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ITS DIOXYGEN DERIVATIVES

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THE CRYSTAL STRUCTURE DETERMINATIONS OF WILKINSON'S CATALYST AND ITS DIOXYGEN DERIVATIVES

by

PETER BLAIR DONALDSON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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EDMONTON, ALBERTA

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled ..The Crystal........ Structure Determinations of Wilkinson's Catalyst and its Dioxygen Derivatives .... submitted by ..Peter Blair Donaldson........................ in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Abstract

A brief chemical introduction is given which includes short discussions of the principles of oxidative addition, the history of the solution studies performed on *tris*-triphenylphosphinechlororhodium(I) - known as Wilkinson's catalyst, and types of dioxygen coordination.

The dioxygen derivatives of the above complex and its iodo analogue were synthesized. The crystal and molecular structures of the red and orange modifications of the catalyst and its *bis* and *tris*-triphenylphosphine dioxygen derivatives were determined.

The *bis*-phosphine dioxygen complex crystallizes in the space group $P\bar{1}$ (a, 13.889(7); b, 13.678(6); c, 11.433(5) Å; α, 105.73(4); β, 115.74(3); γ, 100.97(4)°) with 1 molecule per unit cell (ρ_{obs}, 1.470; ρ_{calc}, 1.469 g-cm^{-3}). The model converged to a final R factor of 0.044. The complex is a dimeric species with dioxygen molecules bridging the rhodium atoms in a novel manner.

The *tris*-phosphine complex crystallizes in the space group Pbca with 8 molecules per unit cell (ρ_{obs}, 1.411; ρ_{calc}, 1.416 g-cm^{-3}). The axial parameters are: a, 24.817(4); b, 18.359(2); c, 23.200(4) Å. The refinement converged at R = 0.049. The molecule contains a π-bonded dioxygen ligand with additional hydrogen bonding being evident. A discussion of the dioxygen bonding in

both derivatives is included.

The orange allotrope of $RhC\ell(P(C_6H_5)_3)_3$ crystallizes in the space group $Pna2_1$ (a, 19.470(3); b, 12.689(2); c, 18.202(3) Å) with 4 molecules per unit cell (ρ_{obs}, 1.363; ρ_{calc}, 1.367 $g\text{-}cm^{-3}$). The refinement converged at a conventional R factor of 0.047. The complex has a square planar central geometry with a small approximately tetrahedral distortion.

The red modification of $RhC\ell(P(C_6H_5)_3)_3$ crystallizes in the space group $Pna2_1$ (a, 32.96(1); b, 12.271(2); c, 11.013 $g\text{-}cm^{-3}$) with 4 molecules per unit cell (ρ_{obs}, 1.382; ρ_{calc}, 1.379 $g\text{-}cm^{-3}$). The refinement converged at $R = 0.042$. The complex has a more distorted central geometry than the orange form. Variations in the rhodium-phosphorus and phosphorus-carbon bond lengths within the same species are discussed and comparisons drawn between the two forms of the catalyst and the two dioxygen derivatives.

Two very brief appendices are included and give explanations of computer programmes used and symbols not defined in the text.

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Chapter I

CHAPTER I

Chemical Introduction

Transition metal complexes are known to be very reactive in promoting chemical reactions and play an important role in the transport of molecular oxygen. One such complex, $RhC\ell(P(C_6H_5)_3)_3$ [1,2], acts as a homogeneous catalyst in a number of chemical reactions [3] and binds molecular oxygen. It was extensively studied when the research described in this thesis was initiated. The following points are important when considering homogeneous catalysis by this complex: (1) the general principles of oxidative addition, (2) the history of the solution studies of $RhC\ell(P(C_6H_5)_3)_3$ and (3) the types of dioxygen coordination in transition metal complexes. These topics will be briefly presented in this chemical introduction.

A number of publications have appeared dealing with transition metal complexes that react in a catalytic manner and these have been classified as proceeding by mechanisms such as oxidative addition [4,5,6], insertion [7], ligand exchange [8] and reactions with Lewis acids or bases [9]. Attempts have also been made to outline the fundamentals of catalysis more generally [10,11], however no scheme has been presented, except perhaps the 16 and

18 electron rule [12], which relates the different reaction types or permits mechanistic predictions.

Principles of Oxidative Addition

The term oxidative addition has been used to describe a large variety of reactions in which an increase in the oxidation number of the metal is accompanied an increase in the metal coordination number. The oxidation number is designated following the accepted convention of assigning to the ligands in the complex the shared electron pairs which constitute the metal-ligand σ-bonds. A typical reaction of this type is the hydrogenation of Vaska's compound [13,14] depicted in equation 1.

$$Ir^{(I)}(CO)C\ell(P(C_6H_5)_3)_2 + H_2 \rightarrow Ir^{(III)}(CO)C\ell(P(C_6H_5)_3)_2H_2 \quad (1)$$

The occurrence of oxidative addition reactions shows an inverse dependence of the preferred coordination number with the d-electron population of the transition metal. This trend illustrates the constraints of the 18 electron (or noble gas) rule where stable configurations of complexes are restricted to those in which the total number of valence electrons (comprising the transition metal d electrons and the σ-bonding electron pairs donated by the ligands) does not exceed 18. Other stable configurations usually having 16 electrons are known as coordinatively unsaturated complexes. These unsaturated complexes undergo a large number of catalytic reactions and coordinative unsaturation is a prerequisite for catalysis and usually a prerequisite for a complex to be able to react by an oxidative addition mechanism. The closed shell configurations corresponding to 18 valence electrons tend to be particularly stable and widespread.

Oxidative addition of Vaska's compound could be represented as[12]

$$ML_4 + L_2 \underset{+2e}{\overset{-2e}{\rightleftarrows}} ML_6 \qquad (2)$$

d^8 (16 electrons) d^6 (18 electrons)

however Vaska *et al.*,[15,16] have shown such a classification proceeding by a two electron step, to be unrealistic. They found that the concept of integral oxidation states for the metal did not agree with the gradual variation in the carbonyl stretching frequencies as ligands of varying electron accepting abilities (acidities) were coordinated. These frequencies varied from 1967 cm^{-1} in the parent d^8 complex, with an oxidation number of 1.0 to a final value of 2075 cm^{-1} for chlorine addition, iridium oxidation state 3.0. The carbonyl stretching frequencies were used to assign relative oxidation states to the metal. It was found that the addition of ligands was easily reversible to a relative oxidation state of 2.24, stable but still reversible from 2.46 to 2.85 and stable irreversible from 2.85 to 3.0. The complex $RhCl(P(C_6H_5)_3)_3$ has no such convenient spectroscopic feature and structural studies are required to furnish similar information.

Oxidative addition reactions of these complexes should not be considered as integral donations of electrons from the metal to the incoming ligand, the coordination number being increased simultaneously, but rather as a gradual sharing of charge depending upon the electronegativity of the new ligand. Ligands accepting only small amounts of charge would not be expected to coordinate strongly or, if diatomic molecules, they would not be particularly perturbed by such donation. Conversely ligands such as Cl_2 accepting large amounts of charge from the metal would be highly perturbed by this charge addition, strongly bound and the original diatomic structure destroyed. Other evidence to support this includes the structural data on dioxygen derivatives of Vaska's compound [17,18,19] and its analogues [20], where it was found that the greater the perturbation of the dioxygen molecule (as indicated by the increase in the oxygen-oxygen distance), the more irreversible was the oxygenation. $(O_2)Ir(CO)C\ell(P(C_6H_5)_3)_2$ has an oxygen-oxygen distance of 1.30(3) Å compared to 1.51(3) Å in the iodo analogue. The first complex can be deoxygenated, whereas the second cannot. This trend was also reflected in the structure of the complex $(O_2)Ir((C_6H_5)_2-PCH_2CH_2P(C_6H_5)_2)_2$ where the oxygen-oxygen distance was 1.63(2) Å and again the oxygenation was irreversible. Vaska and a number of other authors have studied the reactions of related iridium and other d^8 complexes with gaseous molecules. The various influences upon reactivity have been separated and studied as follows.

Vaska et al.,[21] studied the role of the metal by substituting cobalt and rhodium for iridium in the complex $Ir(2{=}phos)_2X$, where 2=phos : cis-$(C_6H_5)_2PCH{=}CHP-(C_6H_5)_2$ and X : $C\ell^-$, I^-, BF_4^-, $B(C_6H_5)_4^-$. Although a number of studies [15,22-24] have been carried out, comparisons had only been made between second and third row transition metal complexes where the usual reactivity order was third row > second row and by assumption also > first row. Vaska et al., found a reactivity order of Co > Ir > Rh. They also noticed that the enthalpies of activation were proportional to the electronic excitation energy of the three complexes and possibly [25,26] to their ligand field stabilization energies. The initial structure of the complex was also found to be important as $CoC\ell(P(C_6H_5)_3)_3$, reportedly tetrahedral [27], was relatively inactive to hydrogenation and oxygenation, whereas the more planar rhodium analogue [138] is reported to be reactive [3]. Ibers *et al.*,[20,28] and Amma[illegible] *al.*,[29] concluded from structural data on similar complexes that the overlap between the ligand and substrate orbitals was less in rhodium than iridium complexes, owing to the higher energies of the rhodium d orbitals.

Vaska, Chen and Senoff [14] examined the role of the halide and found that the reaction rate was proportional to the basicity of the complex in the series $(O_2)IrA(CO)(P(C_6H_5)_3)_2$; A:F, NCO, $OC\ell O_3$, $C\ell$, I etc. In addition the free energy of activation increased with increasing energy of the electronic transition in four halo complexes. The calculated enthalpy changes for oxygenation were also similar to that for oxymyoglobin [30].

Vaska and Chen [31] compared the rates of oxygenation of $IrC\ell(CO)(PR_3)_2$ and found that the rate of formation and stability was directly proportional to the basicity of the phosphine ligand. Steric complications [32] were also apparent as *ortho* substituted groups did not undergo oxygenation whilst *meta* and *para* substituted analogues did. Other bulky ligands also appeared to inhibit the reaction. These effects have been illustrated structurally as the more basic complex $(O_2)Ir(CO)C\ell((C_6H_5)_2(C_2H_5)P)_2$ [33] had a longer oxygen-oxygen bond length (1.46(2) Å) than its less basic analogue $(O_2)Ir(CO)C\ell(P(C_6H_5)_3)_2$, (1.30(3) Å).

Vaska *et al.*, [15,16] and others [34-36] studied the effect caused by changing the incoming covalent molecule and found that the chlorine-iridium-carbon angle varied considerably. They proposed that in keeping with the concept of non-integral metal oxidation states, the geometries could be interpreted as involving fractional coordination numbers of the metal as some structures were clearly intermediate between regular structural types. When the 'acidity' of the incoming molecule was varied, it was found that the greater the acidity, the less reversible and more rapid was the resulting reaction.

Perhaps a better method of comparing these complexes is as a series of compounds either having 16 or 18 electrons depending upon whether the complex is coordinatively unsaturated or saturated. These electrons should not be designated as being specifically associated with either the metal or ligand orbitals but rather as being located in a series of metal-ligand orbitals, the nature of which depend upon the basicity of the initial metal complex and the acidity of the incoming ligand.

