square atomic vibrations ($\text{\AA}^2 \times 10^4$) for
Iridium and phosphorus atoms, with corresponding
standard deviations

	U_{11}	$2U_{12}$	$2U_{13}$	U_{22}	$2U_{23}$	U_{33}
Ir	342(2)	- 24(6)	151(14)	397(2)	- 34(15)	531(3)
P(1)	35(2)	11(4)	- 5(6)	51(2)	- 16(7)	53(3)
P(2)	39(3)	- 1(5)	- 1(6)	60(3)	- 13(6)	68(4)
P(3)	57(3)	23(5)	27(7)	45(3)	- 18(7)	99(6)
P(4)	76(5)	- 23(8)	31(9)	75(4)	- 31(7)	67(4)

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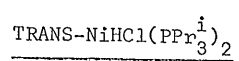
L FC FC A				L FC FC A				L FC FC A				L FC FC A				L FC FC A				L FC FC A																			
0	38	31	170	7	44	45	116	5	55	55	-74	0	62	64	C	4	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0	0	0	0	0
0	20	20	118	0	25	25	103	7	0	0	0	0	67	67	0	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	20	20	118	0	25	25	103	7	0	0	0	0	67	67	0	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0	98	94	0	0	0	0	0				
0	28	21	137	0	31	31	117	0	0	0	0	0	67	67	-2	0	0	0	0	5	105	104	-124	8	62	66	C	0											

[illegible]

Table 2.7.5

Analysis of Agreement between Observed and Calculated
Structure Factors at $R = 6.2\%$

Range $ F_o $	No.	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta F $	Av.w $ \Delta F ^2$	R
0-28	666	15619	15185	2910	32.20	0.186
28-42	788	27159	27337	2661	17.86	0.098
42-56	508	24738	24839	1531	13.64	0.062
56-70	335	21006	20835	999	12.59	0.048
70-84	266	20399	20240	837	12.78	0.041
84-98	188	17021	16968	611	11.73	0.036
98-112	111	11568	11540	384	14.94	0.033
112-126	69	8194	8206	228	10.23	0.028
126-140	62	8209	8205	252	14.70	0.031
140-168	75	11547	11464	390	22.15	0.034
168-224	72	13676	13684	435	20.45	0.031
224-420	29	8019	8098	349	43.15	0.041
Sin θ/λ						
0.0-0.1	20	3854	3917	178	29.70	0.046
0.1-0.2	131	6155	15901	897	38.93	0.056
0.2-0.3	326	32411	32841	1279	16.60	0.039
0.3-0.4	577	42017	41785	1808	12.47	0.043
0.4-0.5	808	45029	44580	2493	13.39	0.055
0.5-0.6	942	36850	36791	3228	18.97	0.088
0.6-0.7	365	10838	10789	1702	35.47	0.157



CHAPTER 2.8

Table 2.8.2

Final positional parameters (fractional co-ordinates, $\times 10^5$ for Nickel, Phosphorus and Chlorine atoms, $\times 10^4$ for the remainder) with corresponding standard deviations and mean square atomic vibrations ($\text{\AA}^2 \times 10^3$) for carbon atoms, with estimated standard deviations.

Atom	x	y	z	U
Ni	25205(7)	02693(11)	01340(6)	
P(1)	30703(13)	-14774(23)	09546(12)	
P(2)	19413(12)	14816(23)	-09444(12)	
Cl	25312(23)	20951(29)	10657(14)	
C(11)	3731(6)	-2797(10)	0405(6)	36(2)
C(12)	4080(7)	-4142(12)	0937(7)	52(3)
C(13)	4409(7)	-1988(12)	-0040(6)	50(3)
C(14)	2262(6)	-2697(10)	1344(6)	36(2)
C(15)	1629(8)	-1728(15)	1797(8)	67(3)
C(16)	1795(7)	-3567(13)	0613(7)	52(3)
C(17)	3611(6)	-0775(10)	1950(6)	37(2)
C(18)	4374(8)	0097(15)	1763(8)	67(3)
C(19)	3807(8)	-1918(15)	2667(8)	70(3)
C(21)	1323(6)	3109(11)	-0626(6)	39(2)
C(22)	0593(9)	2585(16)	-0136(8)	73(4)
C(23)	1076(8)	4260(15)	-1327(8)	69(3)
C(24)	2730(5)	2348(9)	-1575(5)	30(2)
C(25)	3277(7)	1166(12)	-1952(6)	47(2)
C(26)	3272(7)	3426(13)	-1006(7)	55(3)
C(27)	1356(6)	0284(12)	-1712(5)	39(2)
C(28)	0702(7)	-0686(12)	-1287(7)	51(3)
C(29)	0927(7)	1085(12)	-2507(6)	51(3)

Table 2.8.3

Mean square atomic vibrations ($\text{\AA}^2 \times 10^4$) for Nickel, Chlorine and Phosphorus atoms, with estimated standard deviations.

	U_{11}	$2U_{12}$	$2U_{13}$	U_{22}	$2U_{23}$	U_{33}
Ni	282(5)	49(11)	-42(7)	222(4)	18(10)	224(4)
P(1)	265(12)	73(18)	-58(16)	222(9)	1(17)	257(9)
P(2)	219(12)	10(18)	-35(15)	236(9)	-7(17)	235(9)
Cl	1186(27)	583(31)	365(28)	359(14)	-176(21)	293(12)

L FO FC		L FO FC		L FO FC		L FO FC		L FO FC		L FO FC		L FO FC	
L FO K=0	L FO K=5	L FO K=10	L FO K=15	L FO K=20	L FO K=25	L FO K=30	L FO K=35	L FO K=40	L FO K=45	L FO K=50	L FO K=55	L FO K=60	
2 139 142	2 66 70	10 0 0	13 0 0	-5 22 19	-1 27 26	18 23 24							
4 39 51	3 25 26	11 22 22	14 46 45	-2 48 48	1 0 0	20 32 28							
10 0 0	7 75 74	0 0 0	10 0 0	-1 23 20	2 0 0	0 0 0							
8 81 81	5 0 0	H=1 K=11	16 0 0	0 61 61	2 52 52	H=2 K=2							
10 114 120	6 0 0	0 0 0	17 0 0	1 41 43	4 0 0	0 0 0							
10 7 47	7 0 0	1 0 0	19 26 26	2 50 52	5 62 63	-20 25 27							
14 31 28	8 45 46	2 27 29	0 0 0	0 0 0	0 0 0	-18 0 0							
16 0 0	9 43 41	3 0 0	20 0 0	4 44 44	7 0 0	-18 0 0							
18 0 0	10 4 8	4 0 0	H=1 K=3	5 23 19	8 0 0	-17 0 0							
20 26 24	11 40 38	5 0 0	6 40 40	7 0 0	10 0 0	-15 0 0							
H=0 K=1	12 60 60	6 0 0	-19 0 0	8 27 26	11 0 0	-14 0 0							
1 173 164	14 49 47	8 0 0	-18 0 0	12 22 22	13 0 0	-13 44 41							
2 171 172	15 0 0	H=1 K=0	-17 38 38	10 0 0	13 0 0	-12 29 31							
3 16 0	16 0 0	0 0 0	15 47 47	11 44 41	14 0 0	-11 59 61							
4 30 39	17 0 0	-20 0 0	-14 0 0	12 22 20	15 0 0	-10 0 0							
6 101 91	18 0 0	-18 0 0	-13 24 23	13 37 39	0 0 0	-9 53 57							
5 60 54	H=0 K=6	-16 28 28	-11 0 0	15 0 0	H=1 K=9	-8 26 28							
1 53 58	0 61 58	-10 33 34	-9 41 44	17 0 0	-11 0 0	-4 44 43							
2 63 66	1 44 45	10 41 41	-7 68 70	19 0 0	-12 22 22	-4 57 59							
3 70 70	2 27 28	-8 31 31	-6 45 48	0 0 0	-9 0 0	-3 77 81							
11 81 83	3 77 74	-4 47 51	-5 39 35	H=1 K=6	-7 0 0	-1 195 206							
12 0 0	4 0 0	-2 61 65	-3 0 0	-17 0 0	-6 36 36	0 112 111							
14 0 0	5 26 26	4 56 47	-2 0 0	-14 0 0	-4 38 38	-2 22 22							
15 0 0	6 0 0	6 22 22	1 0 0	-12 0 0	-3 0 0	2 116 113							
16 0 0	7 26 24	8 0 0	1 38 36	-11 0 0	-3 0 0	3 75 67							
17 0 0	8 0 0	10 79 87	2 37 39	-10 0 0	-1 0 0	5 37 36							
18 24 23	9 0 0	12 43 43	3 76 76	-9 0 0	0 31 32	6 51 53							
20 0 0	11 53 53	14 22 23	4 74 72	-8 0 0	0 30 30	7 61 59							
21 0 0	12 31 32	16 0 0	5 39 39	-7 58 58	2 23 22	8 0 0							
H=0 K=2	13 41 42	18 0 0	6 54 51	-5 0 0	3 41 42	9 91 89							
0 35 37	14 0 0	20 31 30	7 54 50	-4 0 0	5 0 0	11 59 62							
1 55 50	15 0 0	H=1 K=1	8 0 0	-3 45 48	6 37 38	12 0 0							
3 97 95	16 0 0	-19 25 25	12 0 0	-2 31 32	7 0 0	13 0 0							
4 81 89	H=0 K=7	-17 27 26	13 0 0	-1 67 66	8 0 0	15 0 0							
5 81 90	0 45 44	-16 0 0	14 0 0	1 74 76	9 0 0	17 0 0							
6 110 109	1 45 44	-15 21 23	15 0 0	3 29 25	10 0 0	19 0 0							
7 35 31	2 0 0	-14 0 0	16 0 0	5 0 0	11 0 0	20 0 0							
8 64 66	3 0 0	-13 45 44	17 34 33	6 0 0	13 0 0	0 0 0							
10 0 0	4 0 0	-12 0 0	18 0 0	7 0 0	H=1 K=10	H=2 K=2							
11 0 0	5 0 0	-11 58 56	19 0 0	8 44 45	-11 0 0	-19 33 33							
12 0 0	6 0 0	-10 34 35	20 0 0	9 44 49	-8 0 0	-17 0 0							
13 32 32	8 32 32	-8 33 34	H=1 K=4	10 0 0	-7 22 22	-16 0 0							
14 0 0	9 24 24	-7 33 35	-14 0 0	11 0 0	-6 0 0	-14 27 26							
15 0 0	10 40 39	-6 0 0	-18 0 0	12 0 0	-5 0 0	-14 31 32							
16 24 23	11 23 27	-5 0 0	-17 0 0	13 0 0	-4 0 0	-13 0 0							
17 0 0													

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H= 2 K= 3			H= 2 K= 6			H= 2 K= 9			H= 3 K= 1			H= 3 K= 4			H= 3 K= 7			H= 3 K= 11		
-1	0	0	-10	27	25	-2	25	25	5	52	47	-10	46	48	-9	0	0	-7	0	0
0	0	0	-9	0	0	-1	0	0	6	0	0	-9	0	0	-8	52	51	-6	0	0
1	34	20	-8	0	0	0	0	0	8	24	24	-8	0	0	-7	30	26	-5	0	0
3	172	161	-7	0	0	1	0	0	9	51	53	-7	22	24	-6	44	43	-4	0	0
4	0	0	-6	0	0	2	36	33	10	42	46	-6	0	0	-5	0	0	-2	25	28
5	150	149	-5	47	47	3	0	0	11	40	46	-5	75	71	-4	36	35	-1	0	0
6	39	46	-4	22	21	4	0	0	12	0	0	-4	27	20	-3	31	33	0	27	27
7	0	0	-3	54	52	5	0	0	13	43	45	-3	52	48	-2	52	51	2	24	26
8	80	56	-2	55	55	6	42	43	14	0	0	2	0	0	-1	0	0	3	0	0
9	0	0	0	66	64	7	0	0	15	46	44	2	50	50	0	50	50	4	0	0
10	0	0	1	67	62	8	37	38	16	0	0	4	42	40	1	0	0	5	0	0
11	0	0	2	44	43	9	0	0	17	0	0	5	51	43	2	36	35	6	0	0
12	24	26	3	61	61	10	0	0	18	0	0	5	58	52	3	0	0	7	0	0
13	51	50	4	0	0	12	0	0	19	23	24	6	0	0	4	55	55	8	0	0
14	22	20	5	0	0	13	0	0	20	0	0	7	36	35	5	0	0	9	0	0
15	55	55	6	0	0	0	0	0	0	0	0	8	0	0	4	0	0	10	0	0
16	32	35	7	34	34	0	0	0	0	0	0	9	0	0	3	23	21	11	0	0
17	0	0	8	37	37	0	0	0	0	0	0	10	25	25	2	25	25	12	0	0
18	27	26	9	0	0	0	0	0	0	0	0	11	0	0	0	0	0	13	0	0
19	28	27	10	52	51	0	0	0	0	0	0	12	43	43	0	0	0	14	0	0
20	0	0	11	52	53	0	0	0	0	0	0	13	0	0	0	0	0	15	0	0
H= 2 K= 4			H= 2 K= 7			H= 2 K= 10			H= 3 K= 2			H= 3 K= 5			H= 3 K= 8			H= 4 K= 0		
-19	0	0	-16	0	0	-11	0	0	-20	0	0	-18	0	0	-14	0	0	-20	0	0
-18	0	0	-15	0	0	-10	0	0	-19	0	0	-16	0	0	-13	0	0	-18	0	0
-17	27	25	-14	0	0	-9	0	0	-17	0	0	-15	0	0	-12	0	0	-16	0	0
-16	0	0	-13	30	30	-8	0	0	-16	28	26	-14	0	0	-11	0	0	-15	53	56
-15	40	41	-12	0	0	-7	0	0	-15	25	23	-13	0	0	-10	0	0	-14	31	29
-14	0	0	-11	0	0	-6	0	0	-14	25	23	-12	22	22	-9	0	0	-13	44	43
-13	30	30	-10	0	0	-5	0	0	-13	0	0	-11	48	50	-8	0	0	-12	100	118
-12	0	0	-9	0	0	-4	0	0	-12	22	21	-10	32	30	-7	22	24	0	12	37
-11	0	0	-8	88	90	-3	0	0	-11	0	0	-9	0	0	-6	0	0	4	46	52
-10	0	0	-7	22	22	-2	0	0	-10	25	24	-8	0	0	-5	33	32	6	10	76
-9	0	0	-6	105	101	-1	0	0	-9	75	79	-7	0	0	-4	0	0	8	150	161
-8	88	90	-5	84	85	0	0	0	-8	0	0	-6	0	0	-3	48	48	10	86	82
-7	22	22	-4	30	27	0	0	0	-7	25	25	-5	29	29	-2	0	0	12	0	0
-6	105	101	-3	44	39	0	0	0	-6	0	0	-4	33	32	-1	33	32	14	35	36
-5	84	85	-2	0	0	0	0	0	-5	0	0	-3	53	55	0	0	0	16	0	0
-4	30	27	-1	44	39	0	0	0	-4	23	26	-2	53	55	1	0	0	18	38	38
-3	0	0	0	32	30	0	0	0	-3	22	19	-1	0	0	2	0	0	20	0	0
-2	0	0	0	0	0	0	0	0	-2	22	23	0	62	61	1	52	51	13	47	49
-1	44	39	0	0	0	0	0	0	-1	0	0	0	45	39	0	0	0	11	40	38
0	32	30	-7	0	0	0	0	0	0	0	0	0	4	39	38	0	0	9	33	34
1	0	0	-6	0	0	0	0	0	0	0	0	0	3	44	41	0	0	8	0	0
2	44	51	-5	0	0	0	0	0	0	0	0	0	2	47	45	0	0	7	0	0
3	74	76	-4	48	48	0	0	0	0	0	0	0	1	0	0	0	0	6	0	0
4	26	19	-3	62	61	0	0	0	0	0	0	0	0	0	0	0	0	5	52	51
5	36	33	-2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0
6	38	35	-1	48	48	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0
7	51	50	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0
8	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
9	41	44	2	44	43	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	3	24	24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
11	25	25	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
13	37	37	6	22	19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
14	35	32	7	22	23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
15	30	29	8	36	36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
16	22	20	9	36	33	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
17	0	0	10	28	27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H= 2 K= 5			H= 2 K= 8			H= 3 K= 0			H= 3 K= 3			H= 3 K= 6			H= 3 K= 9			H= 4 K= 1		
-18	0	0	-14	0	0	-20	21	22	-19	0	0	-17	0	0	-12	0	0	-19	0	0
-17	0	0	-13	0	0	-18	38	38	-17	0	0	-16	0	0	-11	0	0	-18	0	0
-16	0	0	-12	0	0	-16	32	34	-16	0	0	-15	0	0	-10	0	0	-17	0	0
-15	0	0	-11	0	0	-14	37	38	-14	44	43	-14	0	0	-9	0	0	-16	36	35
-14	49	51	-10	0	0	-12	62	60	-12	62	60	-12	0	0	-8	0	0	-15	22	21
-13	0	0	-9	0	0	-10	56	58	-10	22	20	-10	0	0	-7	0	0	-14	0	0
-12	43	42	-8	0	0	-8	0	0	-8	0	0	-9	0	0	-6	30	30	-13	47	49
-11	25	21	-7	0	0	-6	0	0	-6	0	0	-8	0	0	-5	0	0	-11	40	38
-10	0	0	-6	45	45	-4	47	46	-4	0	0	-7	0	0	-4	0	0	-10	39	36
-9	32	32	-3	48	48	-2	47	98	-2	70	71	-3	34	35	-3	32	32	-9	33	34
-8	45	45	-2	39	40	4	76	80	-2	43	41	-2	29	29	-2	28	30	-8	0	0
-7	23	25	-1	30	40	6	27	23	-1	32	35	-1	0	0	-1	0	0	-7	0	0
-6	52	50	0	0	0	8	37	38	0	29	31	0	0	0	0	0	0	-6	51	50
-5	0	0	-6	0	0	10	98	105	-6	59	56	-8	0	0	0	0	0	-5	48	46
-4	90	92	-4	0	0	12	41	42	-4	54	47	-7	52	55	5	0	0	-4	0	0
-3	25	26	-3	33	33	14	26	23	-3	33	32	-6	33	32	6	27	28	-3	201	195
-2	39	43	-2	0	0	16	0	0	-2	64	59	-5	0	0	7	0	0	-2	61	65
-1	60	59	-1	0	0	18	29	28	-1	0	0	-4	0	0	8	0	0	-1	129	131
0	0	0	0	23	21	20	38	37	0	0	0	-3	40	38	10	0	0	0	35	-
1	55	53	1	40	41	3	0	0	0	0	0	-2	0	0	11	0	0	1	132	117
2	63	65	2	0	0	4	31	33	0	0	0	-1	7	89	12	0	0	2	54	50
3	41	38	3	0	0	6	41	45	0	0	0	0	0	0	13	0	0	3	0	0
4	37	38	4	45	44	7	66	61	0	0	0	1	73	72	0	0	0	4	110	