Solution Studies of $RhC\ell(P(C_6H_5)_3)_3$

The initial publications of Wilkinson *et al.*,[3] and Bennett and Longstaff [1] suggested that $RhC\ell(P(C_6H_5)_3)_3$ underwent an initial dissociation step with loss of triphenylphosphine upon dissolution. The research mentioned in this thesis was initiated when this was still the accepted viewpoint. If such dissociation did take place then the solution species would either have solvent coordinated to the metal or be coordinatively unsaturated with a minimum of 14 electrons in degassed solutions. In recent years a large amount of research has been directed towards the understanding of the nature of the solution species as it was thought to be highly relevant to the action of $RhC\ell(P(C_6H_5)_3)_3$ as a homogeneous solution catalyst. In addition if such solution behaviour was correct then there appeared to be inconsistencies between the ostensibly similar compound $Ir(CO)C\ell(P(C_6H_5)_3)_2$ and $RhC\ell(P(C_6H_5)_3)_3$ and the rhodium complex would not react by an analogous oxidative addition mechanism.

Eaton and Stuart [37] studied the ^{31}P NMR of $RhC\ell(P(C_6H_5)_3)_3$ in $CDC\ell_3$ and found no peaks of significance associated with free triphenylphosphine. They did however find some evidence of triphenylphosphine oxide and when the concentration of the complex was lowered to 10^{-3} M, some small peaks possibly representing free triphenylphosphine were observed. They concluded that the degree of triphenylphosphine dissociation was less than 5% in solutions with concentrations in excess of 10^{-2} M. In addition there was no evidence of halide dissociation. The coordinated triphenylphosphine *cis-trans* splitting was then studied and the activation energy for *cis-trans* isomerisation found to be ~6 kcal-mole^{-1}. The rate of this isomerisation was greater than the rate of ligand exchange. A simple dissociative mechanism was thus eliminated as the mechanism of isomerisation. They then concluded that although the intermediate could have been a tetrahedral isomer this was not confirmed and the intermolecular mechanism probably involved a structure similar to an ion pair intermediate with one of the triphenylphosphine ligands less strongly bound than the other two. Their study directly contradicted the simple dissociative mechanism predicted by Wilkinson *et al.*, in solutions of concentration greater than 10^{-2} M. These earlier conclusions were based upon osmometric studies so Eaton and Stuart repeated this work and confirmed that the molecular weight of the solution species was approximately 600, thus indicating a *bis*-phosphine complex. The inconsistency between the NMR and osmometric findings thus remained.

Augustine and Van Peppen [38] found that the dissociation of $RhC\ell(P(C_6H_5)_3)_3$ occurred readily in benzene but was completely inhibited by even small amounts of ethanol: their results again being based upon osmometric studies. They also noticed that the amount of oxygen reacting with the complex was quite solvent dependent and postulated the rather unusual species $[(O_2)RhC\ell(P(C_6H_5)_3)_2]_2O$ as a product. However the analytical results leading to this formulation are far from convincing. The isomerisation of olefins by $RhC\ell(P(C_6H_5)_3)_3$ was also found [39] to be most dependent upon the presence of oxygen and the solvent used.

Lehman, Shriver and Wharf [40] suggested that although the solutions used in the osmometric studies had all been stated to be degassed, some oxygen may have been present, causing a lowering of the apparent molecular weight. They rigorously excluded air from their experiments and initially added BF_3 to the solution. If free triphenylphosphine was present they should have obtained the complex $(C_6H_5)_3PBF_3$, however no such species was formed. Freezing point studies were then undertaken with the solvents being first distilled under nitrogen, degassed at high vacuum and transferred in a high vacuum line [41,42]. On four determinations in benzene ranging from 2.39×10^{-3} to 5.85×10^{-3} M, they obtained a molecular weight of

950 ± 40 *cf*. 925 for the parent complex. Using dichloroethane the value was ~920 for a 3.22 x 10^{-2} M solution. A trace of oxygen was then admitted and the apparent molecular weight in both solutions dropped to *ca*. 600 (in agreement with the previous osmometric results). It thus appeared that these earlier results were incorrect and that the presence of oxygen was causing the lowering of the apparent molecular weight. This was supported by the appearance of triphenylphosphine oxide peaks in the ^{31}P NMR studies of Eaton and Stuart as this complex has been shown[43] to be a product from the reaction of similar homogeneous catalysts with oxygen. The ^{31}P NMR results were confirmed at similar concentrations by Shriver et al.

Arai and Halpern[44] then determined the equilibrium constant for dissociation spectrophotometrically in benzene (1.4(± .4) x 10^{-4} M at 25°C) and again supported the amended conclusions that in more concentrated solution (in excess of 10^{-2} M), dissociation was not extensive.

The nature of $RhC\ell(P(C_6H_5)_3)_3$ in benzene and chlorinated hydrocarbons under inert atmospheres thus appeared to be settled. As the hydrogenation reactions involving this complex included an initial interaction with hydrogen it was necessary to find out whether this reaction proceeded by a normal oxidative addition mechanism or involved, as was apparently the case in the oxygenation reaction, expulsion of a triphenylphosphine upon coordination of the gaseous molecule.

Meakin, Jesson and Tolman [45] undertook a UV spectrophotometric study of $RhC\ell(P(C_6H_5)_3)_3$ with hydrogen in methylene chloride and observed that as the concentration of hydrogen was increased only one isosbestic point was obtained (360 mμ). This indicated the presence of only two chromophoric species in solution. From their additional ^{31}P and ^{1}H NMR studies they concluded that these species must correspond to the equilibrium:

$$H_2 + RhC\ell(P(C_6H_5)_3)_3 \rightleftarrows H_2RhC\ell(P(C_6H_5)_3)_3 \qquad (3)$$

This reaction could then be considered as proceeding by an oxidative addition mechanism. Tolman [12] has proposed a complete mechanism for the hydrogenation of a terminal olefin by $RhC\ell(P(C_6H_5)_3)_3$ with two paths arising from the possibility of coordinating hydrogen or olefin initially.

Molecular Oxygen Complexes

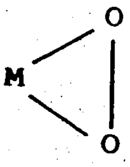
Molecular orbital theory has given an explanation for the biradical nature of the dioxygen molecule in its ground state [46] ($^3\Sigma$). Table 1 shows the molecular orbital configurations for various states of dioxygen. The excited state $^1\Delta O_2$ is diamagnetic and is located at 23.4 Kcal-mole^{-1} [47] above the groundstate. The other diamagnetic

The other diamagnetic state $^1\Sigma$ with opposing spins requires even more energy (37.5 kcal-mole^{-1}). The superoxo ion (O_2^-) and the peroxo ion (O_2^{2-}) should be paramagnetic and diamagnetic respectively.

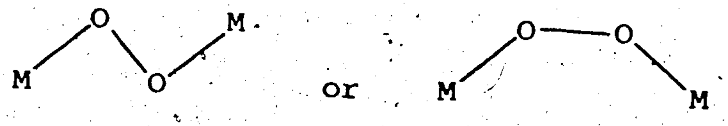
The geometries of the dioxygen molecular orbitals [48,49] are shown in Fig 1 and the oxygen-oxygen distances in O_2 ($^3\Sigma$), O_2^- and O_2^{2-} have been measured and are listed in Table 2. As a result coordinated dioxygen has tended to be classified on its oxygen-oxygen bond length alone and not by consideration of the geometry of the coordination between the metal and the dioxygen molecule. Species such as $(O_2)IrC\ell(CO)(P(C_6H_5)_3)_2$ and $(O_2)IrI(CO)(P(C_6H_5)_3)_2$ with oxygen-oxygen distances of 1.30(3) and 1.51(2) Å respectively, have thus been classified initially as containing either a superoxide or peroxide ion. They should however (as mentioned earlier) be viewed more realistically as involving differing degrees of charge transfer from the ligand to the metal and *vice versa* but not in an integral fashion. Unfortunately these bondlength classifications have been extensively used in the discussion of the bonding within a number of the following dioxygen cobalt complexes (see Table 4).

Compounds undergoing oxygenation have been of interest for some time as oxygen transport in biological systems[50-52] and a number of autoxidation reactions[43-58] are thought to proceed by the formation of an initial oxygenated complex. The first example of a synthetic reversible dioxygen carrying complex was prepared in 1933[59], when it was found that red-brown crystals of *bis*-salicylaldehyde ethylenediimine cobalt(II) darkened on exposure to air. It was five years before this darkening was attributed to the reaction with molecular oxygen[60]. Much research[47,61-63] has been directed into understanding the nature of this complex and other dioxygen species.

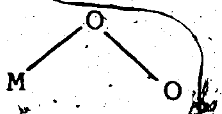
Definitive studies of the structures of dioxygen complexes suggest three major structural categories:



(1)



(11)



(111)

A large number of class (1) complexes have been prepared[47] some of which are represented in Table 3. The bonding in these complexes was first proposed by Griffith[64] and is discussed in later chapters. A number of cobalt complexes with class (11) structures are known, the more important mentioned in Table 4. These complexes have either a planar μ-superoxo dioxygen bridge, the compounds thus being paramagnetic with oxygen-oxygen distances of 1.28 - 1.36 Å; or a non planar μ-peroxo bridge in diamagnetic species with large variations in the torsional angles and oxygen-oxygen distances when compared to H_2O_2. The μ-superoxo complexes can occur in either staggered or eclipsed conformations.

Class (111) complexes are postulated to contain a bent dioxygen-metal bond. This has been observed in the structure of [Co(bzacen)(O_2)]pyridine, bzacen = $((C_6H_5)C(O^-)CHC(CH_3)N(CH_2^-))_2$ [65] where the cobalt-dioxygen angle was 126° and the oxygen-oxygen distance 1.26(4) Å. A number of similar reversible oxygen carrying complexes have been studied [66-69] and along with oxycoboglobin [70] and oxyhemoglobin[71,72] have been postulated to contain similar structures.

A large amount of research has been directed towards understanding the mode of oxygen addition to hemoglobin and the matter still requires resolution. The bonding models of Griffith and Pauling [73] have both been found to represent structures in synthetic analogues. The bent dioxygen-metal bond may be the more favoured current view because of the similarities in the structure of [Co(bzacen)(O_2)] pyridine to that of vitamin B_{12}[74,75] and hemoglobin[76]. The pyridine geometry is analoguous to the histidine imidazole ring close to the metal in the latter two proteins. Studies on a reversible iron(II) complex [77] suggest that the oxygenation of hemoglobin may be heavily influenced by the bulky peptide chains surrounding the active site. These may prevent the formation of a class (11) bridged complex and ensure the bent dioxygen bond.

Other dioxygen structures have been postulated for a variety of synthetic dioxygen complexes [78,79] with little or no structural justification.

The dioxygen complexes mentioned in this thesis may be viewed as belonging either purely to class (1) or as a mixture of class (1) and class (11) structural categories.