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H=4 K=2			H=4 K=5			H=4 K=8			H=5 K=1			H=5 K=3			H=5 K=6			H=5 K=10		
9	0	0	-3	30	25	3	0	0	-14	0	0	12	0	0	9	31	34	2	0	0
10	0	0	-2	0	0	4	0	0	-15	30	30	13	35	34	10	0	0	3	0	0
11	0	0	-1	74	69	5	49	49	-14	22	23	14	0	0	11	0	0	4	0	0
12	30	30	0	52	51	6	0	0	-13	41	43	15	35	32	12	0	0	5	0	0
13	0	0	1	81	72	7	61	60	-11	37	35	16	0	0	13	0	0	6	0	0
14	33	33	2	59	53	8	0	0	-10	0	0	17	27	29	14	0	0	7	27	28
15	30	31	3	48	44	9	0	0	-9	17	33	18	0	0	15	0	0	8	0	0
16	0	0	4	0	0	11	0	0	-8	0	0	19	22	20	16	0	0	9	27	24
17	31	30	5	0	0	12	0	0	-7	53	59	-	-	-	-	-	10	0	0	
18	0	0	6	0	0	13	0	0	-6	0	0	-	-	-	-	-	-	-	-	-
19	0	0	7	0	0	14	0	0	-5	0	0	-	-	-	-	-	-	-	-	-
H=4 K=3			H=4 K=9			H=5 K=2			H=5 K=4			H=5 K=7			H=5 K=11			H=6 K=0		
-19	0	0	8	22	24	-12	27	26	-4	30	28	-18	0	0	-16	0	0	-20	0	0
-18	0	0	9	31	28	-10	36	16	-2	0	0	-16	0	0	-14	0	0	-18	0	0
-17	0	0	10	64	63	-9	0	0	-1	0	0	-15	0	0	-12	0	0	-16	0	0
-16	0	0	11	0	0	-8	24	25	0	65	65	-14	0	0	-11	0	0	-14	0	0
-15	0	0	12	63	63	-7	0	0	1	24	25	-13	0	0	-10	22	23	-3	0	0
-14	0	0	13	0	0	-6	0	0	2	0	0	-12	0	0	-9	0	0	-2	0	0
-13	0	0	14	0	0	-5	0	0	3	25	25	-11	0	0	-8	33	35	-1	0	0
-12	0	0	15	0	0	-4	0	0	4	0	0	-10	0	0	-7	26	27	0	23	24
-11	0	0	16	0	0	-3	0	0	5	27	27	-9	29	31	-6	34	33	1	0	0
-10	29	30	17	0	0	-2	0	0	6	0	0	-8	24	25	-5	0	0	2	22	24
-9	64	63	18	0	0	-1	0	0	7	45	48	-7	35	35	-4	26	25	3	0	0
-8	51	48	19	0	0	0	22	22	8	0	0	-6	0	0	-3	0	0	4	0	0
-7	121	117	20	0	0	1	0	0	9	32	37	-5	62	59	-2	26	24	5	0	0
-6	25	28	21	0	0	2	22	20	10	0	0	-4	0	0	-1	0	0	6	0	0
-5	82	76	22	0	0	3	0	0	11	38	40	-3	84	82	0	0	0	7	26	26
-4	66	61	23	0	0	4	0	0	12	46	46	-2	0	0	1	37	37	8	0	0
-3	28	18	24	0	0	5	0	0	13	51	46	-1	0	0	2	41	40	9	0	0
-2	46	40	25	0	0	6	45	45	14	0	0	0	32	28	3	0	0	10	0	0
-1	0	0	26	0	0	7	0	0	15	26	28	2	42	45	4	39	38	11	0	0
0	38	42	27	0	0	8	24	24	16	0	0	3	61	63	5	0	0	12	0	0
1	57	56	28	0	0	9	0	0	17	22	22	4	0	0	6	24	24	13	0	0
2	0	0	29	0	0	10	0	0	18	0	0	5	92	87	7	26	26	14	0	0
3	168	169	30	0	0	11	0	0	19	29	26	6	0	0	8	21	22	15	0	0
4	0	0	31	0	0	12	0	0	20	0	0	7	0	0	10	22	24	16	0	0
5	92	100	32	0	0	13	0	0	21	0	0	8	0	0	11	0	0	17	0	0
6	0	0	33	0	0	14	0	0	22	28	28	9	0	0	12	0	0	18	0	0
7	0	0	34	0	0	15	0	0	23	38	40	10	0	0	13	0	0	19	0	0
8	22	21	35	0	0	16	0	0	24	27	24	11	0	0	14	0	0	20	0	0
9	0	0	36	0	0	17	0	0	25	0	0	12	0	0	15	0	0	21	0	0
10	0	0	37	0	0	18	0	0	26	0	0	13	0	0	16	0	0	22	0	0
11	29	26	38	0	0	19	0	0	27	0	0	14	0	0	17	0	0	23	0	0
12	0	0	39	0	0	20	0	0	28	0	0	15	0	0	18	0	0	24	0	0
13	56	57	40	0	0	21	0	0	29	0	0	16	0	0	19	0	0	25	0	0
14	0	0	41	0	0	22	0	0	30	0	0	17	0	0	20	0	0	26	0	0
15	41	40	42	0	0	23	0	0	31	0	0	18	0	0	21	0	0	27	0	0
16	39	38	43	0	0	24	0	0	32	0	0	19	0	0	22	0	0	28	0	0
17	25	20	44	0	0	25	0	0	33	0	0	20	0	0	23	0	0	29	0	0
18	0	0	45	0	0	26	0	0	34	0	0	21	0	0	24	0	0	30	0	0
19	29	29	46	0	0	27	0	0	35	0	0	22	0	0	25	0	0	31	0	0
H=4 K=4			H=4 K=10			H=5 K=3			H=5 K=5			H=5 K=8			H=5 K=12			H=6 K=1		
-19	0	0	0	34	32	-11	0	0	-20	0	0	-17	0	0	-13	0	0	-20	0	0
-18	0	0	1	61	58	-10	0	0	-19	0	0	-16	0	0	-12	0	0	-19	0	0
-17	32	31	2	0	0	-9	0	0	-18	26	28	-15	0	0	-11	0	0	-18	0	0
-16	0	0	3	30	38	-8	0	0	-17	27	25	-14	0	0	-10	0	0	-17	0	0
-15	37	38	4	0	0	-7	0	0	-16	40	40	-13	0	0	-9	0	0	-16	0	0
-14	0	0	5	26	27	-6	0	0	-15	0	0	-12	0	0	-8	0	0	-15	0	0
-13	0	0	6	37	35	-5	0	0	-14	0	0	-11	0	0	-7	0	0	-14	0	0
-12	0	0	7	0	0	-4	0	0	-13	37	38	-10	0	0	-6	0	0	-13	0	0
-11	0	0	8	45	46	-3	0	0	-12	22	25	-9	0	0	-5	0	0	-12	0	0
-10	0	0	9	32	31	-2	0	0	-11	28	29	-8	0	0	-4	0	0	-11	0	0
-9	0	0	10	26	25	-1	0	0	-10	28	29	-7	0	0	-3	0	0	-10	0	0
-8	0	0	11	67	65	0	0	0	-9	23	23	-6	0	0	-2	0	0	-9	0	0
-7	0	0	12	0	0	0	0	0	-8	65	64	-5	0	0	-1	0	0	-8	0	0
-6	0	0	13	43	44	0	0	0	-7	0	0	-4	0	0	0	0	0	-7	0	0
-5	0	0	14	0	0	0	0	0	-6	88	81	-3	0	0	0	0	0	-6	0	0
-4	0	0	15	0	0	0	0	0	-5	22	21	-2	0	0	0	0	0	-5	0	0
-3	0	0	16	0	0	0	0	0	-4	22	16	-1	0	0	0	0	0	-4	0	0
H=4 K=7			H=4 K=11			H=5 K=4			H=5 K=6			H=5 K=9			H=5 K=13			H=6 K=2		
-19	0	0	5	0	0	0	22	21	-10	42	42	-17	0	0	-13	0	0	-20	0	0
-18	0	0	6	0	0	1	47	48	-9	0	0	-16	0	0	-12	0	0	-19	0	0
-17	32	31	7	0	0	2	0	0	-8	0	0	-15	0	0	-11	0	0	-18	0	0
-16	0	0	8	0	0	3	0	0	-7	0	0	-14	0	0	-10	0	0	-17	0	0
-15	37	38	9	0	0	4	0	0	-6	0	0	-13	0	0	-9	0	0	-16	0	0
-14	0	0	10	0	0	5	0	0	-5	0	0	-12	0	0	-8	0	0	-15	0	0
-13	0	0	11	0	0	6	73	76	-4	56	55	-11	0	0	-7	0	0	-14	0	0
-12	0	0	12	23	23	7	0	0	-3	33	31	-10	0	0	-6	0	0	-13	0	0
-11	0	0	13	0	0	8	98	92	-2	58	62	-9	0	0	-5	0	0	-12	0	0
-10	38	39	14	0	0	9	23	20	-1	0	0	-8	0	0	-4	0	0	-11	0	0
-9	0	0	15	0	0	10	0	0	0	59	57	-7	0	0	-3	0	0	-10	0	0
-8	75	74	16	0	0	11	0	0	0	0	0	-6	0	0	-2	0	0	-9	0	0
-7	84	82	17	0	0	12	0	0	0	0	0	-5	0	0	-1	0	0	-8	0	0
-6	0	0	18	0	0	13	0	0	0	0	0	-4	0	0						

[illegible]

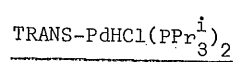
H B K=2			H B K=5			H B K=9			H B K=2			H B K=5			H B K=8			H B K=2		
L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC
14	0	0	12	0	0	-1	0	0	-14	0	0	-14	0	0	7	0	0	-17	0	0
17	0	0	14	0	0	1	0	0	-12	0	0	-14	0	0	8	0	0	-16	0	0
18	0	0	15	0	0	2	25	23	-11	0	0	-15	0	0	8	0	0	-17	0	0
			16	0	0	3	10	0	-10	0	0	-13	0	0	10	0	0	-14	0	0
						4	29	29	-9	0	0	-12	0	0	11	0	0	-13	28	29
						5	22	19	-8	0	0	-11	0	0	0	0	0	-12	22	22
						6	0	0	-7	35	36	-10	25	26				-11	0	0
						7	0	0	-6	42	38	-9	0	0				-10	28	30
						8	0	0	-5	48	45	-8	28	-	-10	0	0	-9	0	0
						9	0	0	-4	0	0	-7	0	0	-9	0	0	-8	28	25
						10	0	0	-3	0	0	-6	23	19	-8	0	0	-7	23	27
						11	0	0	-2	0	0	-5	0	0	-7	0	0	-6	0	0
						12	0	0	-1	0	0	-4	22	25	-6	24	26	-5	50	51
						13	56	56	0	31	30	-3	28	27	-5	0	0	-4	0	0
						14	0	0	0	0	0	-2	36	36	-4	31	32	-3	0	0
						15	0	0	0	0	0	-1	0	0	-3	0	0	-2	44	46
						16	0	0	0	0	0	0	40	41	-2	23	21	-1	0	0
						17	0	0	0	0	0	0	22	22	0	24	27	0	44	49
						18	0	0	0	0	0	0	27	24	0	24	27	1	56	56
						19	0	0	0	0	0	0	32	32	3	0	0	2	37	35
						20	0	0	0	0	0	0	37	37	4	0	0	3	40	41
						21	0	0	0	0	0	0	42	42	5	0	0	4	43	46
						22	0	0	0	0	0	0	47	47	6	0	0	5	46	61
						23	0	0	0	0	0	0	52	52	7	0	0	6	49	51
						24	0	0	0	0	0	0	57	57	8	0	0	7	52	51
						25	0	0	0	0	0	0	62	62	9	0	0	8	0	0
						26	0	0	0	0	0	0	67	67	10	0	0	9	0	0
						27	0	0	0	0	0	0	72	72	11	0	0	10	0	0
						28	0	0	0	0	0	0	77	77	12	0	0	11	28	30
						29	0	0	0	0	0	0	82	82	13	0	0	12	23	0
						30	0	0	0	0	0	0	87	87	14	0	0	13	95	99
						31	56	56	0	31	30	-3	28	27	-5	0	0	14	0	0
						32	0	0	0	0	0	-2	36	36	-4	31	32	15	0	0
						33	0	0	0	0	0	-1	0	0	-3	0	0	16	0	0
						34	0	0	0	0	0	0	40	41	-2	23	21	17	0	0
						35	0	0	0	0	0	0	22	22	0	24	27	18	0	0
						36	0	0	0	0	0	0	27	24	0	24	27	19	0	0
						37	0	0	0	0	0	0	32	32	3	0	0	20	0	0
						38	0	0	0	0	0	0	37	37	4	0	0	21	0	0
						39	0	0	0	0	0	0	42	42	5	0	0	22	0	0
						40	0	0	0	0	0	0	47	47	6	0	0	23	0	0
						41	0	0	0	0	0	0	52	52	7	0	0	24	0	0
						42	0	0	0	0	0	0	57	57	8	0	0	25	0	0
						43	0	0	0	0	0	0	62	62	9	0	0	26	0	0
						44	0	0	0	0	0	0	67	67	10	0	0	27	0	0
						45	0	0	0	0	0	0	72	72	11	0	0	28	0	0
						46	0	0	0	0	0	0	77	77	12	0	0	29	0	0
						47	0	0	0	0	0	0	82	82	13	0	0	30	0	0
						48	0	0	0	0	0	0	87	87	14	0	0	31	0	0
						49	0	0	0	0	0	0	92	92	15	0	0	32	0	0
						50	0	0	0	0	0	0	97	97	16	0	0	33	0	0
						51	0	0	0	0	0	0	102	102	17	0	0	34	0	0
						52	0	0	0	0	0	0	107	107	18	0	0	35	0	0
						53	0	0	0	0	0	0	112	112	19	0	0	36	0	0
						54	0	0	0	0	0	0	117	117	20	0	0	37	0	0
						55	0	0	0	0	0	0	122	122	21	0	0	38	0	0
						56	0	0	0	0	0	0	127	127	22	0	0	39	0	0
						57	0	0	0	0	0	0	132	132	23	0	0	40	0	0
						58	0	0	0	0	0	0	137	137	24	0	0	41	0	0
						59	0	0	0	0	0	0	142	142	25	0	0	42	0	0
						60	0	0	0	0	0	0	147	147	26	0	0	43	0	0
						61	0	0	0	0	0	0	152	152	27	0	0	44	0	0
						62	0	0	0	0	0	0	157	157	28	0	0	45	0	0
						63	0	0	0	0	0	0	162	162	29	0	0	46	0	0
						64	0	0	0	0	0	0	167	167	30	0	0	47	0	0
						65	0	0	0	0	0	0	172	172	31	0	0	48	0	0
						66	0	0	0	0	0	0	177	177	32	0	0	49	0	0
						67	0	0	0	0	0	0	182	182	33	0	0	50	0	0
						68	0	0	0	0	0	0	187	187	34	0	0	51	0	0
						69	0	0	0	0	0	0	192	192	35	0	0	52	0	0
						70	0	0	0	0	0	0	197	197	36	0	0	53	0	0
						71	0	0	0	0	0	0	202	202	37	0	0	54	0	0
						72	0	0	0	0	0	0	207	207	38	0	0	55	0	0
						73	0	0	0	0	0	0	212	212	39	0	0	56	0	0
						74	0	0	0	0	0	0	217	217	40	0	0	57	0	0
						75	0	0	0	0	0	0	222	222	41	0	0	58	0	0
						76	0	0	0	0	0	0	227	227	42	0	0	59	0	0
						77	0	0	0	0	0	0	232	232	43	0	0	60	0	0
						78	0	0	0	0	0	0	237	237	44	0	0	61	0	0
						79	0	0	0	0	0	0	242	242	45	0	0	62	0	0
						80	0	0	0	0	0	0	247	247	46	0	0	63	0	0
						81	0	0	0	0	0	0	252	252	47	0	0	64	0	0
						82	0	0	0	0	0	0	257	257	48	0	0	65	0	0
						83	0	0	0	0	0	0	262	262	49	0	0	66	0	0
						84	0	0	0	0	0	0	267	267	50	0	0	67	0	0
						85	0	0	0	0	0	0	272	272	51	0	0	68	0	0
						86	0	0	0	0	0	0	277	277	52	0	0	69	0	0
						87	0	0	0	0	0	0	282	282	53	0	0	70	0	0
						88	0	0	0	0	0	0	287	287	54	0	0	71	0	0
						89	0	0	0	0	0	0	292	292	55	0	0	72	0	0
						90	0	0	0	0	0	0	297	297	56	0	0	73	0	0
						91	0	0	0	0	0	0	302	302	57	0	0	74	0	0
						92	0	0	0	0	0	0	307	307	58	0	0	75	0	0
						93	0	0	0	0	0	0	312	312	59	0	0	76	0	0
						94	0	0	0	0	0	0	317	317	60	0	0	77	0	0
						95	0	0	0	0	0	0	322	322	61	0	0	78	0	0
						96	0	0	0	0	0	0	327	327	62	0	0	79	0	0
						97	0	0	0	0	0	0	332	332	63	0	0	80		