Table 1

Configurations of Various Dioxygen States

MOLECULAR ORBITAL	STATE				
	O_2^+	$O_2(^3\Sigma)$	$O_2(^1\Delta)$	O_2^-	O_2^{2-}
$\sigma^* p_y$					
$\pi^* p_x$ $\pi^* p_z$	↑	↑ ↑	↑↓	↑↓↑	↑↓↑↓
πp_x πp_z	↑↓↑↓	↑↓↑↓	↑↓↑↓	↑↓↑↓	↑↓↑↓
σp_y	↑↓	↑↓	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓
σ^*_{1s}	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{1s}	↑↓	↑↓	↑↓	↑↓	↑↓

Fig. 1

Dioxygen Molecular Orbital Geometries

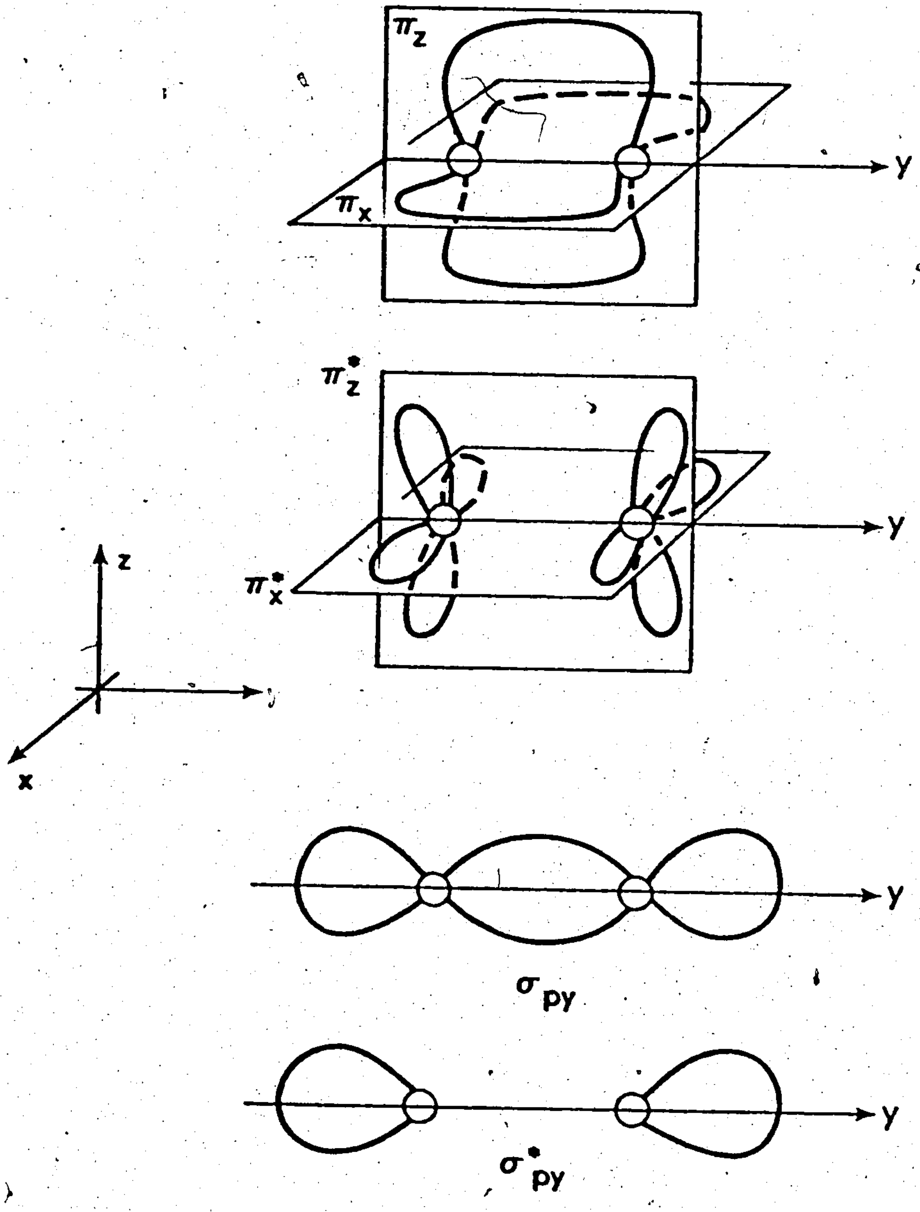


Table 2

A Selection of Simple Oxygen Containing Species

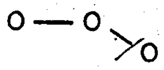
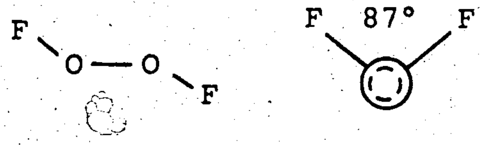
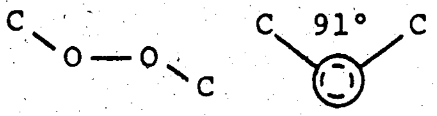
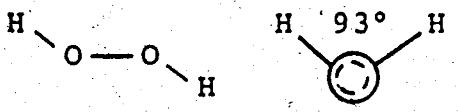
Species	Structure	Oxygen-Oxygen Distance (Å) and Comments	Reference
O_3		1.278(3)	80
O_2F_2		1.217(3) (non planar)	81
O_2^+	linear	1.1227(1)	80
O_2PtF_6	linear	1.17(2)	82
O_2	linear	1.2074(1)	80, 83
KO_2	linear	1.28(2)	80, 84
B-NaO_2	linear	1.33(6)	85, 86
$C_6H_5C(O)(O_2)C(O)C_6H_5$		1.46(2) (non planar)	87
H_2O_2		1.49(1) (non planar)	88
BaO_2	linear	1.49(4)	80, 89

Table 3

A Selection of Class (1) Dioxygen Complexes

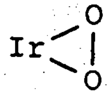
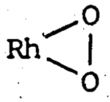
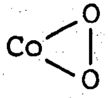
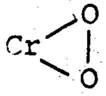
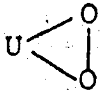
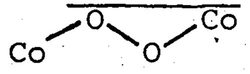
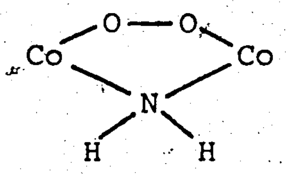
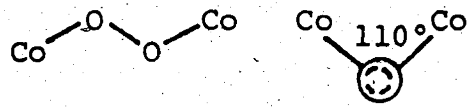
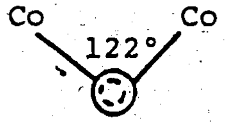
Complex	Structure	Oxygen-Oxygen Distance (Å)	Reference
$(O_2)IrX(CO)\alpha_2$			
$X = C\ell,\ \alpha = P(C_6H_5)_3$		1.30(3)	17
$X = Br,\ \alpha = P(C_6H_5)_3$		1.36(4)	90
$X = I,\ \alpha = P(C_6H_5)_3$		1.47(2), 1.51(2)	18, 10
$X = C\ell,\ \alpha = P(C_6H_5)_2(C_2H_5)$		1.46(2)	33
$[(O_2)Ir(2\text{-phos})_2]^+$		1.66(2)	20, 28
$[(O_2)Rh(2\text{-phos})_2]^+$		1.42(2)	28
$[(O_2)Co(2\text{=phos})_2]^+$		1.42(2)	29
$[(O_2)_4Cr]^{3-}$		1.41(4)	91
$[(O_2)_3UO]^{4-}$		1.51(6)	92

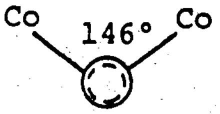
Table 4

A Selection of Class (11) Dioxygen Complexes

Complex	Structure	Oxygen-Oxygen Distance (Å) and comments	Reference
$[(NH_3)_5Co(O_2)Co(NH_3)_5]SO_4(HSO_3)_3$		1.31(3) paramagnetic, planar	93
$[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$	..	1.32(2) paramagnetic, planar	94
$[(Cn)_2Co(O_2)(NH_2)Co(Cn)_2](NO_3)_4$		1.36(3) paramagnetic, nearly planar	95
$[(NH_3)_4Co(O_2)(NH_2)Co(NH_3)_4](NO_3)_4$	..	1.32(1) paramagnetic, nearly planar	96
$[(Co(Safen))_2O_2](dmf)_2$		1.34(1) diamagnetic, non planar	97
$[(H_2O)Co(O_2)N_2F_2C_{16}H_{12}O_2-$ $Co(O_2)N_2F_2C_{16}H_{12}]_2$	.. 	1.31(3) non planar	98

(Table continued)

Table 4 continued

Complex		Structure	Oxygen-Oxygen Distance (Å) and comments	Reference
$[(NH_3)_5Co(O_2)(NH_3)_5](SO_4)_2$	..		1.47(1) diamagnetic, non planar	99
$[(NH_3)_5Co(O_2)Co(NH_3)_5](SCN)_4$	..		1.65(3) diamagnetic, planar	100

CHAPTER II

Synthetic Studies

Experimental

All reactions involving gaseous molecules were performed in sealed vessels. The solutions were degassed by freezing in a liquid nitrogen bath and pumping on the solid material. The gas to be reacted was then introduced and the solution allowed to warm up. This cycle was then repeated several times. Shriver[41] has discussed similar methods for handling air sensitive compounds.

Infrared spectra were obtained using a Perkin Elmer 421 spectrometer with a standard slit width and the ultraviolet studies were carried out with either a Cary 14 M or a Cary 15 recording spectrophotometer. The former machine was used with a Cary 1411 reflectance attachment and a $MgCO_3$ standard block for the diffuse reflectance spectra. In this study only a white light source was used as the UV lamps did not produce high enough outputs to give a spectrum.

Melting points were determined on a Koffler Hot Stage and during the slow heating of the sample, the microcrystalline structure was examined continuously by means of a microscope.

The micro- analyses (unless otherwise stated) were performed in this department by Mrs. D. Mahlow and Mrs. A. Dunn. The gas chromatography results were obtained by Mr. A. Clement of this department with a Sargent recorder and using an 8 ft. Linde molecular sieve at 82°C with a helium flow rate of 60 c.c.-min^{-1}. A Cahn Instruments Inc. Gouy Balance was used by Dr. D. Day who undertook the magnetic measurements. All mass spectroscopic studies were performed in this department with either an A.E.I. MS9 high resolution spectrometer or an A.E.I. MS12 medium resolution instrument. Both machines were operated at 70 ev.

Chemicals were either commercially available or prepared as mentioned below.

Methylene Chloride

Three different brands of this solvent were tried with the reactions proceeding only in the brand with the most stringent specifications (Fisher Scientific Co.). This solvent was initially redistilled but as no effect was observed on the reactions when the Fisher samples were used without further treatment, later studies did not include this precaution.

Rhodium Trichloride

This compound was purchased from the Fisher

Scientific Co. or from A.D. Mackay Ltd., the latter material being recrystallized before use.

Tris-triphenylphosphinechlororhodium (I) $[RhCl(P(C_6H_5)_3)_3]$

This complex was usually prepared by the method described in the literature [1,3] although one batch was obtained from Fluka AG, Switzerland. The crystals of the orange allotrope of this complex were produced by a variation of the usual method. A solution containing 1 g $RhCl_3 \cdot 3H_2O$ in 40 ml ethanol was added very slowly to a solution of 10 g triphenylphosphine in 100 ml ethanol, by diffusion through a filter paper over a number of days at 35°C. Microanalytical analysis (Calcd. C, 70.1; H, 4.9; Cl, 3.8; P, 10.0; Rh, 11.1; Found: C, 70.0; H, 4.9; Cl, 3.8; P, 10.1; Rh, 11.2) were performed by Pascher Microanalytisches Laboratorium, Bonn, Germany. These values were in excellent agreement. The melting point of the compound was 134-136°C.

Crystals of the red form of $RhCl(P(C_6H_5)_3)_3$ prepared for the structural study were obtained in an identical manner except that the triphenylphosphine ethanolic solution was added to the rhodium solution. Microanalytical analyses (Found: C, 70.6; H, 4.9) agreed with the literature values although the chlorine analyses proved unsatisfactory, owing to interference from rhodium or phosphorus. The melting point (138-140°C) agreed with the literature value (138°C). The diffuse reflectance spectra of both forms is given in Fig. 2.