L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC
H= 10 K= 5			H= 10 K= 6			H= 11 K= 2			H= 11 K= 5			H= 11 K= 10			H= 12 K= 3			H= 12 K= 6		
-16	0	0	8	0	0	-7	0	0	0	36	33	-4	0	0	-5	0	0	7	27	22
-14	0	0	9	0	0	-6	31	30	-1	0	0	-3	0	0	-4	0	0	8	0	0
-13	0	0	10	0	0	-5	0	0	-2	30	30	-2	0	0	-3	87	82	9	0	0
-12	0	0				-4	0	0	3	0	0	-1	26	25	-2	0	0	10	0	0
-11	0	0	H= 10 K= 9			-3	0	0	4	24	25	0	0	0	-1	79	80	11	0	0
-10	31	35				-1	0	0	5	0	0	1	0	0	0	0	0	12	0	0
-9	34	31	-9	0	0	1	0	0	6	25	26	3	0	0	1	0	0			
-8	41	41	-8	0	0	2	0	0	7	0	0	8	0	0	2	0	0	H= 12 K= 7		
-7	0	0	-7	0	0	3	0	0	8	0	0	-16	0	0	3	0	0	-12	0	0
-6	0	0	-6	0	0	4	0	0	9	0	0	-14	0	0	4	0	0	-11	0	0
-5	0	0	-5	0	0	5	0	0	10	0	0	-14	0	0	5	0	0	-10	0	0
-4	23	21	-4	26	25	6	34	32	11	23	23	-12	0	0	8	24	21	-9	0	0
-3	24	22	-3	0	0	7	0	0	12	0	0	-10	30	29	9	53	53	-8	0	0
-2	29	30	-2	0	0	8	43	44	13	0	0	-8	67	70	10	0	0	-7	41	40
-1	34	36	-1	21	19	9	0	0				-6	81	81	11	23	21	-6	0	0
0	37	38	0	0	0	10	29	27	H= 11 K= 6			-4	0	0	12	0	0	-5	27	26
1	37	36	1	0	0	11	0	0	-13	0	0	0	39	37	13	0	0	-4	0	0
2	23	26	2	22	22	12	0	0	-12	0	0	2	65	70	14	0	0	-3	23	19
3	25	26	3	0	0	13	0	0	-11	0	0	4	72	70	15	0	0	-2	0	0
4	0	0	4	0	0	14	27	30	-10	0	0	6	0	0	16	0	0	-1	32	29
5	24	23	5	0	0	15	34	34	-9	22	25	8	0	0				0	0	0
6	34	37	6	0	0	16	0	0	-8	0	0	10	0	0	H= 12 K= 4			1	0	0
7	38	36	7	0	0	H= 11 K= 3			-7	0	0	12	0	0	-16	0	0	2	0	0
8	50	50	8	0	0	-17	0	0	-6	0	0	14	29	29	-15	0	0	3	48	45
9	0	0	9	0	0	-15	0	0	-5	0	0	16	0	0	-15	0	0	4	0	0
10	24	21	10	0	0	-14	0	0	-4	0	0				-14	24	24	5	33	33
11	0	0	H= 10 K= 10			-13	23	20	-3	22	22	-11	0	0	-12	41	39	6	0	0
12	0	0	-6	21	22	-12	0	0	-2	29	31	-10	0	0	-11	0	0	7	0	0
13	0	0	-5	0	0	-11	21	19	0	0	0	-17	0	0	-10	23	23	8	0	0
14	0	0	-4	0	0	-9	0	0	1	36	34	-16	0	0	-9	0	0	H= 12 K= 8		
15	0	0	-3	0	0	-8	0	0	2	0	0	-15	0	0	-8	0	0	-9	0	0
H= 10 K= 6			-2	0	0	-7	27	30	3	26	25	-14	0	0	-7	0	0	-8	0	0
-15	0	0	-1	0	0	-6	28	26	4	0	0	-13	0	0	-6	0	0	-7	0	0
-14	0	0	0	22	23	-5	0	0	5	0	0	-11	0	0	-5	0	0	-6	0	0
-13	0	0	1	0	0	-4	27	29	6	0	0	-9	35	37	-4	42	39	-5	32	30
-12	0	0	2	0	0	-3	0	0	7	0	0	-8	0	0	-3	0	0	-4	0	0
-11	26	26	3	0	0	-2	0	0	8	0	0	-6	67	69	-2	65	66	-3	0	0
-10	0	0	4	0	0	0	0	0	9	0	0	-5	22	22	-1	0	0	-2	0	0
-9	31	31	5	0	0	1	0	0	10	0	0	-5	37	36	0	28	31	-1	0	0
-8	27	28	6	0	0	2	0	0	11	0	0	-4	69	67	1	0	0	0	0	0
-7	24	22	7	0	0	3	0	0	12	0	0	-3	23	25	2	0	0	-1	0	0
-6	35	34	8	0	0	4	32	33	13	0	0	-2	25	27	3	0	0	1	29	31
-5	0	0	9	29	29	5	25	27	-1	36	37	-1	16	37	4	0	0	2	0	0
-4	29	29	10	0	0	6	23	20	0	35	40	0	35	40	5	31	32	3	0	0
-3	0	0	11	0	0	7	32	28	1	42	39	1	42	39	6	22	21	4	0	0
-2	0	0	12	26	24	8	0	0	2	48	28	2	48	28	7	59	56	5	0	0
-1	0	0	13	0	0	9	26	28	3	73	70	4	0	0	8	48	53	6	0	0
0	0	0	14	0	0	10	0	0	4	0	0	4	0	0	9	0	0	7	0	0
1	0	0	15	25	26	11	0	0	5	67	68	5	67	68	10	39	36	8	0	0
2	0	0	16	0	0	12	0	0	6	36	37	6	36	37	11	0	0	H= 12 K= 9		
3	0	0	17	0	0	13	0	0	7	0	0	7	0	0	12	0	0	-4	0	0
4	38	39	18	0	0	14	0	0	8	0	0	8	0	0	13	0	0	-5	0	0
5	23	28	19	0	0	15	22	23	9	0	0	9	0	0	14	0	0	-4	0	0
6	40	37	20	0	0	16	0	0	10	0	0	10	0	0	15	22	23	-3	0	0
7	27	29	21	0	0	H= 11 K= 4			11	0	0	11	0	0	-15	0	0	-2	0	0
8	0	0	22	22	23	-16	0	0	-1	0	0	12	23	21	-13	0	0	-1	0	0
9	30	27	23	0	0	-15	0	0	0	25	28	14	0	0	-12	25	23	0	0	0
10	0	0	24	0	0	-14	0	0	1	0	0	15	0	0	-11	0	0	2	0	0
11	0	0	25	24	24	-13	0	0	2	26	26	16	23	23	-10	43	43	3	0	0
12	0	0	26	0	0	-12	0	0	3	0	0	17	0	0	-9	0	0	5	0	0
H= 10 K= 7			-11	0	0	-11	0	0	4	25	23	18	0	0	-8	0	0	H= 13 K= 0		
-13	0	0	-10	0	0	-10	0	0	5	0	0	-17	0	0	-7	0	0	-16	0	0
-12	23	24	-9	0	0	-9	0	0	6	0	0	-15	33	31	-6	25	23	-14	28	25
-11	26	23	-8	0	0	-8	0	0	7	0	0	-14	22	20	-5	0	0	-12	0	0
-10	0	0	-7	0	0	-7	26	22	8	0	0	-13	0	0	-4	0	0	-10	0	0
-9	0	0	-6	0	0	-6	0	0	9	0	0	-12	0	0	-3	0	0	-8	0	0
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-7	39	39	-4	0	0	-4	0	0	11	0	0	-10	0	0	-1	0	0	-6	0	0
-6	45	44	-3	33	36	-3	33	36	12	0	0	-9	0	0	0	0	0	-5	25	24
-5	0	0	-2	0	0	-2	0	0	13	0	0	-8	31	33	-1	36	35	-4	22	27
-4	0	0	-1	0	0	-1	34	33	14	0	0	-7	0	0	0	0	0	-3	0	0
-3	0	0	0	0	0	0	0	0	15	0	0	-6	23	21	1	31	31	-2	0	0
-2	0	0	1	0	0	1	0	0	16	0	0	-5	48	47	2	29	29	0	0	0
-1	32	32	2	0	0	2	24	22	17	0	0	-4	37	37	3	24	24	4	31	29
0	0	0	3	18	19	3	27	26	18	0	0	-3	26	26	4	0	0	6	0	0
1	0	0	4	29	27	4	41	45	19	0	0	-2	76	76	5	0	0	8	0	0
2	0	0	5	54	52	5	41	45	20	0	0	-1	24	22	6	47	49	10	29	28
3	18	19	6	0	0	6	0	0	21	0	0	0	60	60	7	0	0	12	30	33
4	29	27	7	0	0	7	0	0	22	0	0	1	56	51	8	36	36	14	31	31
5	54	52	8	0	0	8	0	0	23	0	0	2	30	30	9	0	0	H= 13 K= 1		
6	0	0	9	24	23	9	0	0	24	0	0	3	32	34	10	0	0	-17	0	0
7	0	0	10	29	28	10	29	28	25	0	0	4	32	32	11	0	0	-15	0	0
8	14	32	11	0	0	11	0	0	26	0	0	5	41	38	-13	0	0	-14	0	0
9	25	25	12	0	0	12	0	0	27	0	0	6	57	57	-12	0	0	-13	0	0
10	0	0	13	0	0	13	0	0	28	0	0	7	33	37	-11</					

Table 2.8.5

Analysis of Agreement between Observed and Calculated
Structure Factors at R=5.5%

Range $ F_o $	No.	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta F $	$Av.w \Delta F ^2$	R
0-25	429	9987	9905	737	3.65	0.074
25-34	601	17627	17491	1030	3.40	0.058
34-42	307	11614	11526	617	3.74	0.053
42-51	218	10067	10056	489	3.90	0.049
51-59	130	7137	7084	356	5.27	0.050
59-68	87	5517	5485	235	3.65	0.043
68-76	53	3802	3759	139	2.74	0.037
76-85	34	2741	2696	154	7.48	0.056
85-102	37	3415	3391	189	8.91	0.055
102-119	21	2307	2308	110	4.81	0.048
119-254	29	4517	4387	265	6.93	0.059
Sin θ/λ						
0.0-0.1	11	1267	1304	86	8.60	0.068
0.1-0.2	95	6206	6016	489	12.99	0.079
0.2-0.3	245	13904	13797	968	7.96	0.070
0.3-0.4	431	19644	19477	990	3.73	0.050
0.4-0.5	524	18698	18620	867	2.61	0.046
0.5-0.6	482	14906	14758	701	2.15	0.047
0.6-0.7	158	4105	4116	221	2.23	0.054



CHAPTER 2.9

Table 2.9.2

Final positional parameters (fractional co-ordinates, $\times 10^5$ for Palladium, Chlorine and Phosphorus atoms, $\times 10^4$ for the remainder) with corresponding standard deviations and mean square atomic vibrations ($\text{\AA}^2 \times 10^3$) for carbon atoms, with estimated standard deviations

Atom	x	y	z	U
Pd	25083(6)	01951(10)	01066(5)	
P(1)	30897(21)	-15771(40)	09789(19)	
P(2)	19082(20)	15499(40)	-09747(18)	
Cl	25077(36)	21586(51)	10985(23)	
C(11)	3730(10)	- 2955(18)	0443(9)	47(4)
C(12)	4102(12)	- 4250(22)	0975(11)	66(5)
C(13)	4394(12)	- 2225(22)	- 0043(11)	66(5)
C(14)	2300(11)	- 2735(19)	1426(10)	51(4)
C(15)	1695(15)	- 1706(28)	1909(14)	88(7)
C(16)	1784(14)	- 3577(26)	0746(13)	85(6)
C(17)	3654(10)	- 0740(19)	1882(10)	51(4)
C(18)	4411(16)	0185(29)	1631(14)	94(7)
C(19)	3894(15)	- 1852(28)	2615(14)	93(7)
C(21)	1319(10)	3162(18)	- 0607(9)	46(4)
C(22)	0570(13)	2578(24)	- 0137(12)	70(5)
C(23)	1045(13)	4349(24)	- 1249(12)	77(6)
C(24)	2720(8)	2420(15)	- 1595(8)	38(3)
C(25)	3279(11)	1256(20)	- 1950(10)	56(4)
C(26)	3233(11)	3519(21)	- 1035(10)	61(4)
C(27)	1304(9)	0386(18)	- 1724(8)	43(3)
C(28)	0659(11)	- 0618(21)	- 1319(11)	63(5)
C(29)	0855(12)	1295(21)	- 2458(11)	63(5)

Table 2.9.3

Mean square atomic vibrations ($\text{\AA}^2 \times 10^4$) for Palladium, Chlorine and Phosphorus atoms, with estimated standard deviations

	U_{11}	$2U_{12}$	$2U_{13}$	U_{22}	$2U_{23}$	U_{33}
Pd	237(3)	57(12)	34(6)	346(4)	- 14(11)	257(3)
P(1)	267(21)	78(30)	62(25)	375(18)	- 8(30)	315(15)
P(2)	236(20)	69(30)	6(23)	411(19)	20(29)	257(14)
Cl	1130(43)	589(54)	-304(44)	506(26)	-167(37)	348(19)