Dioxygen *bis*-triphenylphosphinechlororhodium dimer

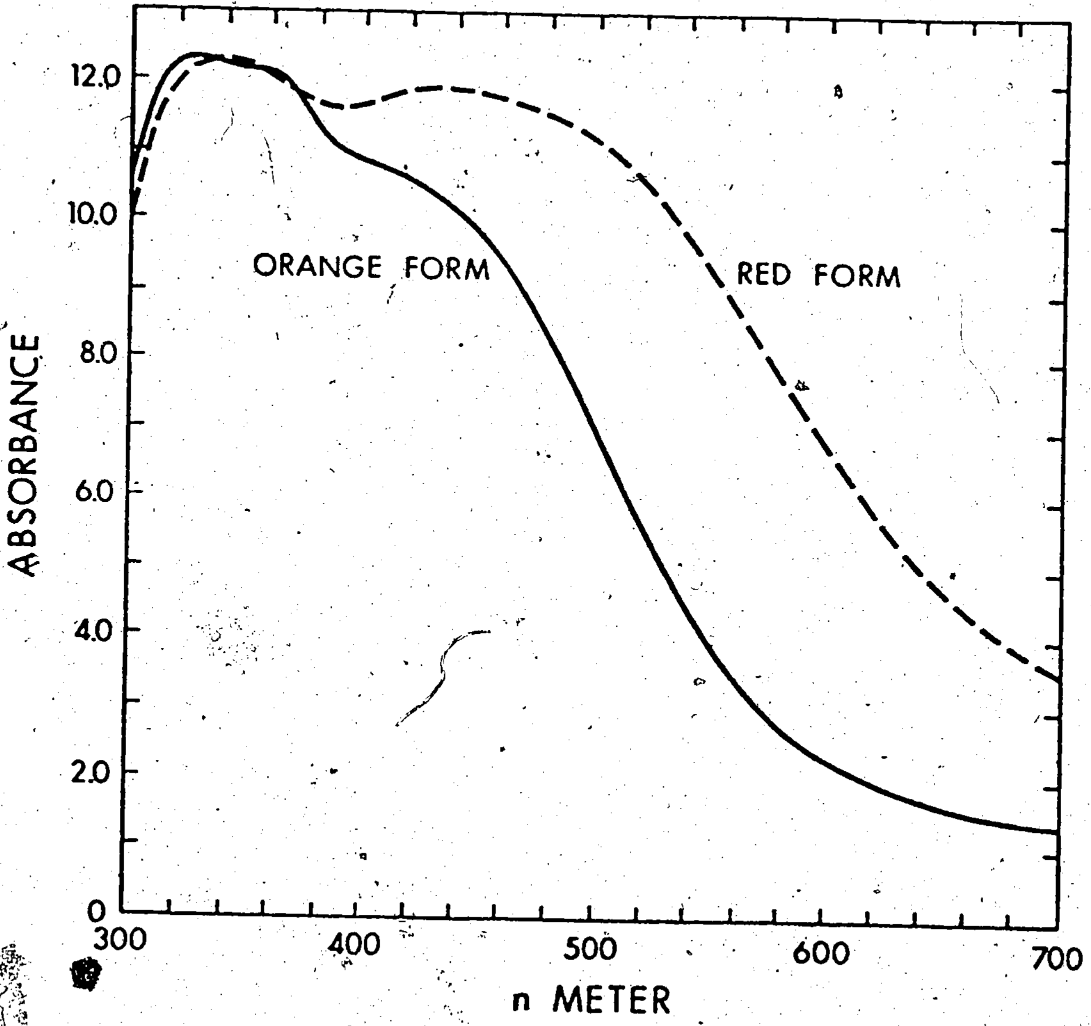
$[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$

When oxygen was bubbled through a solution containing 0.25 g $RhCl(P(C_6H_5)_3)_3$ in 15 ml methylene chloride and the solution slowly evaporated at 7°C for two days a ~50% yield of red-brown diamagnetic crystals was obtained. All measurements were made on this material which appeared to be homogeneous. Carbon and hydrogen analyses (Calcd: C, 57.0; H, 4.1; Found: C, 57.7; H, 4.2) were in reasonable agreement with the formulation but the chlorine analysis again proved difficult (Calcd: 13.6; Found: ~15).

Oxygen was positively identified in the gaseous thermal decomposition products by gas chromatography after heating the complex in vacuo to 20°C. The infrared spectrum of the solid residue showed an absorption (ν, 1120 cm^{-1}) consistent with the formation of complexed triphenylphosphine oxide [43,101]. The dimer undergoes a series of transformations during heating. The first visible transformation (80-85°C) appears to correspond to the complex dissolving in its own solvent of crystallisation. This was followed by loss of solvent (110-120°C)

Fig. 2

Reflectance Spectra of $RhCl(P(C_6H_5)_3)_3$

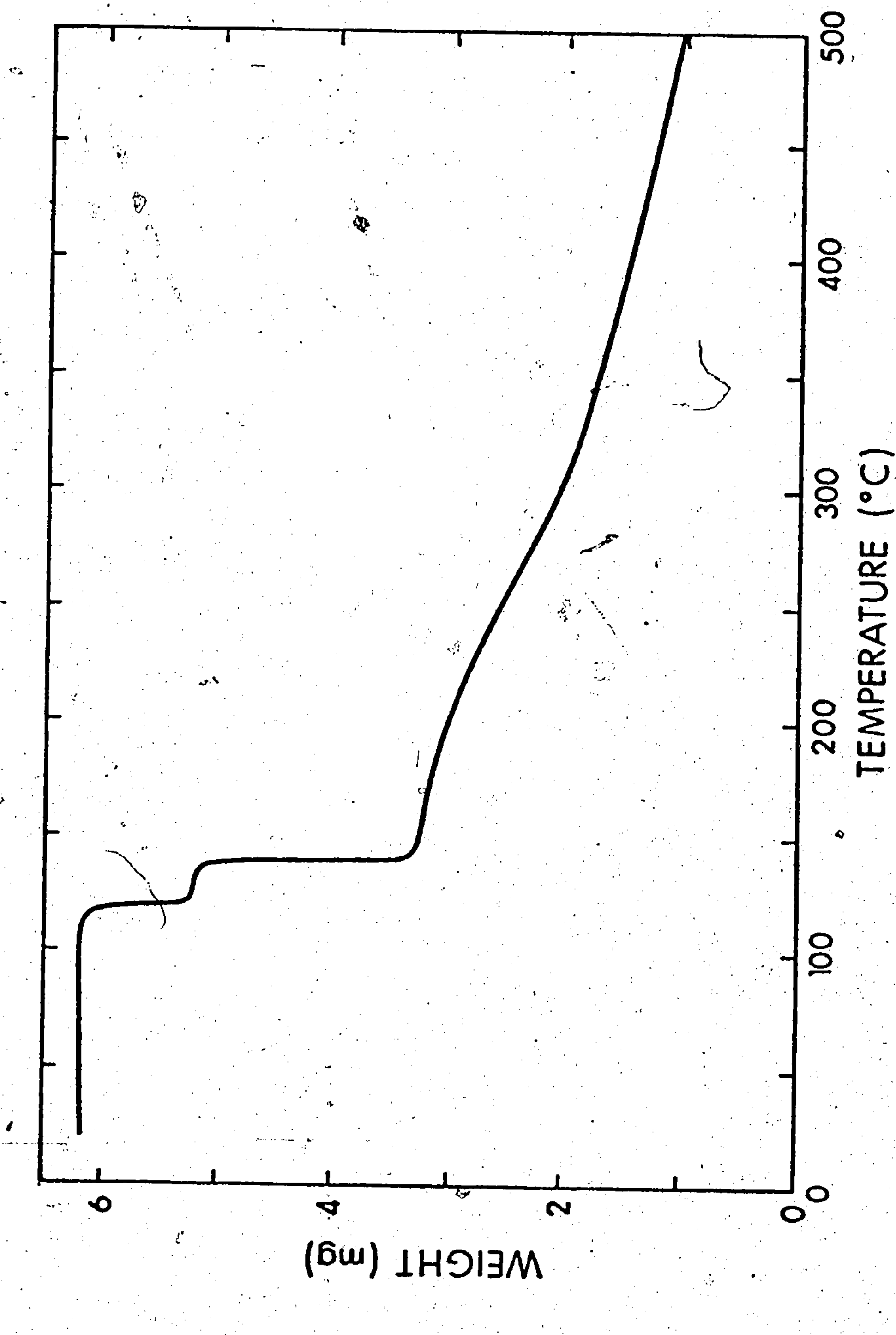


to give a glassy material which when heated to 134°C tends to explode violently. Thermal gravimetric analyses (carried out on a DuPont Thermalgravimetric Analyzer) over two days (Fig. 3) indicated that the complex loses methylene chloride and a triphenylphosphine below 130°C (gradual weight loss occurring above this temperature). At 500°C the mass of the residue corresponded to a mass of 150 per rhodium atom. Infrared and proton NMR spectra (Varian A60) verified the presence of free triphenylphosphine in the sublimate collected on the cool sides of the evacuated reaction tube. Mass spectrometric studies on the dimer (inlet temperature, 120°C) showed no parent peak or any recognisable peaks except triphenylphosphine, triphenylphosphine oxide and their degradation products. Identical behaviour was exhibited by all other compounds tested although a range of inlet temperatures was always tried.

$[(O_2)RhC\ell(P(C_6H_5)_3)_2 \cdot CH_2C\ell_2]_2$ is extremely stable chemically, being inert to either strong acid or base and almost insoluble in all solvents tested. Recrystallisation was thus impossible, however no evidence of impurities was found. The complex does dissolve after prolonged exposure to pyridine and an orange crystalline product is formed. Analysis of this complex proved unsatisfactory. The infrared spectrum of the dimer (nujol

Fig. 3

$[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$ Thermal Weight Loss



mull, Fig. 4) showed the presence of an absorption at 845 cm^{-1} attributable to rhodium-dioxygen coordination [17].

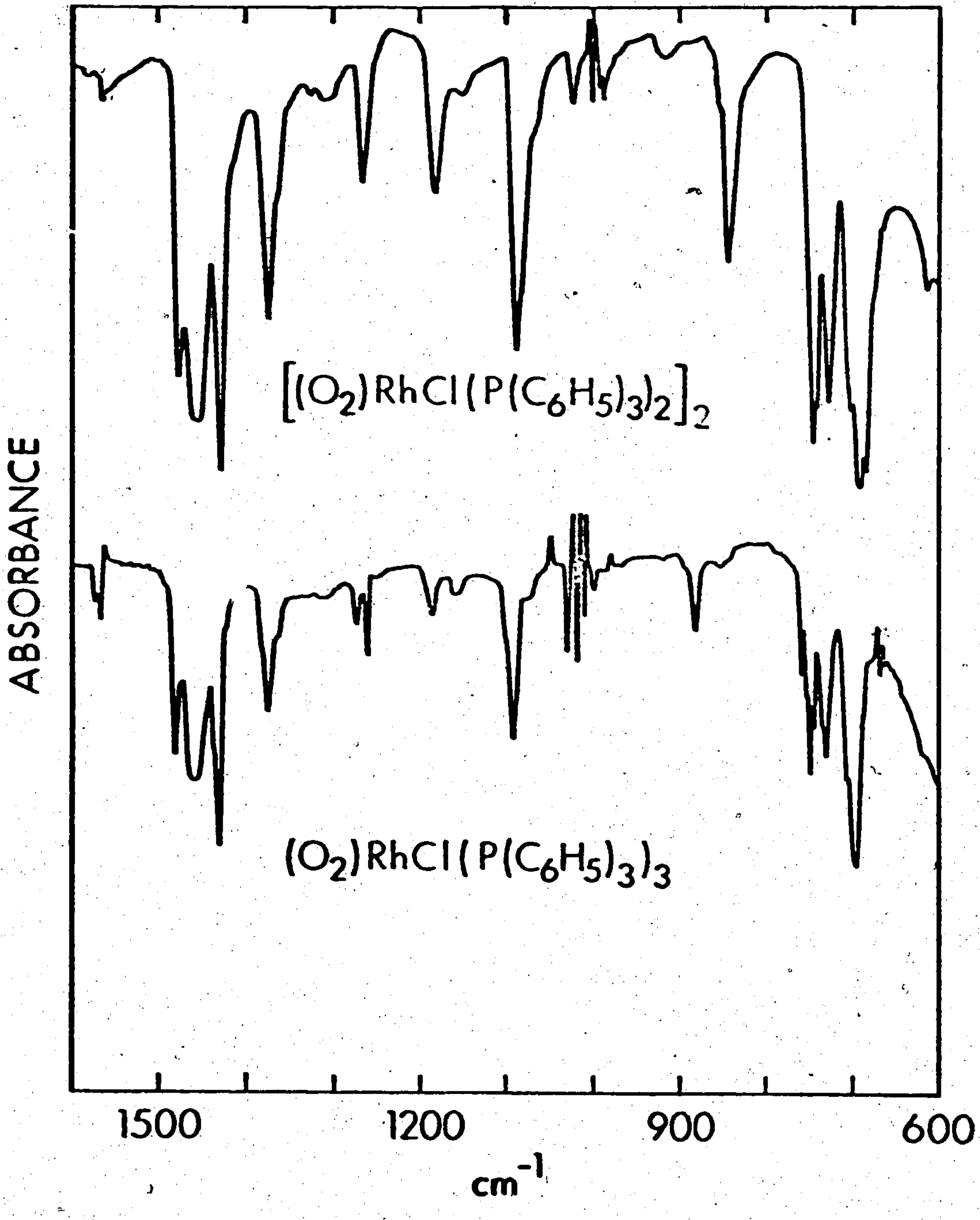
Dioxygen *tris*-triphenylphosphinechloro rhodium
$[(O_2)RhC\ell(P(C_6H_5)_3)_3 \cdot 2CH_2C\ell_2]$

Oxygen was bubbled through a solution, containing 0.5 g $RhC\ell(P(C_6H_5)_3)_3$ in 5 ml methylene chloride, for two minutes. After slow evaporation for 2 days at 7°C, yellow crystals of the complex (always accompanied by the dimer) were filtered off and washed with cyclohexane. The complex may also be produced by adding 0.25 g triphenylphosphine to 0.25 g $RhC\ell(P(C_6H_5)_3)_3$ and repeating the above procedure. Handpicked crystals were used in all subsequent tests.

Microanalytical analyses (Calcd: C, 59.7; H, 4.4; Found: C, 59.3; H, 4.4) were in reasonable agreement with the formulation although the chlorine analysis proved difficult. The compound melted at 82-84°C and decomposed at 126-128°C. The infrared spectrum (nujol mull) (Fig. 4) showed an absorption at 880 cm^{-1} assigned to the coordinated dioxygen. Similar studies on the products after heating to 200°C in vacuo indicated the presence of triphenylphosphine oxide in the solid residue. Oxygen was identified in the gaseous products by gas chromatography. Confirmation of the solid state formulation is contained in Chapter IV. Attempts to

Fig. 4

Infrared Spectra of Dioxygen Derivatives.



identify the *tris*-phosphine dioxygen complex in solution by the appearance of isosbestic points in the UV spectra were unsuccessful.

Tris-triphenylphosphineiodorhodium (I) $[RhI(P(C_6H_5)_3)_3]$

RhI$_3$ (obtained by treating RhCℓ_3 in a water/ethanol solution with excess lithium iodide) was reacted with triphenylphosphine as described in the literature[3]. Microanalytical analyses (Calcd: C, 63.8; H, 4.4; I, 12.5; Found: C, 63.4; H, 4.6; I, 12.5) were in excellent agreement with the formulation and no evidence of chlorine was found. Melting point, 116-118°C, Lit., 118-120°C.

Dioxygen *bis*-triphenylphosphineiodorhodium $[(O_2)RhI(P(C_6H_5)_3)_2]$

When 3.0 g of $RhI(P(C_6H_5)_3)_3$ in 20 ml methylene chloride was reacted with molecular oxygen for 2 minutes and the solution evaporated at 7°C for two days, black crystals were obtained in about 60% yield. Microanalytical analyses (Calcd: C, 54.9; H, 3.8; I, 16.1; Found: C, 54.2; H, 4.0; I, 16.2) were in good agreement with the formulation. Chlorine analysis failed to indicate the presence of methylene chloride although evidence of methylene chloride was found in the infrared spectrum (nujol mull), $\nu = 740\ cm^{-1}$. Strong absorptions at 857 cm^{-1} with shoulders at 850 cm^{-1} and 838 cm^{-1} were assigned to coordinated dioxygen. Examination of fresh crystals under the microscope showed that a rapid breakdown of the crystals was occurring, possibly due to evolution of methylene chloride of crystallisation. This may explain the lack of chlorine in the analysis as this was performed after the infrared spectrum was obtained. The melting point was 166-168°C.

CHAPTER III

The Crystal and Molecular Structures of $[(O_2)RhCl(P(C_6H_5)_3)_2\cdot CH_2Cl_2]_2$

Experimental

Brown crystals of $[(O_2)RhCl(P(C_6H_5)_3)_2\cdot CH_2Cl_2]_2$ were obtained using the procedure outlined in Chapter II. These were examined under a microscope and found to be red-yellow pleochroic crystals, a large number of which were twinned. This twinning took the form of a diagonal missetting of the two crystal halves but was avoided by choosing one of a small number of crystals already cleaved in this direction.

Examination of preliminary Weissenberg and precession photographs indicated that the compound crystallized in the triclinic crystal system. The space group was therefore limited to P1 or P$\bar{1}$, the latter being verified by the successful solution and refinement of the structure.

Lattice parameters were found using the technique of centering the reflection in the diffractometer counter windows by adjusting the χ, ω and 2θ circles and checking at -2θ. Crude photographic lattice parameters were then subjected to a least squares refinement[102] to give the best agreement between the calculated and observed 2θ values. Lattice parameters were: a, 13.889(7); b, 13.678(6); c, 11.433(5) Å, α, 105.73(4); β, 115.74(3);

γ, 100.97(4)°). The density of the compound was measured by flotation in aqueous potassium iodide as 1.470 g-cm^{-3} which is in excellent agreement with the calculated density of 1.469 g-cm^{-3}.

The crystal was mounted on the end of a thin glass fibre so that the c* axis was coincident with the ϕ axis of the diffractometer. Intensity data were collected on a Picker manual 4-circle diffractometer using the coupled $\omega/2\theta$ scan method. Copper Kα X-radiation was employed and the diffractometer settings were calculated with the programme MIXG2 .[103]. Intense peaks were carefully scanned to detect any twinning of the crystal and no evidence (such as splitting) was found. The diffractometer was equipped with a graphite crystal monochromator (002 reflecting plane) and a 2° take off angle was used. Each data point was scanned from $2\theta - 1°$ to $2\theta + 1°$ using a scan speed of 2° per minute. Background counts were estimated from a linear interpolation of 30 second stationary counts taken at the limits of the scan.

Data were only measured to 90° in 2θ as indicated by the preliminary photography. This rapid fall off in intensity was consistent with a relatively low degree of order in the crystals. A total of 2151 reflections were measured and of this number 1658 were found to be statistically reliable using the criterion $I \lesssim 3\sigma$. During the data collection 7 reflections were recollected at intervals of 8 hours and changes in intensity noted. It was found that the crystal did decompose and that the relationship between the decomposition and time was logarithmic with an additional dependance upon the sin θ/λ value of the reflection. After data collection was completed all peaks with a count rate greater than 10^4 counts-sec^{-1} (i.e., more than the linear counting rate of the counter) were recollected at lower voltages and scaled into the data by comparison with other peaks of lower intensity recollected under the same conditions. The Miller indices of the crystal faces were identified as: 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, $00\bar{1}$, $\bar{3}21$ and the dimensions of the crystal measured to allow an absorption correction to be made.

Reflection data were corrected for Lorentz[104] (L) and polarization (P) effects

$$L = 1/\sin 2\theta$$

$$P = (\cos^2 2\theta_{\text{monochromator}} + \cos^2 2\theta)/2$$

and the decomposition correction was applied. The absorption correction of the form

$$I = I_o e^{-\mu t}$$

where I_o = uncorrected intensity

μ = linear absorption coeff. (cm^{-1})

t = thickness (cm)

was made using the programme GONO9 [105] with $\mu = 72.13\ \text{cm}^{-1}$. The transmission factors varied from 0.809 to 0.633. Structure amplitudes ($|F_{rel}|$) and their standard deviations ($\sigma|F_{rel}|$) were then calculated with an uncertainty factor (p) of 0.03 from the equations: [106]

$$|F_{rel}| = \sqrt{I/LP}$$

where $I = [CT - 0.5(t_c/t_b)(B_1 + B_2)]$

now $$d|F_{rel}| = dI/2\sqrt{LPI}$$

and $$\frac{d|F_{rel}|}{|F_{rel}|} = \frac{1}{2}\frac{dI}{I}$$

making the approximation that $d|F_{rel}| = \sigma(|F_{rel}|)$ and $dI = \sigma(I)$ then

$$\sigma(|F_{rel}|) = \sigma(I)/2\sqrt{LPI}$$

where

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1+B_2) + (pI)^2]^{1/2}$$

CT - total integrated peak count obtained in a scan time t_c, B_1 and B_2 being the background counts, each obtained in time t_b.

Solution of Structure and Refinement

The atomic coordinates of the heavy atoms, i.e., rhodium, chlorine and phosphorus were found by calculating a Patterson map [107] using the programme FORDAP [108]. Table 5 contains a listing of the prominent peaks in the Patterson map, together with their assignment and expected magnitude. Approximate coordinates consistent with the space group P$\bar{1}$ were obtained for these atoms.

From the results of the Patterson map it was apparent that the rhodium atoms were located approximately 3.5 Å apart, the molecule thus being dimeric. The other six atoms found were not situated in bridging positions so the molecule appeared to be bridged by either dioxygen or methylene chloride. The rhodium, chlorine and phosphorus atoms were included in the first refinement using SFLS5 [109]. The conventional R factor [110] (R_1) and R_2 (the weighted R factor) were 0.288 and 0.342 respectively, where

$$R_1 = \frac{\Sigma\left|\,|F_o| - |F_c|\,\right|}{\Sigma|F_o|} \quad \text{and} \quad R_2 = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

and $\quad w = 1/\sigma^2(F)$

The remaining atoms in the unit cell were located as outlined in Table 6.

The carbon rings of the phenyl groups were constrained to D_{6h} symmetry, with carbon-carbon bond lengths fixed at 1.392 Å, and refined as rigid bodies to minimize the number of parameters. The atomic scattering factors for the rhodium, chlorine, phosphorus and carbon atoms were derived from Cromer's coefficients [111] and included the real and imaginary terms for anomalous dispersion [112], for the rhodium, chlorine and phosphorus atoms. Hydrogen atoms were included at their calculated positions (carbon-hydrogen bond lengths, 1.0 Å) with isotropic temperature factors 10% larger than those of the carbon atoms to which they were attached. The hydrogen scattering factors were those of Mason and Robertson [113].