L FO FC			L FO FC			L FO FC			L FO FC			L FO FC			L FO FC			L FO FC		
M	C	K	M	C	K	M	C	K	M	C	K	M	C	K	M	C	K	M	C	K
2	200	197 +	4	42	39 +	18	0	0 +	-19	0	0 +	-6	0	0 +	15	0	0 +	12	42	38 -
6	66	65 +	5	0	0 +				-18	0	0 +	-5	45	52 -	17	0	0 +	13	36	39 -
8	162	143 +	6	12	10 +	M=1 K=1			-16	0	0 +	-4	0	0 +				14	43	44 -
10	160	156 +	7	0	0 +	M=1 K=2			-17	0	0 +	-4	0	0 +	M=2 K=1			14	43	44 -
12	83	84 +	8	40	37 +				-15	0	0 +	-1	33	36 -				16	0	0 +
14	0	0 +	9	0	0 +	-20	0	0 +	-16	0	0 +	1	29	28 -	-19	31	32 -	M=2 K=5		
16	0	0 +	10	57	59 +	-16	40	42 +	-13	32	33 -	5	60	62 -	-17	0	0 +	-19	0	0 +
18	34	31 +	11	46	47 -	-14	58	60 +	-12	29	33 -	4	0	0 +	-17	0	0 +			
M=2 K=1			12	38	38 +	-12	38	38 +	-11	42	46 +	5	60	62 -	-15	0	0 +	-19	0	0 +
			13	0	0 +	-12	32	30 +	-10	33	34 -	6	0	0 +	-13	0	0 +	-17	0	0 +
			14	13	0 +	-11	0	0 +	-9	0	0 +	7	31	30 -	-14	56	56 -	-16	0	0 +
			15	0	0 +	-8	86	86 +	-8	44	45 +	8	0	0 +	-13	0	0 +	-15	0	0 +
			16	0	0 +	-7	0	0 +	-7	0	0 +	9	0	0 +	-10	0	0 +	-12	49	54 -
			17	0	0 +	-5	0	0 +	-5	37	32 -	10	0	0 +	-10	51	50 -	-11	0	0 +
			18	0	0 +	-4	0	0 +	-4	0	0 +	11	0	0 +	-10	51	50 -	-12	49	54 -
			19	0	0 +	-2	39	37 -	-2	54	57 -	-13	0	0 +	-7	0	0 +	-10	0	0 +
			20	0	0 +	-1	43	49 -	-1	0	0 +	-12	0	0 +	-6	131	129 -	-9	60	66 -
1	196	219 +	2	1	0 +				-11	0	0 +	-10	0	0 +	-9	0	0 +	-8	0	0 +
2	174	156 +	3	1	0 +				-10	0	0 +	-9	0	0 +	-8	0	0 +	-7	0	0 +
3	66	67 +	4	1	0 +				-9	0	0 +	-8	0	0 +	-7	0	0 +	-6	0	0 +
4	0	0 +	5	170	156 +	3	42	42 +	-8	0	0 +	-7	0	0 +	-6	0	0 +	-5	0	0 +
5	0	0 +	6	0	0 +	4	0	0 +	-6	0	0 +	-6	0	0 +	-5	0	0 +	-4	0	0 +
6	0	0 +	7	116	115 +	5	0	0 +	-5	0	0 +	-5	0	0 +	-4	0	0 +	-3	0	0 +
7	0	0 +	8	0	0 +	6	0	0 +	-4	0	0 +	-4	0	0 +	-3	0	0 +	-2	0	0 +
8	0	0 +	9	0	0 +	7	0	0 +	-3	0	0 +	-3	0	0 +	-2	0	0 +	-1	0	0 +
9	0	0 +	10	0	0 +	8	0	0 +	-2	0	0 +	-2	0	0 +	-1	0	0 +			
10	0	0 +	11	0	0 +	9	0	0 +	-1	0	0 +	-1	0	0 +						
11	0	0 +	12	0	0 +	10	0	0 +	0	0	0 +									
12	0	0 +	13	0	0 +	11	0	0 +	0	0	0 +									
13	0	0 +	14	0	0 +	10	0	0 +	0	0	0 +									
14	0	0 +	15	0	0 +	9	0	0 +	0	0	0 +									
15	0	0 +	16	0	0 +	8	0	0 +	0	0	0 +									
16	0	0 +	17	0	0 +	7	0	0 +	0	0	0 +									
17	0	0 +	18	0	0 +	6	0	0 +	0	0	0 +									
18	0	0 +	19	0	0 +	5	0	0 +	0	0	0 +									
19	0	0 +	20	0	0 +	4	0	0 +	0	0	0 +									
20	0	0 +	21	0	0 +	3	0	0 +	0	0	0 +									
21	0	0 +	22	0	0 +	2	0	0 +	0	0	0 +									
22	0	0 +	23	0	0 +	1	0	0 +	0	0	0 +									
23	0	0 +	24	0	0 +	0	0	0 +												
24	0	0 +	25	0	0 +	0	0	0 +												
25	0	0 +	26	0	0 +	0	0	0 +												
26	0	0 +	27	0	0 +	0	0	0 +												
27	0	0 +	28	0	0 +	0	0	0 +												
28	0	0 +	29	0	0 +	0	0	0 +												
29	0	0 +	30	0	0 +	0	0	0 +												
30	0	0 +	31	0	0 +	0	0	0 +												
31	0	0 +	32	0	0 +	0	0	0 +												
32	0	0 +	33	0	0 +	0	0	0 +												
33	0	0 +	34	0	0 +	0	0	0 +												
34	0	0 +	35	0	0 +	0	0	0 +												
35	0	0 +	36	0	0 +	0	0	0 +												
36	0	0 +	37	0	0 +	0	0	0 +												
37	0	0 +	38	0	0 +	0	0	0 +												
38	0	0 +	39	0	0 +	0	0	0 +												
39	0	0 +	40	0	0 +	0	0	0 +												
40	0	0 +	41	0	0 +	0	0	0 +												
41	0	0 +	42	0	0 +	0	0	0 +												
42	0	0 +	43	0	0 +	0	0	0 +												
43	0	0 +	44	0	0 +	0	0	0 +												
44	0	0 +	45	0	0 +	0	0	0 +												
45	0	0 +	46	0	0 +	0	0	0 +												
46	0	0 +	47	0	0 +	0	0	0 +												
47	0	0 +	48	0	0 +	0	0	0 +												
48	0	0 +	49	0	0 +	0	0	0 +												
49	0	0 +	50	0	0 +	0	0	0 +												
50	0	0 +	51	0	0 +	0	0	0 +												
51	0	0 +	52	0	0 +	0	0	0 +												
52	0	0 +	53	0	0 +	0	0	0 +												
53	0	0 +	54	0	0 +	0	0	0 +												
54	0	0 +	55	0	0 +	0	0	0 +												
55	0	0 +	56	0	0 +	0	0	0 +												
56	0	0 +	57	0	0 +	0	0	0 +												
57	0	0 +	58	0	0 +	0	0	0 +												
58	0	0 +	59	0	0 +	0	0	0 +												
59	0	0 +	60	0	0 +	0	0	0 +												
60	0	0 +	61	0	0 +	0	0	0 +												
61	0	0 +	62	0	0 +	0	0	0 +												
62	0	0 +	63	0	0 +	0	0	0 +												
63	0	0 +	64	0	0 +	0	0	0 +												
64	0	0 +	65	0	0 +	0	0	0 +												
65	0	0 +	66	0	0 +	0	0	0 +												
66	0	0 +	67	0	0 +	0	0	0 +												
67	0	0 +	68	0	0 +	0	0	0 +												
68	0	0 +	69	0	0 +	0	0	0 +												
69	0	0 +	70	0	0 +	0	0	0 +												
70	0	0 +	71	0	0 +	0	0	0 +												
71	0	0 +	72	0	0 +	0	0	0 +												
72	0	0 +	73	0	0 +	0	0	0 +												
73	0	0 +	74	0	0 +	0	0	0 +												
74	0	0 +	75	0	0 +	0	0	0 +												
75	0	0 +	76	0	0 +	0	0	0 +												
76	0	0 +	77	0	0 +	0	0	0 +												
77	0	0 +	78	0	0 +	0	0	0 +												
78	0	0 +	79	0	0 +	0	0	0 +												
79	0	0 +	80	0	0 +	0	0	0 +												
80	0	0 +	81	0	0 +	0	0	0 +												
81	0	0 +	82	0	0 +	0	0	0 +												
82	0	0 +	83	0	0 +	0	0	0 +												
83	0	0 +	84	0	0 +	0	0	0 +												
84	0	0 +	85	0	0 +	0	0	0 +												
85	0	0 +	86	0	0 +	0	0	0 +												
86	0	0 +	87	0	0 +	0	0	0 +												
87	0	0 +	88	0	0 +	0	0	0 +												
88	0	0 +	89	0	0 +	0	0	0 +												
89	0	0 +	90	0	0 +	0	0	0 +												
90	0	0 +	91	0	0 +	0	0	0 +												
91	0	0 +	92	0	0 +	0	0	0 +												
92	0	0 +	93	0	0 +	0	0	0 +												
93	0	0 +	94	0	0 +	0	0	0 +												
94	0	0 +	95	0	0 +	0	0	0 +												
95	0	0 +	96	0	0 +	0	0	0 +												
96	0	0 +	97	0	0 +	0	0	0 +												
97	0	0 +	98	0	0 +	0	0	0 +												
98	0	0 +	99	0	0 +	0	0	0 +												
99	0	0 +	100	0	0 +	0	0	0 +												

L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC
H=2 K=8			H=3 K=2			H=3 K=5			H=3 K=8			H=4 K=2			H=4 K=5			H=4 K=8		
-8	0	0	-20	0	0	-18	0	0	-4	0	0	-20	0	0	-18	0	0	-4	0	0
-7	38	37	-18	38	42	-17	0	0	-3	48	52	-19	0	0	-17	0	0	-3	0	0
-6	0	0	-16	47	46	-16	0	0	-1	37	36	-18	0	0	-16	38	37	-2	29	30
-4	0	0	-15	0	0	-15	0	0	1	0	0	-16	34	36	-15	0	0	0	46	42
-3	0	0	-14	45	42	-14	0	0	3	59	56	-15	0	0	-14	37	40	1	30	31
-2	0	0	-13	0	0	-13	0	0	4	0	0	-14	43	44	-13	0	0	2	0	0
0	36	35	-12	39	37	-12	0	0	5	55	51	-13	0	0	-12	0	0	4	0	0
1	36	45	-11	0	0	-11	36	36	6	0	0	-12	36	36	-11	40	42	6	0	0
2	38	40	-10	36	35	-10	44	41	7	0	0	-11	54	56	-10	0	0	5	51	48
3	0	0	-9	35	36	-9	0	0	8	0	0	-10	50	47	-9	0	0	6	36	36
4	0	0	-8	85	83	-8	38	38	9	0	0	-9	56	58	-8	0	0	7	46	44
5	42	44	-7	37	33	-7	0	0	10	0	0	-8	94	93	-7	42	42	8	0	0
6	32	30	-6	67	66	-6	0	0				-6	120	120	-6	38	39			
7	59	59	-5	0	0	-5	33	32				-5	137	120	-5	58	59			
8	0	0	-4	0	0	-4	36	38				-4	173	176	-4	48	51			
9	0	0	-3	0	0	-3	0	0				-3	81	69	-3	70	75			
10	0	0	-2	0	0	-2	61	62				-2	116	116	-2	0	0			
			-1	50	50	-1	0	0				-1	138	128	-1	109	101			
H=2 K=9			H=3 K=3			H=3 K=6			H=3 K=10			H=4 K=3			H=4 K=6			H=4 K=11		
-12	0	0	-19	29	30	-17	0	0	-10	0	0	-20	0	0	-17	0	0	-4	0	0
-10	0	0	-17	43	44	-16	0	0	-9	31	28	-19	0	0	-16	0	0	0	0	0
-9	0	0	-16	0	0	-15	0	0	-8	0	0	-18	0	0	-15	0	0			
-8	32	26	-15	56	56	-14	0	0	-7	0	0	-17	35	35	-14	36	37			
-7	31	28	-14	46	46	-13	0	0	-6	0	0	-16	0	0	-13	0	0			
-6	0	0	-13	46	46	-12	0	0	-5	0	0	-15	0	0	-12	42	43			
-5	0	0	-12	0	0	-11	0	0	-4	0	0	-14	0	0	-11	0	0			
-4	0	0	-11	0	0	-10	0	0	-3	0	0	-13	0	0	-10	37	41			
-3	0	0	-10	0	0	-9	48	51	-2	0	0	-12	0	0	-9	0	0			
-2	0	0	-9	31	26	-8	0	0	-1	0	0	-11	0	0	-8	0	0			
-1	0	0	-8	0	0	-7	61	63	0	0	0	-10	0	0	-7	0	0			
0	0	0	-7	56	54	-6	33	34	0	36	30	-9	0	0	-6	0	0			
			-6	40	42	-5	32	31	0	28	28	-8	0	0	-5	0	0			
H=2 K=10			H=3 K=4			H=3 K=7			H=4 K=0			H=4 K=1			H=4 K=4			H=4 K=7		
-12	0	0	-19	29	30	-17	0	0	-20	0	0	-18	29	32	-17	0	0	-19	39	41
-10	0	0	-17	43	44	-16	0	0	-19	0	0	-16	0	0	-15	0	0	-17	40	38
-9	0	0	-16	0	0	-15	0	0	-18	0	0	-15	0	0	-14	0	0	-16	48	50
-8	32	26	-15	56	56	-14	0	0	-17	35	35	-14	36	37	-13	0	0	-15	48	50
-7	31	28	-14	46	46	-13	0	0	-16	0	0	-13	0	0	-12	42	43	-14	0	0
-6	0	0	-13	46	46	-12	0	0	-15	0	0	-12	0	0	-11	0	0	-13	55	53
-5	0	0	-12	0	0	-11	0	0	-14	0	0	-11	0	0	-10	37	41	-11	56	51
-4	0	0	-11	0	0	-10	0	0	-13	0	0	-10	0	0	-9	0	0	-10	0	0
-3	0	0	-10	0	0	-9	48	51	-12	0	0	-9	0	0	-8	0	0	-9	56	52
-2	0	0	-9	31	26	-8	0	0	-11	0	0	-8	0	0	-7	0	0	-8	0	0
-1	0	0	-8	0	0	-7	61	63	-10	0	0	-7	0	0	-6	0	0	-7	64	69
0	0	0	-7	56	54	-6	33	34	-9	0	0	-6	0	0	-5	0	0	-6	0	0
			-6	40	42	-5	32	31	-8	0	0	-5	0	0	-4	0	0	-5	0	0
H=2 K=11			H=3 K=5			H=3 K=8			H=4 K=2			H=4 K=5			H=4 K=8			H=4 K=11		
-12	0	0	-19	29	30	-17	0	0	-20	0	0	-18	0	0	-16	0	0	-12	40	43
-10	0	0	-17	43	44	-16	0	0	-19	0	0	-16	0	0	-15	0	0	-10	40	43
-9	0	0	-16	0	0	-15	0	0	-18	0	0	-15	0	0	-14	0	0	-9	40	43
-8	32	26	-15	56	56	-14	0	0	-17	35	35	-14	36	37	-13	0	0	-8	40	43
-7	31	28	-14	46	46	-13	0	0	-16	0	0	-13	0	0	-12	42	43	-7	40	43
-6	0	0	-13	46	46	-12	0	0	-15	0	0	-12	0	0	-11	0	0	-6	40	43
-5	0	0	-12	0	0	-11	0	0	-14	0	0	-11	0	0	-10	37	41	-5	40	43
-4	0	0	-11	0	0	-10	0	0	-13	0	0	-10	0	0	-9	0	0	-4	40	43
-3	0	0	-10	0	0	-9	48	51	-12	0	0	-9	0	0	-8	0	0	-3	40	43
-2	0	0	-9	31	26	-8	0	0	-11	0	0	-8	0	0	-7	0	0	-2	40	43
-1	0	0	-8	0	0	-7	61	63	-10	0	0	-7	0	0	-6	0	0	-1	40	43
0	0	0	-7	56	54	-6	33	34	-9	0	0	-6	0	0	-5	0	0	0	40	43
			-6	40	42	-5	32	31	-8	0	0	-5	0	0	-4	0	0			
H=2 K=12			H=3 K=6			H=3 K=9			H=4 K=3			H=4 K=6			H=4 K=9			H=4 K=12		
-12	0	0	-19	29	30	-17	0	0	-20	0	0	-18	0	0	-16	0	0	-12	40	43
-10	0	0	-17	43	44	-16	0	0	-19	0	0	-16	0	0	-15	0	0	-10	40	43
-9	0	0	-16	0	0	-15	0	0	-18	0	0	-15	0	0	-14	0	0	-9	40	43
-8	32	26	-15	56	56	-14	0	0	-17	35	35	-14	36	37	-13	0	0	-8	40	43
-7	31	28	-14	46	46	-13	0	0	-16	0	0	-13	0	0	-12	42	43	-7	40	43
-6	0	0	-13	46	46	-12	0	0	-15	0	0	-12	0	0	-11	0	0	-6	40	43
-5	0	0	-12	0	0	-11	0	0	-14	0	0	-11	0	0	-10	37	41	-5	40	43
-4	0	0	-11	0	0	-10	0	0	-13	0	0	-10	0	0	-9	0	0	-4	40	43
-3	0	0	-10	0	0	-9	48	51	-12	0	0	-9	0	0	-8	0	0	-3	40	43
-2	0	0	-9	31	26	-8	0	0	-11	0	0	-8	0	0	-7	0	0	-2	40	43
-1	0	0	-8	0	0	-7	61	63	-10	0	0	-7	0	0	-6	0	0	-1	40	43
0	0	0	-7	56	54	-6	33	34	-9	0	0	-6	0	0	-5	0	0	0	40	43
			-6	40	42	-5	32	31	-8	0	0	-5	0	0	-4	0	0			