Initially ($R_1 = 0.146$) (Table 7), the nature of the methylene chloride electron density peaks indicated a disordered molecule, however methylene chloride was included as a single site model and further examination deferred until later in the refinement. The refinement (with $\Sigma w(|F_o| - |F_c|)^2$ being minimized) converged to give a conventional R factor of 0.055 for this model (cycle 10). At this point an electron density difference map was calculated and residual electron density around the position of the methylene chloride noted. Several models were tried to describe this disordered molecule. On the basis of minimal residual in electron density maps one model was chosen for the remainder of the refinement. This model used a single site (single occupancy) for the carbon atom and one chlorine atom (Cℓ4); the second chlorine atom being resolved into two sites with variable occupancy factors (Cℓ2, 0.42(4); Cℓ3, 0.62(4)). The single site model for the carbon (C1) and chlorine (Cℓ4) atoms may be physically incorrect but the data do not permit resolution of the separate sites. The total model was then refined to convergence (shift/sigma, ~0.07) to give R_1, 0.044; R_2, 0.055.

Since the observed structure was so novel it was considered necessary to be absolutely certain that the bridging units were dioxygen molecules. When the scattering factors for nitrogen were used for these atoms the atomic thermal parameters assumed physically impossible values and R_1 increased to 0.051. Thus all evidence, both chemical (Chapter 2) and crystallographic (a Hamilton test [114] rejects the N_2 at better than the 0.005 confidence level) confirms the assignment of oxygen for these atoms.

A final electron density difference map was then calculated. The largest positive and negative peaks were 0.4 and -0.4 e-$\mathring{A}^{-3}$ respectively (c.f. carbon ~3 e-$\mathring{A}^{-3}$) and were located in the vicinity of the disordered methylene chloride molecule.

The atomic coordinates and their standard deviations of all atoms were then used to calculate interatomic bond lengths, angles and intra and intermolecular nonbonded contacts with their respective standard deviations, with the programme ORFFE II [115].

As the equivalent isotropic temperature factor of the chlorine atom (Cℓ1) was relatively large (4.17) a riding correction was applied to the rhodium-chlorine bond length. This compensates for the false shortening of this bond caused by the thermal motion description and its interpretation by the bond length programme. A similar correction was also applied to the rhodium-phosphorus bond lengths as a check. The thermal motion in these latter atoms was small so only slight changes were expected. This was indeed found to be the case. All atoms in these corrections were assumed to ride on a "stationary" rhodium atom.

Table 5

Assignment of Patterson Map Peaks

Peak Coordinates*	Relative Height (origin=999)	Assignment	Calculated Height	Calculated Coordinates (from Solution)
u v w				u' v' w'
0.172,-0.126, 0.124	228	$2x_a,2y_a,2z_a$	320	0.156,-0.114, 0.132
-0.185, 0.116,-0.136	236	$2\bar{x}_a,2\bar{y}_a,2\bar{z}_a$	320	-0.156, 0.114,-0.132
-0.080,-0.060,-0.214	102	x_a-x_b,y_a-y_b,z_a-z_b	120	-0.083,-0.060,-0.250
-0.269, 0.050,-0.370	108	$\bar{x}_a-x_b,\bar{y}_a-y_b,\bar{z}_a-z_b$	120	-0.273, 0.053,-0.383
0.004, 0.160,-0.006	158	x_a-x_c,y_a-y_c,z_a-z_c	107	0.032, 0.178, 0.022
-0.164, 0.292,-0.110	123	$\bar{x}_a-x_c,\bar{y}_a-y_c,\bar{z}_a-z_c$	107	-0.162, 0.292,-0.110
-0.164 0.038,-0.006	106	x_a-x_d,y_a-y_d,z_a-z_d	107	-0.170,-0.044,-0.007
-0.353, 0.072,-0.136	112	x_a-x_d,y_a-y_d,z_a-z_d	107	-0.360, 0.070,-0.139

Space group $P\bar{1}$ solution a = Rh x, 0.078; $\bar{y}$, 0.060; z, 0.065

b = Cℓ1 x, 0.175, 0.005, 0.292

c = P1 x, 0.080, -0.226, 0.058

d = P2 x, 0.259, -0.009, 0.072

* These peaks with their combinations were the fourteen strongest peaks observed.

Table 6

Structure Solution Refinement Sequence

Refinement Cycle	Atoms used in Phasing	R_1	Atoms Located in Diff. Map.
1	Rh, Cℓ1, P1, P2,	0.288	O1, O2, C111-C116, C131-C136, C222-C226
2	Rh, Cℓ1, P1, P2, O1, O2 C111-C116, C131-C136, C222-C226	0.204	
3	..	0.186	C121-C126, C211-C216, C231-C236
4	Rh, Cℓ1, P1, P2, O1, O2 C111-C116, C121-C126, C131-C136, C211-C216, C221-C226, C231-C236	0.146	Methylene chloride located (included as a single site model)

Table 7

Refinement Sequence for Model

Refinement Cycle	Model Description	R_1	R_2
5	All atoms included, anomalous dispersion correction applied	0.112	0.136
6	..	0.091	0.116
7	Central atoms assigned anisotropic thermal parameters	0.077	0.090
8	..	0.071	0.083
9	Hydrogen atoms included	0.061	0.073
10	..	0.055	0.066
11	Methylene chloride represented as disordered model	0.049	0.060
12	..	0.046	0.057
13	..	0.044	0.055
14	Oxygen atoms replaced by nitrogen atoms	0.053	0.071
15	..	0.051	0.069

Results

Table 8 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes (electrons x 10). The atomic coordinates of all atoms are listed in Table 9 and the anisotropic temperature factors (U_{ij}) for the central atoms are given in Table 10. Interatomic distances (Table 11), interatomic angles (Table 12), intramolecular and intermolecular non bonded-contacts (Tables 13 and 14 respectively) are included with the standard deviations in parentheses.

A view[116] of the whole molecule is shown in Fig. 5. The central coordination geometry is represented in Fig. 6 and a view down the P1-O2' axis is given in Fig. 7.

Table 8

Observed and Calculated Structure Amplitudes (electrons x 10)

H	K	FOBS	FCAL
L = 0**			
1	0	1400	1438
2	0	288	278
3	0	986	916
4	0	749	785
5	0	1232	1186
6	0	727	687
7	0	287	245
-10	1	390	395
-9	1	306	326
-8	1	292	200
-6	1	370	378
-5	1	594	629
-4	1	859	835
-3	1	461	473
-2	1	341	324
-1	1	181	79
0	1	1573	1588
1	1	510	492
2	1	722	735
3	1	357	353
4	1	172	170
6	1	481	480
7	1	410	402
8	1	117	134
-10	2	284	285
-9	2	324	331
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-2	2	467	529
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2	2	749	759
3	2	579	611
4	2	165	148
6	2	141	159
7	2	182	207
-10	3	218	220
-9	3	247	248
-8	3	410	373
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	3	186	165
	3	111	83
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-1	3	260	265
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1	3	1326	1362
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3	3	230	225
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6	3	571	610
7	3	450	401
8	3	188	144
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-7	4	595	615
-6	4	134	146
-5	4	216	192
-4	4	696	684
-3	4	1122	1088
-2	4	792	790
-1	4	418	397
0	4	713	730
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2	4	161	157
4	4	475	480
6	4	463	411
7	4	323	295
-10	5	176	187
-8	5	276	306
-7	5	591	573
-6	5	559	507
-4	5	386	392
-3	5	756	734
-2	5	870	845
-1	5	1035	1023
0	5	186	187
1	5	488	482
2	5	185	165
3	5	223	195
4	5	449	441
5	5	397	370
-8	6	412	405
-7	6	708	683
-6	6	360	345
-5	6	143	155
-3	6	715	722
-2	6	794	820
-1	6	1159	1155
0	6	333	323
2	6	264	269
3	6	417	420
4	6	694	688
5	6	568	509
-9	7	209	280
-8	7	315	289
-7	7	798	791
-6	7	658	634
-5	7	850	636
-3	7	506	480
-2	7	874	869
-1	7	656	719
0	7	203	226
2	7	130	132
4	7	390	374
5	7	324	327
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-7	8	555	565
-6	8	644	630
-5	8	470	462
-4	8	294	314
-2	8	374	362
-1	8	133	111
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2	8	202	143
4	8	279	276
-8	9	171	137
-7	9	234	241
-6	9	360	343
-5	9	266	250
-4	9	368	335
-2	9	224	252
-1	9	197	174
0	9	160	155
2	9	136	120
-7	10	221	213
-6	10	331	323
-5	10	144	144
-4	10	380	356
-3	10	170	195
-2	10	229	222
-1	10	313	292
0	10	242	235
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3	-11	589	576
4	-11	471	467
5	-11	235	261
0	-10	137	86
3	-10	272	298
4	-10	330	347
6	-10	262	260
0	-9	400	401
3	-9	478	501
4	-9	515	520
7	-9	198	195
-4	-8	205	211
0	-8	442	446
1	-8	576	574
2	-8	272	243
3	-8	389	401
4	-8	595	619
5	-8	477	482
6	-8	365	330
7	-8	224	167
8	-8	225	188
-5	-7	214	225
-4	-7	335	341
-2	-7	546	582
-1	-7	172	178
0	-7	208	192
1	-7	698	708
2	-7	391	393
3	-7	128	189
4	-7	341	355
5	-7	493	492
6	-7	514	539
7	-7	333	338
9	-7	169	140
-6	-6	253	260
-5	-6	519	550
-4	-6	448	468
-3	-6	147	128
-2	-6	293	320
-1	-6	153	204
0	-6	916	923
1	-6	1308	1320
2	-6	818	826
4	-6	285	273
5	-6	242	270
6	-6	391	448
7	-6	399	418
8	-6	320	291
-5	-5	536	538
-4	-5	595	611
-3	-5	498	485
-1	-5	319	341
0	-5	445	429
1	-5	1247	1257
2	-5	1276	1257
3	-5	525	531
4	-5	175	180
7	-5	528	515
8	-5	351	341
-8	-4	212	223
-7	-4	345	360
-6	-4	603	644
-4	-4	725	721
-3	-4	355	377
-2	-4	125	107
-1	-4	290	309
1	-4	828	819
3	-4	243	221
4	-4	450	431
5	-4	395	397
6	-4	190	165
7	-4	184	212
8	-4	312	300
9	-4	173	195
-9	-3	206	232
-7	-3	173	148
-6	-3	411	400
-5	-3	343	322
-4	-3	188	194
-2	-3	221	217
-1	-3	1012	994
0	-3	633	639
1	-3	534	491
2	-3	1181	1141
4	-3	182	175
5	-3	325	330
6	-3	135	171
7	-3	605	657
8	-3	375	405
9	-3	193	182
-8	-2	211	212
-7	-2	280	289
-6	-2	404	370
-4	-2	384	415
-3	-2	1061	1095
-2	-2	281	264
-1	-2	612	651
0	-2	445	405
2	-2	1421	1401
3	-2	188	180
4	-2	391	382
5	-2	343	344
7	-2	471	526
8	-2	505	547
9	-2	393	390
-8	-1	142	131
-7	-1	377	356
-6	-1	364	413
-5	-1	516	537
-3	-1	1526	1511
-2	-1	967	960
-1	-1	1021	943
0	-1	1026	1071
1	-1	424	461
2	-1	418	405
3	-1	590	610
4	-1	266	265
5	-1	492	517
6	-1	578	605
8	-1	428	406
9	-1	366	399
-7	0	469	489
-6	0	705	720
-5	0	700	678
-4	0	433	458
-3	0	725	668
-2	0	361	275
-1	0	1666	1707
0	0	1463	1476
1	0	508	524
2	0	667	629
4	0	777	741
5	0	946	974
6	0	806	796
8	0	157	170
9	0	149	140
-10	1	224	199
-9	1	315	306
-8	1	318	285
-7	1	235	247
-6	1	956	957
-5	1	901	907
-4	1	427	421
-3	1	142	105
-2	1	95	70
-1	1	725	727
0	1	1036	1066
1	1	684	677
3	1	289	297
4	1	123	121
5	1	568	569
6	1	816	793
7	1	249	208
-10	2	288	275
-8	2	502	535
-7	2	188	253
-6	2	341	335
-5	2	640	637
-4	2	533	558
-3	2	774	715
-1	2	142	125
0	2	960	907
1	2	403	412
2	2	246	249
3	2	261	265
5	2	584	550
6	2	535	516
7	2	166	177
-10	3	299	159
-8	3	592	602
-7	3	183	171
-6	3	364	374
-5	3	403	611
-4	3	691	675
-3	3	279	265
-2	3	794	779
-1	3	172	201
0	3	628	632
1	3	370	366
2	3	189	190
3	3	145	148
4	3	154	179
5	3	511	508
6	3	609	619
7	3	469	476
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-9	4	237	214
-8	4	507	500
-7	4	398	345
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-5	4	351	350
-4	4	483	483
-3	4	825	831
-2	4	661	653
-1	4	154	139
0	4	352	328
1	4	353	354
2	4	214	236
3	4	576	561
4	4	252	265
5	4	297	308
6	4	490	479
-9	5	208	155
-8	5	554	547
-7	5	712	703
-6	5	215	166
-5	5	366	382
-4	5	612	589
-3	5	972	966
-2	5	705	692
-1	5	380	340
0	5	150	119
2	5	714	705
3	5	710	711
4	5	447	418
6	5	235	204
-8	6	696	705
-7	6	730	768
-5	6	265	242
-4	6	425	408
-3	6	352	363
-2	6	580	570
-1	6	721	703
2	6	370	362
3	6	561	582
4	6	727	709
5	6	223	248
-10	7	147	126
-8	7	668	621
-7	7	703	702
-6	7	498	491
-5	7	214	185
-3	7	360	369
-2	7	503	494
-1	7	483	471
0	7	265	262
1	7	158	205
3	7	497	507
4	7	532	551
-9	8	199	196
-8	8	418	381
-7	8	825	785
-6	8	443	415
-5	8	234	240
-4	8	249	252
-2	8	159	173
-1	8	381	373
0	8	374	384
1	8	181	201
-7	9	504	487
-4	9	227	226
-3	9	135	110
-2	9	316	307
-1	9	218	222
-7	10	366	377
-4	10	248	265
-2	10	171	210
-1	10	222	204
L = 2**			
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3	-11	608	614
4	-11	170	144
-2	-10	374	335
-1	-10	241	224
0	-10	147	160
2	-10	223	257
3	-10	591	609
-4	-9	310	341
-3	-9	156	124
-2	-9	334	342
-1	-9	536	563
0	-9	357	363
1	-9	248	226
2	-9	369	354
3	-9	687	666
5	-9	155	124
-5	-8	216	277
-4	-8	280	297
-3	-8	164	169
-2	-8	234	259