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H= 5 K= 2			H= 5 K= 5			H= 5 K= 8			H= 6 K= 1			H= 6 K= 4			H= 6 K= 7		
-11 0 0 +	-12 0 0 +	-10 41 42 +	-11 50 48 +	-10 44 45 +	-9 35 36 +	-8 0 0 +	-7 0 0 +	-6 77 71 +	-5 0 0 +	-4 0 0 +	-3 0 0 +	-2 0 0 +	-1 36 42 +	0 0 0 +	1 43 48 +	2 0 0 +	3 0 0 +
4 0 0 +	5 0 0 +	6 79 84 +	7 0 0 +	8 93 89 +	9 0 0 +	10 0 0 +	11 0 0 +	12 36 35 -	13 59 58 -	14 54 52 -	15 0 0 +	16 33 35 -	17 0 0 +	18 0 0 +	19 30 30 +	20 38 38 -	21 35 35 -
22 30 30 +	23 38 38 -	24 40 40 +	25 48 48 +	26 50 50 +	27 58 58 +	28 60 60 +	29 68 68 +	30 70 70 +	31 78 78 +	32 80 80 +	33 88 88 +	34 90 90 +	35 98 98 +	36 100 100 +	37 108 108 +	38 110 110 +	39 118 118 +
40 120 120 +	41 130 130 +	42 140 140 +	43 150 150 +	44 160 160 +	45 170 170 +	46 180 180 +	47 190 190 +	48 200 200 +	49 210 210 +	50 220 220 +	51 230 230 +	52 240 240 +	53 250 250 +	54 260 260 +	55 270 270 +	56 280 280 +	57 290 290 +
58 300 300 +	59 310 310 +	60 320 320 +	61 330 330 +	62 340 340 +	63 350 350 +	64 360 360 +	65 370 370 +	66 380 380 +	67 390 390 +	68 400 400 +	69 410 410 +	70 420 420 +	71 430 430 +	72 440 440 +	73 450 450 +	74 460 460 +	75 470 470 +
76 480 480 +	77 490 490 +	78 500 500 +	79 510 510 +	80 520 520 +	81 530 530 +	82 540 540 +	83 550 550 +	84 560 560 +	85 570 570 +	86 580 580 +	87 590 590 +	88 600 600 +	89 610 610 +	90 620 620 +	91 630 630 +	92 640 640 +	93 650 650 +
94 660 660 +	95 670 670 +	96 680 680 +	97 690 690 +	98 700 700 +	99 710 710 +	100 720 720 +	101 730 730 +	102 740 740 +	103 750 750 +	104 760 760 +	105 770 770 +	106 780 780 +	107 790 790 +	108 800 800 +	109 810 810 +	110 820 820 +	111 830 830 +
112 840 840 +	113 850 850 +	114 860 860 +	115 870 870 +	116 880 880 +	117 890 890 +	118 900 900 +	119 910 910 +	120 920 920 +	121 930 930 +	122 940 940 +	123 950 950 +	124 960 960 +	125 970 970 +	126 980 980 +	127 990 990 +	128 1000 1000 +	129 1010 1010 +
130 1020 1020 +	131 1030 1030 +	132 1040 1040 +	133 1050 1050 +	134 1060 1060 +	135 1070 1070 +	136 1080 1080 +	137 1090 1090 +	138 1100 1100 +	139 1110 1110 +	140 1120 1120 +	141 1130 1130 +	142 1140 1140 +	143 1150 1150 +	144 1160 1160 +	145 1170 1170 +	146 1180 1180 +	147 1190 1190 +
148 1200 1200 +	149 1210 1210 +	150 1220 1220 +	151 1230 1230 +	152 1240 1240 +	153 1250 1250 +	154 1260 1260 +	155 1270 1270 +	156 1280 1280 +	157 1290 1290 +	158 1300 1300 +	159 1310 1310 +	160 1320 1320 +	161 1330 1330 +	162 1340 1340 +	163 1350 1350 +	164 1360 1360 +	165 1370 1370 +
166 1380 1380 +	167 1390 1390 +	168 1400 1400 +	169 1410 1410 +	170 1420 1420 +	171 1430 1430 +	172 1440 1440 +	173 1450 1450 +	174 1460 1460 +	175 1470 1470 +	176 1480 1480 +	177 1490 1490 +	178 1500 1500 +	179 1510 1510 +	180 1520 1520 +	181 1530 1530 +	182 1540 1540 +	183 1550 1550 +
184 1560 1560 +	185 1570 1570 +	186 1580 1580 +	187 1590 1590 +	188 1600 1600 +	189 1610 1610 +	190 1620 1620 +	191 1630 1630 +	192 1640 1640 +	193 1650 1650 +	194 1660 1660 +	195 1670 1670 +	196 1680 1680 +	197 1690 1690 +	198 1700 1700 +	199 1710 1710 +	200 1720 1720 +	201 1730 1730 +
202 1740 1740 +	203 1750 1750 +	204 1760 1760 +	205 1770 1770 +	206 1780 1780 +	207 1790 1790 +	208 1800 1800 +	209 1810 1810 +	210 1820 1820 +	211 1830 1830 +	212 1840 1840 +	213 1850 1850 +	214 1860 1860 +	215 1870 1870 +	216 1880 1880 +	217 1890 1890 +	218 1900 1900 +	219 1910 1910 +
220 1920 1920 +	221 1930 1930 +	222 1940 1940 +	223 1950 1950 +	224 1960 1960 +	225 1970 1970 +	226 1980 1980 +	227 1990 1990 +	228 2000 2000 +	229 2010 2010 +	230 2020 2020 +	231 2030 2030 +	232 2040 2040 +	233 2050 2050 +	234 2060 2060 +	235 2070 2070 +	236 2080 2080 +	237 2090 2090 +
238 2100 2100 +	239 2110 2110 +	240 2120 2120 +	241 2130 2130 +	242 2140 2140 +	243 2150 2150 +	244 2160 2160 +	245 2170 2170 +	246 2180 2180 +	247 2190 2190 +	248 2200 2200 +	249 2210 2210 +	250 2220 2220 +	251 2230 2230 +	252 2240 2240 +	253 2250 2250 +	254 2260 2260 +	255 2270 2270 +
256 2280 2280 +	257 2290 2290 +	258 2300 2300 +	259 2310 2310 +	260 2320 2320 +	261 2330 2330 +	262 2340 2340 +	263 2350 2350 +	264 2360 2360 +	265 2370 2370 +	266 2380 2380 +	267 2390 2390 +	268 2400 2400 +	269 2410 2410 +	270 2420 2420 +	271 2430 2430 +	272 2440 2440 +	273 2450 2450 +
274 2460 2460 +	275 2470 2470 +	276 2480 2480 +	277 2490 2490 +	278 2500 2500 +	279 2510 2510 +	280 2520 2520 +	281 2530 2530 +	282 2540 2540 +	283 2550 2550 +	284 2560 2560 +	285 2570 2570 +	286 2580 2580 +	287 2590 2590 +	288 2600 2600 +	289 2610 2610 +	290 2620 2620 +	291 2630 2630 +
292 2640 2640 +	293 2650 2650 +	294 2660 2660 +	295 2670 2670 +	296 2680 2680 +	297 2690 2690 +	298 2700 2700 +	299 2710 2710 +	300 2720 2720 +	301 2730 2730 +	302 2740 2740 +	303 2750 2750 +	304 2760 2760 +	305 2770 2770 +	306 2780 2780 +	307 2790 2790 +	308 2800 2800 +	309 2810 2810 +
310 2820 2820 +	311 2830 2830 +	312 2840 2840 +	313 2850 2850 +	314 2860 2860 +	315 2870 2870 +	316 2880 2880 +	317 2890 2890 +	318 2900 2900 +	319 2910 2910 +	320 2920 2920 +	321 2930 2930 +	322 2940 2940 +	323 2950 2950 +	324 2960 2960 +	325 2970 2970 +	326 2980 2980 +	327 2990 2990 +
328 3000 3000 +	329 3010 3010 +	330 3020 3020 +	331 3030 3030 +	332 3040 3040 +	333 3050 3050 +	334 3060 3060 +	335 3070 3070 +	336 3080 3080 +	337 3090 3090 +	338 3100 3100 +	339 3110 3110 +	340 3120 3120 +	341 3130 3130 +	342 3140 3140 +	343 3150 3150 +	344 3160 3160 +	345 3170 3170 +
346 3180 3180 +	347 3190 3190 +	348 3200 3200 +	349 3210 3210 +	350 3220 3220 +	351 3230 3230 +	352 3240 3240 +	353 3250 3250 +	354 3260 3260 +	355 3270 3270 +	356 3280 3280 +	357 3290 3290 +	358 3300 3300 +	359 3310 3310 +	360 3320 3320 +	361 3330 3330 +	362 3340 3340 +	363 3350 3350 +
364 3360 3360 +	365 3370 3370 +	366 3380 3380 +	367 3390 3390 +	368 3400 3400 +	369 3410 3410 +	370 3420 3420 +	371 3430 3430 +	372 3440 3440 +	373 3450 3450 +	374 3460 3460 +	375 3470 3470 +	376 3480 3480 +	377 3490 3490 +	378 3500 3500 +	379 3510 3510 +	380 3520 3520 +	381 3530 3530 +
382 3540 3540 +	383 3550 3550 +	384 3560 3560 +	385 3570 3570 +	386 3580 3580 +	387 3590 3590 +	388 3600 3600 +	389 3610 3610 +	390 3620 3620 +	391 3630 3630 +	392 3640 3640 +	393 3650 3650 +	394 3660 3660 +	395 3670 3670 +	396 3680 3680 +	397 3690 3690 +	398 3700 3700 +	399 3710 3710 +
400 3720 3720 +	401 3730 3730 +	402 3740 3740 +	403 3750 3750 +	404 3760 3760 +	405 3770 3770 +	406 3780 3780 +	407 3790 3790 +	408 3800 3800 +	409 3810 3810 +	410 3820 3820 +	411 3830 3830 +	412 3840 3840 +	413 3850 3850 +	414 3860 3860 +	415 3870 3870 +	416 3880 3880 +	417 3890 3890 +
418 3900 3900 +	419 3910 3910 +	420 3920 3920 +	421 3930 3930 +	422 3940 3940 +	423 3950 3950 +	424 3960 3960 +	425 3970 3970 +	426 3980 3980 +	427 3990 3990 +	428 4000 4000 +	429 4010 4010 +	430 4020 4020 +	431 4030 4030 +	432 4040 4040 +	433 4050 4050 +	434 4060 4060 +	435 4070 4070 +
436 4080 4080 +	437 4090 4090 +	438 4100 4100 +	439 4110 4110 +	440 4120 4120 +	441 4130 4130 +	442 4140 4140 +	443 4150 4150 +	444 4160 4160 +	445 4170 4170 +	446 4180 4180 +	447 4190 4190 +	448 4200 4200 +	449 4210 4210 +	450 4220 4220 +	451 4230 4230 +	452 4240 4240 +	453 4250 4250 +
454 4260 4260 +	455 4270 4270 +	456 4280 4280 +	457 4290 4290 +	458 4300 4300 +	459 4310 4310 +	460 4320 4320 +	461 4330 4330 +	462 4340 4340 +	463 4350 4350 +	464 4360 4360 +	465 4370 4370 +	466 4380 4380 +	467 4390 4390 +	468 4400 4400 +	469 4410 4410 +	470 4420 4420 +	471 4430 4430 +
472 4440 4440 +	473 4450 4450 +	474 4460 4460 +	475 4470 4470 +	476 4480 4480 +	477 4490 4490 +	478 4500 4500 +	479 4510 4510 +	480 4520 4520 +	481 4530 4530 +	482 4540 4540 +	483 4550 4550 +	484 4560 4560 +	485 4570 4570 +	486 4580 4580 +	487 4590 4590 +	488 4600 4600 +	489 4610 4610 +
490 4620 4620 +	491 4630 4630 +	492 4640 4640 +	493 4650 4650 +	494 4660 4660 +	495 4670 4670 +	496 4680 4680 +	497 4690 4690 +	498 4700 4700 +	499 4710 4710 +	500 4720 4720 +	501 4730 4730 +	502 4740 4740 +	503 4750 4750 +	504 4760 4760 +	505 4770 4770 +	506 4780 4780 +	507 4790 4790 +
508 4800 4800 +	509 4810 4810 +	510 4820 4820 +	511 4830 4830 +	512 4840 4840 +	513 4850 4850 +	514 4860 4860 +	515 4870 4870 +	516 4880 4880 +	517 4890 4890 +	518 4900 4900 +	519 4910 4910 +	520 4920 4920 +	521 4930 4930 +	522 4940 4940 +	523 4950 4950 +	524 4960 4960 +	525 4970 4970 +
526 4980 4980 +	527 4990 4990 +	528 5000 5000 +	529 5010 5010 +	530 5020 5020 +	531 5030 5030 +	532 5040 5040 +	533 5050 5050 +	534 5060 5060 +	535 5070 5070 +	536 5080 5080 +	537 5090 5090 +	538 5100 5100 +	539 5110 5110 +	540 5120 5120 +	541 5130 5130 +	542 5140 5140 +	543 5150 5150 +
544 5160 5160 +	545 5170 5170 +	546 5180 5180 +	547 5190 5190 +	548 5200 5200 +	549 5210 5210 +	550 5220 5220 +	551 5230 5230 +	552 5240 5240 +	553 5250 5250 +	554 5260 5260 +	555 5270 5270 +	556 5280 5280 +	557 5290 5290 +	558 5300 5300 +	559 5310 5310 +	560 5320 5320 +	561 5330 5330 +
562 5340 5340 +	563 5350 5350 +	564 5360 5360 +	565 5370 5370 +	566 5380 5380 +	567 5390 5390 +	568 5400 5400 +	569 5410 5410 +	570 5420 5420 +	571 5430 5430 +	572 5440 5440 +	573 5450 5450 +	574 5460 5460 +	575 5470 5470 +	576 5480 5480 +	577 5490 5490 +	578 5500 5500 +	579 5510 5510 +
580 5520 5520 +	581 5530 5530 +	582 5540 5540 +	583 5550 5550 +	584 5560 5560 +	585 5570 5570 +	586 5580 5580 +	587 5590 5590 +	588 5600 5600 +	589 5610 5610 +	590 5620 5620 +	591 5630 5630 +	592 5640 5640 +	593 5650 5650 +	594 5660 5660 +	595 5670 5670 +	596 5680 5680 +	597 5690 5690 +
598 5700 5700 +	599 5710 5710 +	600 5720 5720 +	601 5730 5730 +	602 5740 5740 +	603 5750 5750 +	604 5760 5760 +	605 5770 5770 +	606 5780 5780 +	607 5790 5790 +	608 5800 5800 +	609 5810 5810 +	610 5820 5820 +	611 5830 5830 +	612 5840 5840 +	613 5850 5850 +	614 5860 5860 +	615 5870 5870 +
616 5880 5880 +	617 5890 5890 +	618 5900 5900 +	619 5910 5910 +	620 5920 5920 +	621 5930 5930 +	622 5940 5940 +	623 5950 5950 +	624 5960 5960 +	625 5970 5970 +	626 5980 5980 +	627 5990 5990 +	628 6000 6000 +	629 6010 6010 +	630 6020 6020 +	631 6030 6030 +	632 6040 6040 +	633 6050 6050 +
634 6060 6060 +	635 6070 6070 +																

L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC
H=7 K=4			H=7 K=7			H=8 K=1			H=8 K=8			H=9 K=2			H=9 K=5					
-1	33	30+	5	0	0+	-1	93	87+	2	104	101+	-11	0	0+	-18	33	39+	-10	35	33-
0	0	0+	6	40	37+	0	0	0+	3	50	52+	-10	0	0+	-17	0	0+	-9	31	28+
1	0	0+	7	0	0+	1	89	83+	4	0	0+	-8	0	0+	-16	38	41+	-8	36	36+
2	0	0+	8	0	0+	2	77	75+	5	0	0+	-6	0	0+	-14	33	32+	-7	0	0+
3	47	55+	9	0	0+	3	135	132+	6	0	0+	-5	0	0+	-12	36	36+	-6	0	0+
4	34	35+	10	0	0+	4	41	37+	7	40	40+	-4	0	0+	-10	31	31+	-5	0	0+
5	49	46+	11	0	0+	5	115	114+	8	62	59+	-3	0	0+	-9	0	0+	-4	30	35+
6	0	0+	12	0	0+	6	0	0+	9	45	46+	-2	0	0+	-8	32	34+	-3	0	0+
7	0	0+	13	0	0+	7	91	86+	10	67	67+	-1	0	0+	-7	42	42+	-2	47	42+
8	0	0+	14	0	0+	8	71	65+	11	0	0+	0	0	0+	-6	55	48+	0	52	55+
9	0	0+				9	45	45+	12	38	39+	1	0	0+	-5	0	0+	3	0	0+
10	46	45+	H=7 K=8			11	51	43+	13	0	0+	2	0	0+	-4	0	0+	4	0	0+
11	0	0+	-13	0	0+	12	52	53+	15	0	0+	3	0	0+	-3	0	0+	5	0	0+
12	45	44+	-12	0	0+	13	33	35+	17	0	0+	4	0	0+	-2	0	0+	6	34	36+
13	0	0+	-11	0	0+	14	38	34+	18	0	0+	5	0	0+	-1	0	0+	8	34	37+
14	0	0+	-10	0	0+	15	37	34+	19	0	0+	6	0	0+	0	0	0+	9	0	0+
15	0	0+	-9	31	26+	16	0	0+	H=8 K=5			7	0	0+	3	0	0+	10	0	0+
16	0	0+	-8	0	0+	17	0	0+	-17	0	0+	8	0	0+	4	0	0+	11	34	33+
18	30	31+	-7	32	31+				-15	0	0+	9	0	0+	5	0	0+	12	0	0+
H=7 K=5			-5	47	45+	H=8 K=2			-13	0	0+	10	0	0+	6	39	42+	13	0	0+
-18	0	0+	-4	0	0+	-18	0	0+	-11	32	34+	11	0	0+	7	0	0+	14	0	0+
-17	0	0+	-3	45	40+	-17	0	0+	-10	0	0+	12	0	0+	8	51	53+	15	0	0+
-16	0	0+	-2	0	0+	-16	0	0+	-9	45	44+	13	0	0+	9	0	0+			
-15	0	0+	-1	32	30+	-14	31	33+	-8	40	45+	14	0	0+	10	42	39+	H=9 K=6		
-14	0	0+	0	0	0+	-13	31	36+	-7	54	56+	15	0	0+	11	45	42+	-16	0	0+
-13	34	33+	1	32	31+	-12	56	54+	-6	30	33+	16	48	40+	12	0	0+	-14	0	0+
-12	0	0+	2	57	40+	-11	34	36+	-5	46	52+	17	31	31+	13	0	0+	-13	0	0+
-11	31	32+	3	0	0+	-10	93	92+	-4	60	62+	18	0	0+	14	45	42+	-12	0	0+
-10	36	39+	4	0	0+	-9	0	0+	-3	0	0+	19	0	0+	15	32	36+	-11	0	0+
-9	29	30+	5	47	40+	-8	95	84+	-2	0	0+	20	0	0+	16	48	40+	-10	0	0+
-8	39	38+	6	0	0+	-7	40	39+	-1	56	60+	21	0	0+	17	30	31+	-9	36	35+
-7	40	45+	7	0	0+	-6	0	0+	0	31	34+	22	0	0+	18	0	0+	-8	0	0+
-6	0	0+	8	0	0+	-5	0	0+	1	45	50+	23	0	0+	19	30	31+	-7	34	37+
-5	0	0+	9	0	0+	-4	110	111+	2	55	53+	24	0	0+	20	32	36+	-6	0	0+
-4	37	38+	10	0	0+	-3	51	56+	3	47	43+	25	0	0+	21	43	44+	-5	36	35+
-3	36	28+	11	0	0+	-2	131	129+	4	0	0+	26	0	0+	22	0	0+	-4	0	0+
-2	39	43+	12	0	0+	-1	56	52+	5	46	48+	27	0	0+	23	36	38+	-3	16	36+
-1	0	0+	13	0	0+	0	100	112+	6	33	36+	28	0	0+	24	0	0+	-2	0	0+
0	57	56+	14	0	0+	1	34	37+	7	46	51+	29	0	0+	25	34	31+	-1	50	50+
1	0	0+	15	0	0+	2	111	103+	8	46	51+	30	0	0+	26	0	0+	0	0	0+
2	43	44+	16	0	0+	3	58	65+	9	32	36+	31	0	0+	27	36	38+	1	56	61+
3	0	0+	17	0	0+	4	109	111+	10	32	36+	32	0	0+	28	0	0+	2	0	0+
4	32	33+	18	0	0+	5	0	0+	11	0	0+	33	0	0+	29	0	0+	3	0	0+
5	36	31+	19	0	0+	6	99	93+	12	0	0+	34	0	0+	30	0	0+	4	0	0+
6	0	0+	20	0	0+	7	30	26+	13	0	0+	35	0	0+	31	0	0+	5	0	0+
7	0	0+	21	0	0+	8	54	51+	14	0	0+	36	0	0+	32	0	0+	6	0	0+
8	35	39+	22	0	0+	9	0	0+	15	0	0+	37	0	0+	33	0	0+	7	10	33+
9	29	28+	23	0	0+	10	73	71+	16	0	0+	38	0	0+	34	0	0+	8	0	0+
10	0	0+	24	0	0+	11	31	31+	17	0	0+	39	0	0+	35	0	0+	9	31	31+
11	46	28+	25	0	0+	12	2	2+	18	29	32+	40	0	0+	36	0	0+	10	0	0+
12	0	0+	26	0	0+	13	38	40+	19	0	0+	41	0	0+	37	0	0+	11	0	0+
13	32	32+	27	0	0+	14	0	0+	20	0	0+	42	0	0+	38	0	0+	12	0	0+
14	0	0+	28	0	0+	15	0	0+	21	0	0+	43	0	0+	39	0	0+	13	0	0+
15	0	0+	29	0	0+	16	0	0+	22	0	0+	44	0	0+	40	0	0+	14	0	0+
16	0	0+	30	0	0+	17	0	0+	23	0	0+	45	0	0+	41	0	0+	15	0	0+
H=7 K=6			H=7 K=10			H=8 K=3			H=8 K=6			H=9 K=10			H=9 K=4			H=9 K=7		
-17	0	0+	-8	0	0+	-19	0	0+	-7	0	0+	-18	34	34+	-18	0	0+	-14	0	0+
-16	0	0+	-7	0	0+	-18	0	0+	-6	68	70+	-17	44	46+	-16	0	0+	-13	0	0+
-15	0	0+	-6	0	0+	-17	0	0+	-5	0	0+	-16	44	46+	-15	0	0+	-12	0	0+
-14	0	0+	-5	0	0+	-16	0	0+	-4	76	78+	-15	44	46+	-14	0	0+	-11	0	0+
-13	0	0+	-4	0	0+	-15	0	0+	-3	0	0+	-14	44	46+	-13	0	0+	-10	0	0+
-12	0	0+	-3	38	33+	-14	0	0+	-2	50	52+	-13	44	46+	-12	0	0+	-9	0	0+
-11	29	30+	-2	30	36+	-13	30	30+	-1	0	0+	-12	44	46+	-11	0	0+	-8	36	33+
-10	29	25+	-1	38	26+	-12	0	0+	0	0	0+	-11	44	46+	-10	0	0+	-7	0	0+
-9	35	32+	0	40	36+	-11	78	78+	1	0	0+	-10	44	46+	-9	0	0+	-6	35	36+
-8	31	30+	1	40	36+	-10	78	78+	2	37	39+	-9	44	46+	-8	0	0+	-5	0	0+
-7	34	37+	2	34	29+	-9	78	78+	3	0	0+	-8	44	46+	-7	0	0+	-4	37	37+
-6	37	41+	3	34	29+	-8	0	0+	4	77	86+	-7	44	46+	-6	0	0+	-3	0	0+
-5	0	0+	4	0	0+	-7	46	48+	5	0	0+	-6	44	46+	-5	0	0+	-2	34	38+
-4	0	0+	5	0	0+	-6	0	0+	6	61	65+	-5	44	46+	-4	0	0+	-1	34	38+
-3	32	36+	6	0	0+	-5	62	58+	7	0	0+	-4	44	46+	-3	0	0+	0	0	0+
-2	58	56+	7	0	0+	-4	0	0+	8	0	0+	-3	44	46+	-2	0	0+	1	0	0+
-1	58	56+	8	0	0+	-3	88	90+	9	0	0+	-2	44	46+	-1	0	0+	2	32	37+
0	0	0+	9	0	0+	-2	0	0+	10	0	0+	-1	44	46+	0	0	0+	3	0	0+
1	71	75+	10	0	0+	-1	114	118+	11	30	28+	0	0	0+	1	0	0+	4	32	35+
2	33	35+	11	0	0+	0	0	0+	12	0	0+	-19	0	0+	0	0	0+	5	0	0+
3	0	0+	12	0	0+	1	149	160+	13	0	0+	-18	0	0+	-7	0	0+	6	0	0+
4	0	0+	13	0	0+	2	0	0+	14	0	0+	-17	0	0+	-6	0	0+	7	0	0+
5	0	0+	14	0	0+	3	15	80+	15	0	0+	-16	0	0+	-5	0	0+	8	0	0+
6	0	0+	15	0	0+	4	37	40+	16	0	0+	-15	0	0+	-4	0	0+	9	0	0+
7	33	34+	16	0	0+	5	60	61+	17	0	0+	-14	0	0+	-3	0	0+	10	0	0+
8	0	0+	17	0	0+	6	0	0+	18	0	0+	-13	0	0+	-2	0	0+	11	0	0+

L FU FC			L FU FC			L FU FC			L FU FC			L FU FC			L FU FC			L FU FC		
H 9 K=9	H 9 K=9	H 9 K=9	H 10 K=2	H 10 K=2	H 10 K=2	H 10 K=6	H 10 K=6	H 10 K=6	H 11 K=0	H 11 K=0	H 11 K=0	H 11 K=4	H 11 K=4	H 11 K=4	H 11 K=9	H 11 K=9	H 11 K=9	H 12 K=2	H 12 K=2	H 12 K=2
-10 0 0	0 0	0 0	5 0 0	0 0	0 0	-15 0 0	0 0	0 0	16 0 0	0 0	-2 0 0	0 0	0 0	0 0	-5 39 31	0 0	0 0	13 0 0	0 0	0 0
-8 0 0	0 0	0 0	6 75 71	0 0	0 0	-14 0 0	0 0	0 0	-1 38 37	0 0	-4 0 0	0 0	0 0	0 0	-3 45 37	0 0	0 0	15 0 0	0 0	0 0
-4 32 32	0 0	0 0	8 51 42	0 0	0 0	-11 0 0	0 0	0 0	0 0	0 0	2 0 0	0 0	0 0	0 0	-3 34 35	0 0	0 0	16 0 0	0 0	0 0
-4 39 34	0 0	0 0	9 52 0	0 0	0 0	-9 0 0	0 0	0 0	-17 30 32	0 0	3 31 35	0 0	0 0	0 0	1 0 0	0 0	0 0	0 0	0 0	0 0
-2 40 33	0 0	0 0	10 56 52	0 0	0 0	-8 41 44	0 0	0 0	-15 38 38	0 0	4 0 0	0 0	0 0	0 0	3 39 37	0 0	0 0	0 0	0 0	0 0
0 38 29	0 0	0 0	11 50 50	0 0	0 0	-7 42 33	0 0	0 0	0 43 42	0 0	5 34 41	0 0	0 0	0 0	4 37 40	0 0	0 0	0 0	0 0	0 0
2 31 31	0 0	0 0	12 40 40	0 0	0 0	-6 60 65	0 0	0 0	-11 35 35	0 0	6 0 0	0 0	0 0	0 0	7 0 0	0 0	0 0	-15 0 0	0 0	0 0
4 38 30	0 0	0 0	13 40 39	0 0	0 0	-4 52 51	0 0	0 0	-10 0 0	0 0	7 0 0	0 0	0 0	0 0	8 0 0	0 0	0 0	-16 0 0	0 0	0 0
5 0 0	0 0	0 0	14 0 0	0 0	0 0	-2 31 76	0 0	0 0	-8 29 8	0 0	8 0 0	0 0	0 0	0 0	9 0 0	0 0	0 0	-13 59 61	0 0	0 0
6 30 32	0 0	0 0	16 0 0	0 0	0 0	2 39 42	0 0	0 0	-7 40 40	0 0	10 32 32	0 0	0 0	0 0	0 0	0 0	0 0	-11 56 58	0 0	0 0
8 0 0	0 0	0 0	17 0 0	0 0	0 0	4 59 66	0 0	0 0	-5 0 0	0 0	11 0 0	0 0	0 0	0 0	0 0	0 0	0 0	-7 0 0	0 0	0 0
H 9 K=10	H 10 K=3	H 10 K=3	-17 0 0	0 0	0 0	5 47 47	0 0	0 0	-2 0 0	0 0	13 0 0	0 0	0 0	0 0	-8 0 0	0 0	0 0	-4 0 0	0 0	0 0
-5 0 0	0 0	0 0	-16 0 0	0 0	0 0	7 0 0	0 0	0 0	0 0	0 0	13 0 0	0 0	0 0	0 0	-4 0 0	0 0	0 0	-7 0 0	0 0	0 0
-3 30 25	0 0	0 0	-17 0 0	0 0	0 0	8 0 0	0 0	0 0	0 0	0 0	13 0 0	0 0	0 0	0 0	-4 0 0	0 0	0 0	-7 0 0	0 0	0 0
-2 0 0	0 0	0 0	-13 40 52	0 0	0 0	11 0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	-2 33 31	0 0	0 0	-3 136 116	0 0	0 0
0 0 0	0 0	0 0	-12 0 0	0 0	0 0	12 0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	1 0 0	0 0	0 0	-1 116 102	0 0	0 0
-1 0 0	0 0	0 0	-10 0 0	0 0	0 0	13 0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	4 32 29	0 0	0 0	1 36 35	0 0	0 0
1 34 30	0 0	0 0	-9 56 56	0 0	0 0	14 30 30	0 0	0 0	7 38 37	0 0	-13 0 0	0 0	0 0	0 0	6 0 0	0 0	0 0	2 0 0	0 0	0 0
3 0 0	0 0	0 0	-7 0 0	0 0	0 0	H 10 K=7	H 10 K=7	H 10 K=7	8 0 0	0 0	-13 0 0	0 0	0 0	0 0	0 0	0 0	0 0	2 0 0	0 0	0 0
5 0 0	0 0	0 0	-6 37 31	0 0	0 0	-11 43 43	0 0	0 0	-11 29 31	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	5 40 41	0 0	0 0
H 10 K=0	H 10 K=0	H 10 K=0	-5 52 52	0 0	0 0	13 46 44	0 0	0 0	-10 0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	7 76 80	0 0	0 0
-18 33 33	0 0	0 0	-3 13 109	0 0	0 0	13 0 0	0 0	0 0	-10 0 0	0 0	0 0	0 0	0 0	0 0	-18 0 0	0 0	0 0	9 71 66	0 0	0 0
-14 0 0	0 0	0 0	-1 95 0	0 0	0 0	-9 0 0	0 0	0 0	-7 0 0	0 0	0 0	0 0	0 0	0 0	-12 0 0	0 0	0 0	10 0 0	0 0	0 0
-12 31 25	0 0	0 0	2 0 0	0 0	0 0	-6 0 0	0 0	0 0	-3 0 0	0 0	0 0	0 0	0 0	0 0	-17 0 0	0 0	0 0	12 0 0	0 0	0 0
-8 0 0	0 0	0 0	3 0 0	0 0	0 0	-5 55 55	0 0	0 0	-18 31 33	0 0	-4 38 40	0 0	0 0	0 0	-8 115 109	0 0	0 0	14 0 0	0 0	0 0
-6 216 194	0 0	0 0	4 0 0	0 0	0 0	-3 0 0	0 0	0 0	0 0 0	0 0	-2 46 43	0 0	0 0	0 0	-6 126 102	0 0	0 0	15 0 0	0 0	0 0
12 29 31	0 0	0 0	5 0 0	0 0	0 0	-2 0 0	0 0	0 0	-15 0 0	0 0	0 0	0 0	0 0	0 0	-17 0 0	0 0	0 0	14 0 0	0 0	0 0
-2 0 0	0 0	0 0	7 63 67	0 0	0 0	1 0 0	0 0	0 0	-3 34 35	0 0	1 0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
0 0 0	0 0	0 0	8 0 0	0 0	0 0	2 0 0	0 0	0 0	-12 41 41	0 0	1 0 0	0 0	0 0	0 0	4 105 98	0 0	0 0	-14 31 32	0 0	0 0
2 110 110	0 0	0 0	9 76 76	0 0	0 0	-2 0 0	0 0	0 0	-11 0 0	0 0	2 33 38	0 0	0 0	0 0	6 32 29	0 0	0 0	-12 47 48	0 0	0 0
4 117 125	0 0	0 0	10 0 0	0 0	0 0	3 46 55	0 0	0 0	-10 35 32	0 0	3 0 0	0 0	0 0	0 0	10 46 46	0 0	0 0	-10 41 44	0 0	0 0
6 103 91	0 0	0 0	11 62 55	0 0	0 0	4 0 0	0 0	0 0	-9 0 0	0 0	5 0 0	0 0	0 0	0 0	12 51 47	0 0	0 0	-9 0 0	0 0	0 0
8 0 0	0 0	0 0	12 5 43	0 0	0 0	5 9 54	0 0	0 0	-8 35 39	0 0	5 0 0	0 0	0 0	0 0	14 0 0	0 0	0 0	-7 0 0	0 0	0 0
10 44 36	0 0	0 0	13 0 0	0 0	0 0	6 0 0	0 0	0 0	-6 40 38	0 0	7 0 0	0 0	0 0	0 0	16 0 0	0 0	0 0	-6 32 33	0 0	0 0
12 0 0	0 0	0 0	14 0 0	0 0	0 0	7 0 0	0 0	0 0	-5 0 0	0 0	8 0 0	0 0	0 0	0 0	0 0	0 0	0 0	-5 0 0	0 0	0 0
14 63 57	0 0	0 0	15 0 0	0 0	0 0	8 0 0	0 0	0 0	-4 0 0	0 0	9 0 0	0 0	0 0	0 0	0 0	0 0	0 0	-4 0 0	0 0	0 0
16 31 37	0 0	0 0	16 0 0	0 0	0 0	10 0 0	0 0	0 0	-3 0 0	0 0	10 0 0	0 0	0 0	0 0	0 0	0 0	0 0	-3 0 0	0 0	0 0
18 0 0	0 0	0 0	17 0 0	0 0	0 0	11 0 0	0 0	0 0	-2 0 0	0 0	11 0 0	0 0	0 0	0 0	0 0	0 0	0 0	-2 0 0	0 0	0 0
H 10 K=1	H 10 K=4	H 10 K=4	13 0 0	0 0	0 0	12 0 0	0 0	0 0	-1 0 0	0 0	12 0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
-18 0 0	0 0	0 0	-17 0 0	0 0	0 0	1 0 0	0 0	0 0	0 0	0 0	13 0 0	0 0	0 0	0 0	-17 0 0	0 0	0 0	-16 0 0	0 0	0 0
-17 32 33	0 0	0 0	-14 0 0	0 0	0 0	2 0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	-16 0 0	0 0	0 0	-2 88 86	0 0	0 0
-16 0 0	0 0	0 0	-12 55 57	0 0	0 0	-12 0 0	0 0	0 0	5 0 0	0 0	-14 0 0	0 0	0 0	0 0	-11 31 29	0 0	0 0	2 42 44	0 0	0 0
-14 0 0	0 0	0 0	-10 31 38	0 0	0 0	-10 0 0	0 0	0 0	-4 0 0	0 0	-13 0 0	0 0	0 0	0 0	-9 72 71	0 0	0 0	3 71 70	0 0	0 0
-13 0 0	0 0	0 0	-10 68 67	0 0	0 0	-9 0 0	0 0	0 0	8 48 49	0 0	-13 0 0	0 0	0 0	0 0	-8 0 0	0 0	0 0	4 0 0	0 0	0 0
-12 0 0	0 0	0 0	-9 31 33	0 0	0 0	-8 0 0	0 0	0 0	-12 0 0	0 0	-12 0 0	0 0	0 0	0 0	-7 103 93	0 0	0 0	5 33 41	0 0	0 0
-10 0 0	0 0	0 0	-8 0 0	0 0	0 0	-7 0 0	0 0	0 0	3 12 33	0 0	-10 0 0	0 0	0 0	0 0	-6 0 0	0 0	0 0	6 0 0	0 0	0 0
-11 41 37	0 0	0 0	-7 0 0	0 0	0 0	-6 0 0	0 0	0 0	11 0 0	0 0	-10 0 0	0 0	0 0	0 0	-5 76 69	0 0	0 0	7 49 49	0 0	0 0
-9 0 0	0 0	0 0	-5 52 52	0 0	0 0	-5 0 0	0 0	0 0	-3 32 29	0 0	-9 0 0	0 0	0 0	0 0	-4 77 61	0 0	0 0	8 61 66	0 0	0 0
-8 70 63	0 0	0 0	-4 0 0	0 0	0 0	-4 0 0	0 0	0 0	14 42 42	0 0	-8 0 0	0 0	0 0	0 0	-3 65 67	0 0	0 0	9 64 64	0 0	0 0
-7 120 119	0 0	0 0	-3 0 0	0 0	0 0	-3 0 0	0 0	0 0	16 37 30	0 0	-7 30 29	0 0	0 0	0 0	-2 0 0	0 0	0 0	11 0 0	0 0	0 0
-6 0 0	0 0	0 0	-2 0 0	0 0	0 0	-2 0 0	0 0	0 0	0 0	0 0	-5 0 0	0 0	0 0	0 0	-1 65 73	0 0	0 0	13 0 0	0 0	0 0
-5 111 101	0 0	0 0	-2 91 87	0 0	0 0	0 0 0	0 0	0 0	-1 0 0	0 0	-4 0 0	0 0	0 0	0 0	-1 0 0	0 0	0 0	15 0 0	0 0	0 0
-4 66 55	0 0	0 0	-1 119 117	0 0	0 0	1 0 0	0 0	0 0	-17 0 0	0 0	-3 0 0	0 0	0 0	0 0	1 85 81	0 0	0 0	0 0	0 0	0 0
-3 0 0	0 0	0 0	-1 55 58	0 0	0 0	2 0 0	0 0	0 0	-16 0 0	0 0	-3 0 0	0 0	0 0	0 0	2 0 0	0 0	0 0	0 0	0 0	0 0
-2 45 45	0 0	0 0	-2 65 66	0 0	0 0	3 0 0	0 0	0 0	-15 0 0	0 0	-4 0 0	0 0	0 0	0 0	3 113 107	0 0	0 0	-15 0 0	0 0	0 0
-1 97 89	0 0	0 0	-3 0 0	0 0	0 0	4 0 0	0 0	0 0	-15 31 33	0 0	-1 36 38	0 0	0 0	0 0	4 0 0	0 0	0 0	-13 0 0	0 0	0 0
0 0 0	0 0	0 0	-4 0 0	0 0	0 0	5 0 0	0 0	0 0	-14 0 0	0 0	-2 0 0	0 0	0 0	0 0	5 88 86	0 0	0 0	-11 0 0	0 0	0 0
2 111 100	0 0	0 0	-5 0 0	0 0	0 0	6 0 0	0 0	0 0	-13 35 37	0 0	3 0 0	0 0	0 0	0 0	6 32 31	0 0	0 0	-10 0 0	0 0	0 0
2 58 60	0 0	0 0	-6 41 42	0 0	0 0	7 0 0	0 0	0 0	-12 0 0	0 0	4 0 0	0 0	0 0	0 0	7 34 36	0 0	0 0	-9 0 0	0 0	0 0
4 0 0	0 0	0 0	-7 113 57	0 0	0 0	8 0 0	0 0	0 0	-11 0 0	0 0	5 0 0	0 0	0 0	0 0	8 0 0	0 0	0 0	-8 0 0	0 0	0 0
4 0 0	0 0	0 0	-8 81 77	0 0	0 0	-9 30 30	0 0	0 0	-10 0 0	0 0	6 0 0	0 0	0 0	0 0	9 38 33	0 0	0 0	-7 0 0	0 0	0 0
5 114 109	0 0	0 0	-9 36 36	0 0	0 0	-8 0 0	0 0	0 0	-9 0 0	0 0	7 0 0	0 0	0 0	0 0	10 0 0	0 0	0 0	-6 0 0	0 0	0 0
6 0 0	0 0	0 0	-10 51 50	0 0	0 0	-7 0 0	0 0	0 0	-8 34 34	0 0	8 0 0	0 0</								