Table 8 (continued)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
00L =		30000		-2	-8	370	362	4	-2	172	187	-5	5	562	547	-8	-4	334	298
-4	3	187	128	0	-8	180	191	5	-2	326	307	-4	5	291	260	-7	-4	187	147
-3	3	741	783	2	-8	288	291	6	-2	484	513	-3	5	434	432	-6	-4	584	562
-2	3	172	153	3	-8	388	385	-11	-1	203	248	-1	5	767	794	-2	-4	204	284
-1	3	170	153	4	-8	490	488	-10	-1	212	227	0	5	561	535	-1	-4	213	262
0	3	534	520	5	-8	233	216	-9	-1	402	332	2	5	336	325	0	-4	382	374
1	3	277	296	-7	-7	241	211	-8	-1	251	200	-10	6	443	438	1	-4	291	273
2	3	167	152	-6	-7	312	287	-5	-1	210	198	-9	6	761	701	2	-4	191	171
3	3	125	113	-5	-7	215	194	-4	-1	251	278	-8	6	514	469	3	-4	271	268
4	3	433	426	-4	-7	409	407	-3	-1	797	779	-6	6	414	396	5	-4	164	131
5	3	329	336	-3	-7	578	581	-2	-1	942	920	-5	6	769	781	-10	-3	292	304
-9	4	175	155	-2	-7	449	472	-1	-1	612	614	-4	6	729	738	-9	-3	203	188
-8	4	199	169	-1	-7	460	442	0	-1	617	611	-3	6	486	468	-8	-3	145	133
-7	4	161	136	0	-7	284	285	1	-1	1052	1040	-1	6	502	484	-6	-3	233	212
-6	4	359	351	2	-7	710	703	2	-1	999	1001	0	6	348	366	-5	-3	715	728
-4	4	189	206	3	-7	391	428	3	-1	553	566	1	6	192	178	-4	-3	148	158
-3	4	272	282	4	-7	741	717	4	-1	286	289	-9	7	428	441	-3	-3	199	231
-2	4	302	304	5	-7	269	246	5	-1	135	114	-8	7	500	513	-2	-3	154	144
-1	4	586	590	6	-7	185	155	6	-1	396	414	-7	7	338	360	-1	-3	471	455
0	4	758	788	7	-7	408	415	-10	0	567	562	-5	7	362	380	0	-3	583	569
1	4	305	285	-8	-6	452	384	-9	0	751	717	-4	7	498	475	1	-3	318	286
2	4	146	126	-7	-6	375	362	-8	0	417	407	-3	7	531	541	2	-3	207	223
4	4	254	248	-6	-6	477	482	-7	0	583	567	0	7	174	190	3	-3	370	340
-11	5	399	377	-4	-6	176	202	-6	0	229	232	-8	8	426	418	-10	-2	210	197
-10	5	311	297	-3	-6	355	376	-5	0	293	312	-4	8	223	239	-9	-2	283	285
-9	5	309	296	-2	-6	491	480	-4	0	810	822	-3	8	507	501	-7	-2	153	144
-8	5	207	184	-1	-6	502	523	-3	0	756	719	00L =		50000		-5	-2	749	739
-7	5	143	105	0	-6	382	391	-2	0	801	793	-3	-10	305	316	-4	-2	421	410
-6	5	239	225	1	-6	554	535	-1	0	721	736	-1	-10	145	117	-3	-2	477	453
-5	5	839	832	2	-6	131	119	0	0	471	448	0	-10	149	120	-2	-2	174	181
-4	5	737	698	3	-6	728	745	1	0	425	440	1	-10	346	338	-1	-2	746	729
-3	5	340	354	4	-6	753	730	2	0	634	661	2	-10	511	502	0	-2	1154	1169
-1	5	601	602	5	-6	693	694	3	0	545	532	-4	-9	272	278	1	-2	744	776
0	5	874	889	6	-6	550	573	4	0	380	371	-3	-9	189	177	2	-2	220	231
1	5	583	549	-9	-5	201	186	5	0	245	256	-1	-9	146	152	4	-2	228	250
2	5	405	430	-8	-5	228	195	-10	1	257	276	0	-9	230	227	5	-2	309	319
3	5	165	125	-7	-5	269	267	-9	1	368	388	1	-9	169	182	-11	-1	315	288
-10	6	491	496	-6	-5	636	656	-8	1	682	699	2	-9	240	262	-10	-1	202	149
-9	6	703	728	-5	-5	809	801	-7	1	655	671	3	-9	262	259	-9	-1	163	133
-8	6	492	509	-3	-5	135	110	-6	1	369	352	-4	-8	371	394	-8	-1	180	210
-7	6	180	206	-2	-5	251	241	-3	1	206	185	-3	-8	288	290	-6	-1	230	228
-5	6	479	482	-1	-5	332	337	-2	1	1030	1017	-2	-8	236	226	-5	-1	542	515
-4	6	738	788	0	-5	782	787	-1	1	844	845	-1	-8	144	113	-4	-1	399	396
-3	6	721	730	1	-5	964	914	0	1	120	67	1	-8	400	397	-3	-1	332	342
-2	6	630	611	3	-5	597	602	1	1	659	660	2	-8	711	702	-2	-1	467	429
0	6	488	492	4	-5	313	281	2	1	484	488	3	-8	617	554	0	-1	1096	1105
1	6	417	428	5	-5	583	640	3	1	176	216	5	-8	288	274	1	-1	774	768
2	6	545	579	6	-5	454	498	4	1	244	238	-5	-7	308	303	2	-1	477	450
-9	7	463	453	-9	-4	178	212	-11	2	278	[illegible]	-4	-7	521	504	3	-1	252	263
-8	7	636	613	-7	-4	267	278	-8	2	155	[illegible]	-3	-7	338	331	4	-1	250	263
-7	7	586	572	-6	-4	439	452	-6	2	760	752	-2	-7	305	323	-11	0	317	342
-6	7	311	281	-5	-4	665	660	-5	2	747	769	-1	-7	392	401	-10	0	452	463
-5	7	270	273	-4	-4	128	138	-4	2	519	482	0	-7	230	210	-9	0	632	620
-4	7	272	245	-3	-4	524	538	-2	2	800	802	1	-7	705	680	-8	0	692	730
-3	7	665	657	-2	-4	190	209	-1	2	699	712	2	-7	831	843	-7	0	467	452
-2	7	642	665	0	-4	129	111	0	2	196	167	3	-7	783	769	-5	0	570	531
-8	8	288	304	1	-4	470	506	1	2	446	427	4	-7	[illegible]	286	-4	0	805	822
-7	8	293	288	4	-4	301	313	3	2	170	192	-8	-6	[illegible]	386	-3	0	567	557
-6	8	234	219	5	-4	187	216	4	2	192	206	-7	-6	328	334	-2	0	786	775
-5	8	191	184	6	-4	208	217	-11	3	284	268	-6	-6	449	433	-1	0	286	282
-3	8	479	495	-10	-3	443	426	-8	3	136	88	-5	-6	133	117	0	0	625	625
-2	8	307	352	-9	-3	367	360	-7	3	348	343	-4	-6	132	142	1	0	515	497
0	8	[illegible]	105	-7	-3	193	191	-6	3	436	444	-3	-6	285	297	2	0	365	354
-7	9	[illegible]	335	-6	-3	270	235	-4	3	317	313	-2	-6	621	628	3	0	151	175
-4	9	221	252	-5	-3	593	590	-3	3	117	139	-1	-6	474	458	4	0	382	386
-3	9	496	479	-4	-3	401	379	-2	3	514	527	0	-6	517	504	-11	1	222	237
00L =		40000		-3	-3	266	245	-1	3	637	658	2	-6	498	490	-10	1	230	254
0	-11	237	228	-2	-3	152	167	0	3	276	266	3	-6	799	803	-9	1	273	277
1	-11	182	200	-1	-3	151	160	2	3	147	132	4	-6	342	369	-8	1	570	514
2	-11	385	376	0	-3	427	425	4	3	238	194	5	-6	540	548	-7	1	1022	1052
3	-11	177	170	1	-3	494	512	-9	4	190	189	-8	-5	300	296	-6	1	598	595
-3	-10	411	396	4	-3	271	295	-7	4	182	181	-7	-5	349	309	-5	1	243	243
-2	-10	191	204	5	-3	382	365	-5	4	363	354	-6	-5	738	735	-4	1	525	525
2	-10	277	264	[illegible]	-3	428	454	-4	4	266	254	-5	-5	303	289	-3	1	767	721
-4	-9	347	333	-10	-2	192	172	-2	4	754	710	-4	-5	345	357	-2	1	806	785
-3	-9	336	359	-9	-2	215	204	-1	4	905	907	-2	-5	271	256	-1	1	673	454
-2	-9	175	161	-8	-2	285	319	0	4	366	312	-1	-5	803	807	0	1	195	192
2	-9	203	230	-7	-2	177	183	1	4	146	150	0	-5	1116	1110	1	1	360	371
3	-9	298	275	-6	-2	736	738	-11	5	247	243	1	-5	421	392	2	1	270	290
4	-9	149	168	-3	-2	215	227	-10	5	200	232	2	-5	725	726	3	1	235	211
6	-9	245	214	-2	-2	582	575	-9	5	289	263	3	-5	482	496	4	1	304	312
-5	-8	211	194	0	-2	1101	1151	-8	5	275	285	4	-5	176	192	-9	2	138	91
-4	-8	481	453	1	-2	989	1000	-7	5	150	155	5	-5	443	407	-8	2	310	334
-3	-8	810	814	2	-2	671	688	-6	5	331	357	6	-5	155	165	-7	2	599	568