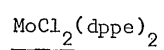
L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC	L	FD	FC
H= 12 K= 6			H= 13 K= 2			H= 13 K= 6			H= 14 K= 2			H= 14 K= 6			H= 15 K= 3			H= 16 K= 0		
4	56	60	-5	0	0	-13	0	0	-15	0	0	-8	52	50	-10	0	0	-12	31	34
5	0	0	-4	0	0	-12	0	0	-14	37	38	-6	37	34	-9	0	0	-10	71	72
6	0	0	-3	0	0	-11	0	0	-12	37	37	-5	0	0	-8	0	0	-8	55	58
7	0	0	-2	0	0	-10	0	0	-11	30	25	-2	0	0	-7	0	0	-6	35	37
8	0	0	-1	0	0	-9	0	0	-10	33	34	-1	0	0	-6	0	0	-4	34	33
9	0	0	0	0	0	-8	0	0	-9	43	42	0	45	48	-5	0	0	-2	51	54
10	0	0	0	0	0	-7	0	0	-7	0	0	2	50	56	-4	0	0	0	110	108
11	0	0	0	0	0	-6	0	0	-6	62	60	3	0	0	-2	0	0	2	102	98
12	36	35	4	0	0	-5	0	0	-5	30	27	4	40	41	0	0	0	4	0	0
H= 12 K= 7			5	0	0	-4	0	0	-4	98	88	5	0	0	2	0	0	6	0	0
-12	0	0	6	0	0	-4	0	0	-4	98	88	5	0	0	2	0	0	6	0	0
-11	0	0	8	35	34	-3	35	35	-2	95	88	6	0	0	3	0	0	8	32	34
-10	0	0	9	0	0	-3	36	33	-2	95	88	6	0	0	4	0	0	10	54	52
-9	0	0	10	29	29	-4	0	0	0	54	55	7	0	0	5	0	0	12	34	37
-8	0	0	11	0	0	1	33	38	1	0	0	-2	0	0	6	0	0	0	0	0
-7	46	44	12	0	0	2	0	0	2	43	48	-1	0	0	7	0	0	-13	0	0
-6	0	0	13	0	0	3	0	0	3	0	0	-2	0	0	8	0	0	-12	0	0
-5	39	39	14	0	0	4	0	0	4	49	54	-1	0	0	9	0	0	-11	42	46
-4	0	0	15	0	0	5	0	0	5	0	0	-8	0	0	10	0	0	-9	56	57
-3	0	0	16	0	0	6	0	0	6	58	64	-7	0	0	11	0	0	-8	0	0
-2	0	0	17	0	0	7	0	0	7	67	67	-6	0	0	12	0	0	-7	45	48
-1	0	0	18	0	0	8	0	0	8	77	77	-5	0	0	13	0	0	-6	0	0
0	0	0	19	0	0	9	0	0	9	88	88	-4	0	0	14	0	0	-5	41	41
H= 13 K= 3			20	0	0	10	0	0	10	0	0	-3	0	0	15	0	0	-4	0	0
1	32	36	21	0	0	11	0	0	11	0	0	-2	0	0	16	0	0	-3	0	0
2	0	0	22	0	0	12	0	0	12	0	0	-1	0	0	17	0	0	-2	0	0
3	46	50	23	0	0	13	0	0	13	0	0	0	0	0	18	0	0	-1	0	0
4	0	0	24	0	0	14	0	0	14	0	0	1	40	39	19	0	0	0	0	0
5	37	36	25	0	0	15	0	0	15	0	0	2	38	37	20	0	0	0	0	0
6	0	0	26	0	0	16	0	0	16	0	0	3	36	35	21	0	0	0	0	0
7	0	0	27	0	0	17	0	0	17	0	0	4	34	33	22	0	0	0	0	0
8	0	0	28	0	0	18	0	0	18	0	0	5	32	31	23	0	0	0	0	0
9	0	0	29	0	0	19	0	0	19	0	0	6	30	29	24	0	0	0	0	0
10	0	0	30	0	0	20	0	0	20	0	0	7	28	27	25	0	0	0	0	0
11	0	0	31	0	0	21	0	0	21	0	0	8	26	25	26	0	0	0	0	0
12	36	35	32	0	0	22	0	0	22	0	0	9	24	23	27	0	0	0	0	0
H= 12 K= 8			33	0	0	23	0	0	23	0	0	10	22	21	28	0	0	0	0	0
-12	0	0	34	0	0	24	0	0	24	0	0	11	20	19	29	0	0	0	0	0
-11	0	0	35	0	0	25	0	0	25	0	0	12	18	17	30	0	0	0	0	0
-10	0	0	36	0	0	26	0	0	26	0	0	13	16	15	31	0	0	0	0	0
-9	0	0	37	0	0	27	0	0	27	0	0	14	14	13	32	0	0	0	0	0
-8	0	0	38	0	0	28	0	0	28	0	0	15	12	11	33	0	0	0	0	0
-7	46	44	39	0	0	29	0	0	29	0	0	16	10	9	34	0	0	0	0	0
-6	0	0	40	0	0	30	0	0	30	0	0	17	8	7	35	0	0	0	0	0
-5	39	39	41	0	0	31	0	0	31	0	0	18	6	5	36	0	0	0	0	0
-4	0	0	42	0	0	32	0	0	32	0	0	19	4	3	37	0	0	0	0	0
-3	0	0	43	0	0	33	0	0	33	0	0	20	2	1	38	0	0	0	0	0
-2	0	0	44	0	0	34	0	0	34	0	0	21	0	0	39	0	0	0	0	0
-1	0	0	45	0	0	35	0	0	35	0	0	22	0	0	40	0	0	0	0	0
0	0	0	46	0	0	36	0	0	36	0	0	23	0	0	41	0	0	0	0	0
H= 13 K= 4			47	0	0	37	0	0	37	0	0	24	0	0	42	0	0	0	0	0
-14	0	0	48	0	0	38	0	0	38	0	0	25	0	0	43	0	0	0	0	0
-13	0	0	49	0	0	39	0	0	39	0	0	26	0	0	44	0	0	0	0	0
-12	0	0	50	0	0	40	0	0	40	0	0	27	0	0	45	0	0	0	0	0
-11	0	0	51	0	0	41	0	0	41	0	0	28	0	0	46	0	0	0	0	0
-10	0	0	52	0	0	42	0	0	42	0	0	29	0	0	47	0	0	0	0	0
-9	0	0	53	0	0	43	0	0	43	0	0	30	0	0	48	0	0	0	0	0
-8	0	0	54	0	0	44	0	0	44	0	0	31	0	0	49	0	0	0	0	0
-7	46	44	55	0	0	45	0	0	45	0	0	32	0	0	50	0	0	0	0	0
-6	0	0	56	0	0	46	0	0	46	0	0	33	0	0	51	0	0	0	0	0
-5	39	39	57	0	0	47	0	0	47	0	0	34	0	0	52	0	0	0	0	0
-4	0	0	58	0	0	48	0	0	48	0	0	35	0	0	53	0	0	0	0	0
-3	0	0	59	0	0	49	0	0	49	0	0	36	0	0	54	0	0	0	0	0
-2	0	0	60	0	0	50	0	0	50	0	0	37	0	0	55	0	0	0	0	0
-1	0	0	61	0	0	51	0	0	51	0	0	38	0	0	56	0	0	0	0	0
0	0	0	62	0	0	52	0	0	52	0	0	39	0	0	57	0	0	0	0	0
H= 12 K= 9			63	0	0	53	0	0	53	0	0	40	0	0	58	0	0	0	0	0
-6	0	0	64	0	0	54	0	0	54	0	0	41	0	0	59	0	0	0	0	0
-5	0	0	65	0	0	55	0	0	55	0	0	42	0	0	60	0	0	0	0	0
-4	0	0	66	0	0	56	0	0	56	0	0	43	0	0	61	0	0	0	0	0
-3	0	0	67	0	0	57	0	0	57	0	0	44	0	0	62	0	0	0	0	0
-2	0	0	68	0	0	58	0	0	58	0	0	45	0	0	63	0	0	0	0	0
-1	0	0	69	0	0	59	0	0	59	0	0	46	0	0	64	0	0	0	0	0
0	0	0	70	0	0	60	0	0	60	0	0	47	0	0	65	0	0	0	0	0
1	29	25	71	0	0	61	0	0	61	0	0	48	0	0	66	0	0	0	0	0
2	0	0	72	0	0	62	0	0	62	0	0	49	0	0	67	0	0	0	0	0
3	0	0	73	0	0	63	0	0	63	0	0	50	0	0	68	0	0	0	0	0
4	0	0	74	0	0	64	0	0	64	0	0	51	0	0	69	0	0	0	0	0
5	0	0	75	0	0	65	0	0	65	0	0	52	0	0	70	0	0	0	0	0
6	0	0	76	0	0	66	0	0	66	0	0	53	0	0	71	0	0	0	0	0
7	0	0	77	0	0	67	0	0	67	0	0	54	0	0	72	0	0	0	0	0
8	0	0	78	0	0	68	0	0	68	0	0	55	0	0	73	0	0	0	0	

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H= 16 K= 5			H= 17 K= 3			H= 18 K= 2			H= 19 K= 4		
-11	0	0 +	5	0	0 +	8	0	0 +	-4	0	0 +
-10	0	0 +	6	0	0 +	9	0	0 +	-3	0	0 +
-9	34	34 +	7	0	0 +				-1	0	0 +
-8	0	0 +	9	0	0 +	H= 18 K= 3			1	0	0 +
-7	33	35 +				-9	0	0 +	3	0	0 +
-6	0	0 +	H= 17 K= 4			-7	51	54 -	4	0	0 +
-5	0	0 +	-11	0	0 +	-5	63	64 -	H= 19 K= 5		
-4	0	0 +	-10	0	0 +	-3	37	39 -	-3	0	0 +
-3	30	28 +	-9	0	0 +	-2	0	0 +	-2	0	0 +
-2	35	31 +	-8	0	0 +	-1	0	0 +	0	0	0 +
-1	42	39 +	-7	0	0 +	1	0	0 +			
0	0	0 +	-5	0	0 +	3	54	52 -	H= 20 K= 0		
1	36	37 +	-4	0	0 +	4	C	0 +	-8	0	0 +
2	31	30 -	-3	0	0 +	5	59	58 -	-6	0	0 +
3	33	35 +	-1	0	0 +	7	0	0 +	-4	44	47 +
4	32	29 -	1	0	0 +	8	C	0 +	-2	63	66 +
5	0	0 +	2	0	0 +	H= 18 K= 4			0	35	42 +
7	0	0 +	3	0	0 +	-9	0	0 +	2	0	0 +
8	0	0 +	4	0	0 +	-8	C	0 +	4	0	0 +
9	0	0 +	5	0	0 +	-7	0	0 +	H= 20 K= 1		
H= 16 K= 6			6	0	0 +	-6	43	46 -	-7	0	0 +
-8	31	33 +	7	0	0 +	-5	0	0 +	-5	0	0 +
-6	0	0 +	H= 17 K= 5			-4	39	42 -	-4	0	0 +
-3	0	0 +	-9	0	0 +	-3	0	0 +	-3	47	50 +
-2	0	0 +	-8	0	0 +	-2	0	0 +	-1	47	52 +
0	49	50 +	-6	0	0 +	0	0	0 +	0	0	0 +
1	0	0 +	-4	0	0 +	1	0	0 +	1	33	35 +
2	39	42 +	-2	0	0 +	2	31	35 -	3	29	30 +
3	0	0 +	C	0	0 +	3	0	0 +	4	0	0 +
4	0	0 +	2	0	0 +	4	44	45 -	5	0	0 +
5	0	0 +	3	0	0 +	6	31	33 -			
H= 16 K= 7			4	0	0 +	H= 18 K= 5			H= 20 K= 2		
-6	0	0 +	5	0	0 +	-7	0	0 +	-6	34	41 +
-5	0	0 +	6	0	0 +	-5	0	0 +	-5	0	0 +
-3	0	0 +	7	0	0 +	-4	0	0 +	-4	0	0 +
-2	0	0 +	H= 17 K= 6			-3	0	0 +	-3	0	0 +
-1	31	29 +	-7	0	0 +	-2	0	0 +	-2	0	0 +
0	0	0 +	-5	0	0 +	-1	34	33 -	-1	0	0 +
1	36	33 +	-3	0	0 +	0	C	0 +	0	34	36 +
3	0	0 +	-1	0	0 +	1	34	34 -	1	0	0 +
H= 17 K= 0			1	0	0 +	2	0	0 +	2	40	41 +
-12	0	0 +	2	0	0 +	3	30	24 -	4	38	41 +
-10	0	0 +	3	0	0 +	4	C	0 +	H= 20 K= 3		
-8	0	0 +	4	0	0 +	5	0	0 +	-5	41	42 +
-6	0	0 +	5	0	0 +	H= 18 K= 6			-3	0	0 +
-4	0	0 +	H= 18 K= 0			-2	39	36 -	-1	0	0 +
4	0	0 +	-12	35	41 -	-1	0	0 +	1	30	34 +
6	0	0 +	-10	44	52 -	0	38	42 -			
8	0	0 +	-8	33	35 -	1	0	0 +	H= 19 K= 0		
10	0	0 +	-6	0	0 +	H= 19 K= 1			-10	0	0 +
H= 17 K= 1			-4	36	37 -	-8	0	0 +	-8	0	0 +
-13	0	0 +	-2	68	68 -	-6	0	0 +	-6	0	0 +
-11	0	0 +	0	72	73 -	-4	0	0 +	-4	0	0 +
-9	0	0 +	2	41	46 -	-2	0	0 +	-2	0	0 +
-7	0	0 +	4	0	0 +	2	0	0 +	2	0	0 +
-5	0	0 +	8	39	40 -	4	C	0 +	4	C	0 +
-2	0	0 +	10	47	47 -	6	C	0 +	6	C	0 +
3	0	0 +	H= 18 K= 1			8	0	0 +			
5	0	0 +	-11	35	42 -	H= 19 K= 2					
7	0	0 +	-10	0	0 +	-9	0	0 +			
8	0	0 +	-9	36	40 -	-7	0	0 +			
11	0	0 +	-8	0	0 +	-5	0	0 +			
H= 17 K= 2			-7	0	0 +	-2	0	0 +			
-12	0	0 +	-5	0	0 +	3	0	0 +			
-11	0	0 +	-4	0	0 +	5	0	0 +			
-10	0	0 +	-3	54	51 -	7	C	0 +			
-9	0	0 +	-2	0	0 +	H= 19 K= 3					
-8	0	0 +	-1	68	68 -	-8	C	0 +			
-7	0	0 +	1	46	52 -	-7	0	0 +			
-6	0	0 +	2	0	0 +	-6	0	0 +			
-5	0	0 +	3	29	31 -	-5	0	0 +			
-4	0	0 +	4	0	0 +	-4	0	0 +			
-3	0	0 +	5	33	31 -	-3	0	0 +			
-2	0	0 +	6	0	0 +	-2	0	0 +			
-1	0	0 +	7	31	36 -	-1	0	0 +			
1	0	0 +	8	0	0 +	3	0	0 +			
3	0	0 +	9	41	40 -	4	0	0 +			
4	0	0 +	H= 18 K= 2			6	0	0 +			
5	0	0 +	-10	0	0 +	7	0	0 +			
6	0	0 +	-9	0	0 +	H= 19 K= 4					
8	0	0 +	-8	37	39 -	-8	C	0 +			
10	0	0 +	-7	0	0 +	-7	0	0 +			
H= 17 K= 3			-6	52	53 -	-6	0	0 +			
-11	0	0 +	-5	0	0 +	-5	0	0 +			
-9	0	0 +	-4	40	45 -	-4	0	0 +			
-8	0	0 +	-3	0	0 +	-2	0	0 +			
-7	0	0 +	-2	45	41 -	0	0	0 +			
-6	0	0 +	-1	0	0 +	2	0	0 +			
-5	0	0 +	0	39	41 -	3	0	0 +			
-4	0	0 +	1	0	0 +	4	0	0 +			
-3	0	0 +	2	37	39 -	5	0	0 +			
-2	0	0 +	3	0	0 +						
0	0	0 +	4	58	56 -						
2	0	0 +	5	0	0 +						
3	0	0 +	6	48	49 -						
4	0	0 +	7	0	0 +						

Table 2.9.5

Analysis of Agreement between Observed and Calculated
Structure Factors at R=6.1%

Range $ F_o $	No.	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta F $	$Av.w \Delta F ^2$	R
0-33	356	11043	11010	804	7.03	0.073
33-44	656	24905	24810	1626	8.71	0.065
44-55	341	16703	16700	965	10.21	0.058
55-66	203	12114	12057	664	14.06	0.055
66-77	119	8479	8460	433	12.28	0.051
77-88	56	4623	4510	248	18.16	0.054
88-99	56	5223	5066	321	31.95	0.062
99-110	38	3989	3954	194	18.64	0.049
110-132	48	5725	5625	383	35.72	0.067
132-154	25	3510	3455	208	27.80	0.059
154-176	15	2450	2369	137	30.43	0.056
176-199	12	2232	2248	129	43.87	0.058
199-331	11	2689	2671	203	74.83	0.086
Sin θ/λ						
0.0-0.1	14	1960	2024	138	50.66	0.071
0.1-0.2	90	8250	7994	660	39.55	0.080
0.2-0.3	236	18386	18396	1104	19.71	0.060
0.3-0.4	430	25389	25000	1415	11.43	0.056
0.4-0.5	592	27676	27637	1574	8.41	0.057
0.5-0.6	455	17860	17723	1104	8.23	0.062
0.6-0.7	119	4160	4161	319	9.95	0.077



CHAPTER 3.1

Table 3.1.2

Final Positional Parameters (fractional coordinates, $\times 10^4$) with estimated standard deviations, and mean square atomic vibrations (\AA^2 , $\times 10^3$), with estimated standard deviations.

Atom	x	y	z	U
Mo	1351(3)	1779(15)	0509(11)	8(4)
P(1)	0880(8)	1707(48)	-0375(25)	45(13)
P(2)	1448(9)	0718(42)	-0799(32)	29(15)
P(3)	1786(13)	2121(58)	1260(43)	43(23)
P(4)	1211(10)	2669(43)	1651(33)	31(16)
Cl(1)	1373(9)	-0164(40)	1147(28)	32(15)
Cl(2)	1362(10)	3700(40)	-0203(32)	40(17)
C(11)	0902(38)	1842(202)	-1540(120)	59(73)
C(21)	1141(28)	0583(132)	-1208(96)	7(51)
C(31)	1847(52)	2530(241)	2517(174)	79(114)
C(41)	1409(18)	2184(75)	2320(58)	- 9(24)
C(111)	0254(20)	-1345(82)	-0287(64)	
C(112)	0202(17)	-0313(104)	-0737(57)	
C(113)	0404(25)	0579(75)	-0733(57)	
C(114)	0659(20)	0440(82)	-0279(64)	
C(115)	0711(17)	-0593(104)	0171(57)	
C(116)	0509(25)	-1484(75)	0166(57)	
C(121)	0663(25)	3125(112)	-0317(91)	
C(122)	0508(30)	3093(108)	0262(80)	
C(123)	0358(24)	4117(157)	0416(68)	
C(124)	0364(25)	5174(112)	-0008(91)	
C(125)	0519(30)	5205(108)	-0588(80)	
C(126)	0669(24)	4181(157)	-0742(68)	
C(211)	1571(22)	-0821(72)	-0794(60)	
C(212)	1846(19)	-1115(88)	-0802(63)	
C(213)	1933(15)	-2326(103)	-0725(63)	
C(214)	1744(22)	-3246(72)	-0639(60)	
C(215)	1469(19)	-2952(88)	-0631(63)	
C(216)	1382(15)	-1741(103)	-0709(63)	

Table 3.1.2 (contd.)

Atom	x	y	z
C(221)	1879(26)	1936(118)	-2393(51)
C(222)	1705(21)	1256(89)	-2014(75)
C(223)	1704(21)	1460(101)	-1257(75)
C(224)	1876(26)	2344(118)	-0878(51)
C(225)	2050(21)	3024(89)	-1258(75)
C(226)	2051(21)	2820(101)	-2014(75)
C(311)	2362(23)	5406(94)	0732(73)
C(312)	2474(17)	4235(113)	0808(72)
C(313)	2325(24)	3284(81)	1058(73)
C(314)	2063(23)	3503(94)	1234(73)
C(315)	1951(17)	4675(113)	1158(72)
C(316)	2101(24)	5626(81)	0907(73)
C(321)	2017(29)	0922(145)	1205(129)
C(322)	2197(44)	0954(144)	1878(105)
C(323)	2392(33)	0032(214)	2053(73)
C(324)	2406(29)	-0924(145)	1554(129)
C(325)	2225(45)	-0956(144)	0880(105)
C(326)	2031(33)	-0034(214)	0706(73)
C(411)	0844(25)	0979(126)	2139(84)
C(412)	0604(31)	0519(92)	2349(87)
C(413)	0401(22)	1314(138)	2519(85)
C(414)	0439(25)	2572(126)	2479(84)
C(415)	0680(31)	3032(92)	2268(87)
C(416)	0882(22)	2236(138)	2098(85)
C(421)	1205(23)	4418(75)	1863(89)
C(422)	1092(20)	5140(132)	1260(60)
C(423)	1076(20)	6402(123)	1342(68)
C(424)	1173(23)	6942(75)	2028(89)
C(425)	1285(20)	6219(132)	2632(60)
C(426)	1301(20)	4958(123)	2549(68)

TABLE 3.1.3

Group vibrational parameters for ligand phenyl rings
(\AA^2 , $\times 10^3$) with estimated standard deviations.

Ring	U
P1: C(111)-C(116)	47(20)
C(121)-C(126)	66(29)
P2: C(211)-C(216)	59(21)
C(221)-C(226)	40(25)
P3: C(311)-C(316)	59(25)
C(321)-C(326)	112(41)
P4: C(411)-C(416)	118(33)
C(421)-C(426)	44(23)

TRANS- Mo(O)Cl(dppe)₂ · ZnCl₃(acetone) · acetone

CHAPTER 3.2

Table 3.2.2

Final positional parameters (fractional coordinates, $\times 10^5$ for Mo, Zn, P, Cl atoms, $\times 10^4$ for the remainder) with estimated standard deviations, and mean square atomic vibrations ($\text{\AA}^2 \times 10^3$), with estimated standard deviations.

Atom	x	y	z	U
Mo	15821(8)	13720(11)	22094(9)	18(1)
Cl(1)	14927(26)	26926(33)	20534(25)	31(2)
P(1)	17642(26)	12965(39)	11883(28)	27(2)
P(2)	25814(25)	15925(35)	21823(29)	26(2)
P(3)	05703(24)	12631(35)	22062(31)	24(2)
P(4)	13696(26)	16524(35)	32127(26)	21(2)
O(1)	1615(7)	0470(9)	2340(6)	30(5)
C(11)	2360(12)	1816(15)	1076(12)	38(8)
C(21)	2801(8)	1596(12)	1457(9)	17(6)
C(31)	0381(10)	1138(13)	2915(10)	21(7)
C(41)	0639(9)	1773(11)	3285(9)	17(5)
Zn	41315(12)	15365(16)	05878(13)	33(1)
Cl(2)	34378(31)	19278(36)	01090(28)	42(2)
Cl(3)	48332(29)	11579(38)	01272(32)	46(2)
Cl(4)	42864(31)	22008(40)	13331(32)	48(2)
O(2)	3824(8)	0526(11)	0864(8)	56(6)
C(1)	4044(11)	- 0014(16)	1065(12)	45(8)
C(2)	3722(15)	- 0706(20)	1146(15)	74(12)
C(3)	4614(12)	- 0074(17)	1188(13)	51(10)
O(3)	3749(9)	0292(13)	4502(10)	92(7)
C(4)	3817(13)	0942(20)	4470(15)	68(10)
C(5)	3479(13)	1434(18)	4121(12)	71(9)
C(6)	4232(13)	1306(18)	4789(13)	67(9)
C(111)	0632(7)	1448(10)	- 0008(8)	
C(112)	0617(7)	2195(10)	- 0117(7)	
C(113)	0957(8)	2668(7)	0155(8)	
C(114)	1313(7)	2396(10)	0536(8)	
C(115)	1329(7)	1649(10)	0645(7)	
C(116)	0989(8)	1176(7)	0374(8)	
C(121)	2065(8)	- 1067(7)	0594(8)	
C(122)	1649(7)	- 0903(9)	0945(8)	
C(123)	1577(7)	- 0190(11)	1127(7)	
C(124)	1920(8)	0360(7)	0959(8)	
C(125)	2336(7)	0195(9)	0608(8)	
C(126)	2409(7)	- 0518(11)	0426(7)	

Table 3.2.2 (contd.)

Atom	x	y	z
C(211)	2865(7)	0157(13)	2465(9)
C(212)	3026(8)	0883(11)	2442(10)
C(213)	3550(10)	1065(9)	2547(10)
C(214)	3913(7)	0520(13)	2676(9)
C(215)	3752(8)	- 0206(11)	2699(10)
C(216)	3228(10)	- 0388(9)	2594(10)
C(221)	2828(7)	2452(8)	2463(8)
C(222)	2848(8)	2527(9)	3028(8)
C(223)	3006(8)	3185(11)	3259(6)
C(224)	3145(7)	3770(8)	2925(8)
C(225)	3126(8)	3695(9)	2360(8)
C(226)	2967(8)	3036(11)	2129(6)
C(311)	0044(8)	- 0894(9)	1388(8)
C(312)	- 0101(8)	- 0227(12)	1160(7)
C(313)	0042(8)	0423(9)	1416(9)
C(314)	0331(8)	0406(9)	1899(8)
C(315)	0476(8)	- 0261(12)	2126(7)
C(316)	0333(8)	- 0911(9)	1871(9)
C(321)	0256(7)	2280(11)	1426(8)
C(322)	0149(8)	1991(10)	1939(8)
C(323)	- 0290(8)	2231(11)	2231(6)
C(324)	- 0622(7)	2759(11)	2009(8)
C(325)	- 0515(8)	3048(10)	1496(8)
C(326)	- 0076(8)	2809(11)	1205(6)
C(411)	1600(8)	2429(9)	3630(8)
C(412)	1400(7)	3123(11)	3527(7)
C(413)	1541(8)	3706(8)	3862(8)
C(414)	1883(8)	3595(9)	4299(8)
C(415)	2084(7)	2901(11)	4401(7)
C(416)	1943(8)	2318(8)	4067(8)
C(421)	1520(10)	0861(10)	3647(9)
C(422)	2031(9)	0585(13)	3609(9)
C(423)	2182(7)	- 0006(13)	3931(10)
C(424)	1823(10)	- 0320(10)	4291(9)
C(425)	1312(9)	- 0044(13)	4329(9)
C(426)	1161(7)	0547(13)	4008(10)

TABLE 3.2.3

Group Vibrational Parameters for Ligand Phenyl Groups
(\AA^3 , $\times 10^3$), with estimated standard deviations.

Ring	U
P1: C(111)-C(116) C(121)-C(126)	46(3) 44(4)
P2: C(211)-C(216) C(221)-C(226)	58(5) 40(4)
P3: C(311)-C(316) C(321)-C(326)	51(4) 44(4)
P4: C(411)-C(416) C(421)-C(426)	44(4) 56(5)

L PO PC				L PO PC				L PO PC				L PO PC				L PO PC			
H=0 K=12				H=0 K=11				H=0 K=10				H=0 K=9				H=0 K=8			
1	157	165	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
2	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
3	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
4	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
5	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
6	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
7	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
8	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
9	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
10	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
11	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
12	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
13	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
14	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
15	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
16	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
17	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
18	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
19	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
20	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
21	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
22	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
23	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
24	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
25	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
26	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
27	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
28	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
29	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
30	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
31	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
32	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
33	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
34	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
35	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
36	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
37	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
38	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
39	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
40	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
41	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
42	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
43	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
44	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
45	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
46	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
47	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
48	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
49	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
50	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
51	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
52	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
53	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
54	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
55	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
56	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
57	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
58	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
59	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
60	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
61	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
62	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
63	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
64	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
65	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
66	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
67	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
68	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
69	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
70	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
71	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
72	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
73	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
74	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
75	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
76	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
77	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
78	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
79	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
80	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
81	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
82	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
83	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
84	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
85	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
86	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
87	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
88	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
89	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
90	121	117	0	17	0	0	0	5	212	264	0	17	0	0	0	10	0	0	0
91	121</																		

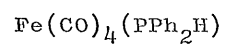
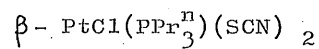
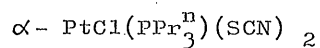
Table 3.2.5

Analysis of Agreement between Observed and Calculated
Structure Factors at R=6.6%

Range $ F_o $	No	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta F $	Av.w $ \Delta F ^2$	R
0-66	1	60	59	1	1.70	0.022
66-98	164	15005	14988	1609	149.26	0.107
98-131	612	70530	69240	5793	139.92	0.082
131-164	439	64102	63056	4382	156.81	0.068
164-197	233	41760	40892	2385	167.30	0.057
197-230	133	28263	27838	1686	256.89	0.060
230-262	72	17597	17253	869	228.28	0.049
262-295	45	12507	12363	586	240.70	0.047
295-328	33	10286	10064	449	280.52	0.044
328-394	39	13792	13584	577	373.64	0.042
394-722	27	12308	12585	472	467.20	0.036
Sin θ/λ						
0.00-0.10	37	8833	8673	470	642.60	0.053
0.10-0.20	210	43599	41696	2940	312.65	0.067
0.20-0.30	477	82804	82225	5101	183.62	0.062
0.30-0.40	487	74046	72902	4786	152.42	0.065
0.40-0.50	435	60878	59559	4329	151.06	0.071
0.50-0.60	153	17634	17714	1320	112.51	0.075

APPENDIX IIIFURTHER STRUCTURES STUDIED

The structures of the following complexes were also solved during the period covered by my Studentship:



For these three compounds, the preliminary work was done by Miss M C Barrett, and the diffractometer data was collected by Dr J A J Jarvis.

APPENDIX IV
PUBLICATIONS

1. The structure of a hydridonaphthyl-ruthenium (II) complex:
S.D. Ibekwe, B.T. Kilbourn, U.A. Raeburn, and D.R. Russell; Chem. Comm., 1969, 433.
2. Hydrido complexes of osmium (II):
trans-OsH₂(Ph₂P-CH₂-PPh₂)₂ and the Os-H bond in trans-OsHCl(Ph₂P-CH₂-PPh₂)₂C₆H₆:
S.D. Ibekwe and U.A. Raeburn; J. Organometal. Chem., 19 (1969), 447.
3. Structures of hydrides formed by addition of an organic molecule to a transition-metal complex, Part I. The crystal and molecular structure of bis (1,2-bis(dimethylphosphino)ethane)naphthyl-hydrido-ruthenium (II) and its osmium analogue:
S.D. Ibekwe, B.T. Kilbourn, U.A. Raeburn, and D.R. Russell; J. Chem. Soc. (A), Paper O/573 in press.
4. Oxochlorobis-(1,2-bis(diphenylphosphino)ethane)-molybdenum (IV) Trichloro(acetone)zincate:
(MoOCl(Ph₂P(CH₂)₂PPh₂)₂)⁺(ZnCl₃.OC(CH₃)₂)⁻:
V.C. Adam, U.A. Gregory, and B.T. Kilbourn; J. Chem. Soc. (D), 1970, 1400.
5. Crystal and molecular structure of diphenyl-phosphinetetracarbonyl iron:
B.T. Kilbourn, U.A. Raeburn, and D.T. Thompson; J. Chem. Soc. (A), 1969, 1906.
6. The molecular structure of dinuclear complexes of platinum (II), Part II, α - and β - forms of dichloro- μ -dithiocyanatobis tri-n-propylphosphine diplatinum (II):
U.A. Gregory, J.A.J. Jarvis, B.T. Kilbourn and P.G. Owston; J. Chem. Soc. (A), 1970, 2770.

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