Table 8 (continued)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 5**				3	-6	206	186	-3	2	226	212	-4	-3	179	189	-3	-6	248	227
-8	2	408	420	4	-6	205	178	-2	2	187	205	-3	-3	191	199	1	-6	467	453
-5	2	231	226	-9	-5	391	360	-1	2	172	201	-2	-3	303	268	-8	-5	269	318
-3	2	403	419	-7	-5	220	250	1	2	192	187	-1	-3	228	193	-7	-5	211	220
-2	2	371	373	-6	-5	623	602	-10	3	271	291	0	-3	428	455	-5	-5	272	285
-1	2	345	361	-5	-5	396	358	-8	3	340	321	2	-3	203	180	-4	-5	404	427
0	2	208	204	-3	-5	508	502	-7	3	583	578	3	-3	185	210	-3	-5	421	424
1	2	232	231	-2	-5	326	318	-5	3	283	279	-10	-2	250	263	-2	-5	332	300
-9	3	179	156	-1	-5	509	517	-4	3	369	392	-9	-2	197	149	-1	-5	270	237
-8	3	277	293	0	-5	359	344	-3	3	210	206	-7	-2	425	405	0	-5	248	227
-7	3	390	389	1	-5	281	253	-2	3	301	307	-6	-2	631	614	1	-5	183	195
-6	3	363	363	2	-5	443	438	-1	3	166	143	-5	-2	330	356	-7	-4	313	298
-4	3	324	307	-7	-4	285	243	1	3	150	175	-4	-2	312	341	-6	-4	189	185
-3	3	363	352	-6	-4	667	639	-10	4	192	178	-3	-2	344	321	-5	-4	227	183
-2	3	405	415	-5	-4	472	465	-9	4	189	173	-2	-2	198	212	-4	-4	155	118
-1	3	396	374	-3	-4	457	440	-8	4	364	379	-1	-2	318	308	-3	-4	238	98
1	3	190	214	-2	-4	404	392	-7	4	276	288	0	-2	451	417	-2	-4	162	177
3	3	155	158	-1	-4	401	396	-5	4	258	272	1	-2	243	241	-1	-4	268	288
-10	4	260	265	0	-4	288	300	-4	4	208	241	-10	-1	287	233	0	-4	299	331
-9	4	335	305	1	-4	152	119	-2	4	348	341	-9	-1	267	190	-9	-3	167	31
-7	4	407	409	2	-4	289	331	-1	4	415	392	-7	-1	389	364	-7	-3	183	197
-6	4	582	587	-10	-3	194	156	-8	5	343	346	-6	-1	710	698	-6	-3	270	252
-5	4	300	313	-9	-3	238	272	-7	5	509	487	-5	-1	415	389	-4	-3	197	166
-4	4	130	164	-7	-3	150	30	-6	5	293	271	-4	-1	127	55	-1	-3	302	311
-3	4	268	289	-6	-3	613	614	-3	5	171	234	-2	-1	182	168	-9	-2	252	276
-2	4	471	471	-5	-3	563	538	-2	5	345	352	-1	-1	437	424	-6	-2	335	315
-1	4	667	687	-3	-3	366	328	-8	6	276	240	0	-1	501	495	-4	-2	167	186
0	4	292	274	-2	-3	429	438	-7	6	560	541	1	-1	539	529	-2	-2	192	192
-10	5	447	445	-1	-3	328	345	-6	6	445	420	-10	0	526	559	-1	-2	502	478
-9	5	404	438	0	-3	384	412	-5	6	397	422	-9	0	290	233	0	-2	322	341
-8	5	154	135	2	-3	179	250	-4	6	339	354	-8	0	373	353	-9	-1	205	195
-7	5	451	461	-8	-2	164	157	**L = 7****				-7	0	259	231	-7	-1	455	447
-6	5	472	489	-7	-2	214	177	-4	-9	319	330	-6	0	768	744	-6	-1	553	520
-5	5	200	192	-6	-2	644	613	-1	-9	188	165	-5	0	712	715	-5	-1	265	271
-2	5	131	157	-5	-2	650	587	0	-9	431	395	-4	0	371	366	-2	-1	287	291
-1	5	567	624	-3	-2	545	526	[illegible]	-9	196	198	-3	0	438	421	-1	-1	581	524
0	5	148	127	-2	-2	311	303	-5	-8	291	278	-1	0	233	216	0	-1	604	598
1	5	298	356	-1	-2	221	222	-4	-8	444	484	0	0	490	478	-7	0	306	309
-10	6	396	408	0	-2	333	371	-2	-8	234	247	1	0	616	602	-6	0	649	608
-9	6	499	513	1	-2	286	321	-1	-8	187	198	-10	1	550	537	-5	0	676	682
-8	6	167	172	-11	-1	184	187	0	-8	231	243	-9	1	367	295	-4	0	439	455
-7	6	417	415	-10	-1	242	223	1	-8	588	572	-8	1	406	441	-3	0	281	293
-5	6	486	476	-9	-1	322	314	2	-8	485	452	-6	1	511	451	-1	0	497	482
-4	6	271	283	-8	-1	301	309	-5	-7	454	453	-5	1	475	453	-6	1	281	278
-3	6	191	168	-6	-1	407	388	-4	-7	682	673	-4	1	449	449	-5	1	384	327
-1	6	361	367	-5	-1	690	677	-3	-7	509	512	-3	1	607	604	-4	1	426	434
-8	7	397	408	-4	-1	694	658	-1	-7	232	233	-2	1	455	442	-3	1	403	389
-7	7	210	279	-1	-1	762	755	0	-7	353	341	0	1	302	293	-2	1	222	238
-6	7	453	485	0	-1	688	692	1	-7	709	684	1	1	401	442	-7	2	171	178
-5	7	309	325	1	-1	451	479	2	-7	538	526	-9	2	364	383	-6	2	231	166
-4	7	363	331	-11	0	328	286	-8	-6	241	202	-8	2	437	421	-3	2	282	268
-3	7	389	389	-10	0	512	496	-7	-6	405	385	-6	2	391	375	-7	3	267	253
L = 6**				-9	0	525	544	-5	-6	165	147	-5	2	322	342	-6	3	289	253
0	-10	241	248	-8	0	472	461	-4	-6	518	499	-2	2	262	257	**L = [illegible]			
1	-10	540	517	-7	0	327	335	-3	-6	833	835	-1	2	190	184	-5	-6	487	465
-4	-9	318	317	-6	0	499	543	-2	-6	275	263	0	2	182	157	-4	-6	355	365
1	-9	210	235	-5	0	1011	1010	-1	-6	174	116	-9	3	189	167	-3	-6	201	216
3	-9	208	170	-4	0	867	859	1	-6	367	358	-8	3	217	220	-5	-5	456	423
-4	-8	352	330	-3	0	214	198	2	-6	572	590	-7	3	162	153	-4	-5	592	592
-3	-8	419	412	-2	0	226	258	-8	-5	289	244	-5	3	195	198	-3	-5	355	355
0	-8	356	356	-1	0	230	229	-7	-5	670	695	-3	3	221	237	-2	-5	201	240
1	-8	753	740	0	0	243	266	-6	-5	381	343	-2	3	342	309	-6	-4	222	173
2	-8	692	672	1	0	410	397	-4	-5	604	644	-9	4	148	143	-3	-4	180	163
4	-8	302	285	2	0	333	343	-3	-5	632	614	-8	4	272	228	-2	-4	197	200
-7	-7	255	271	3	0	390	390	-2	-5	283	270	-7	4	345	323	-6	-3	278	300
-5	-7	305	295	-11	1	328	316	-1	-5	184	185	-5	4	248	251	-3	-3	217	202
-4	-7	730	736	-10	1	302	295	0	-5	164	140	-4	4	148	177	-8	-2	216	192
-3	-7	640	648	-9	1	392	382	2	-5	416	433	-3	4	294	285	-7	-2	268	256
-2	-7	466	450	-8	1	675	703	-9	-4	205	168	-7	5	483	524	-6	-2	239	238
0	-7	325	314	-7	1	365	359	-7	-4	417	385	-6	5	206	150	-5	-2	200	226
1	-7	865	846	-6	1	516	520	-6	-4	397	406	**L = 8****				-4	-2	291	245
2	-7	754	738	-5	1	580	573	-4	-4	382	375	-4	-8	177	172	-3	-2	314	303
3	-7	362	388	-4	1	280	266	-3	-4	260	243	-2	-8	173	169	-2	-2	363	398
4	-7	165	139	-3	1	218	236	-2	-4	321	302	-1	-8	160	144	-8	-1	283	237
-8	-6	295	225	-2	1	257	239	-1	-4	241	223	-6	-7	321	296	-7	-1	505	522
-7	-6	406	410	-1	1	389	400	0	-4	283	274	-5	-7	553	518	-6	-1	542	517
-6	-6	380	392	1	1	273	262	2	-4	382	394	-4	-7	316	330	-5	-1	285	296
-4	-6	380	389	2	1	192	201	3	-4	164	165	-2	-7	275	270	-3	-1	317	344
-3	-6	661	666	-9	2	235	208	-10	-3	288	269	0	-7	213	239	-7	0	264	245
-2	-6	578	585	-8	2	472	439	-7	-3	326	300	-6	-6	294	285	-6	0	491	494
-1	-6	227	259	-7	2	489	494	-6	-3	426	447	-5	-6	592	576	-5	0	493	442
1	-6	345	377	-5	2	155	220	-5	-3	245	264	-4	-6	564	599	-4	0	285	276
2	-6	588	604	-4	2	326	311												

Table 9.

Atomic Coordinates and Isotropic Temperature Factors for the Unique Contents of the Unit Cell.

Atom	x	y	z	B *
Rh	0.09542(7)	-0.05735(7)	0.06606(9)	2.45
Cℓ1	0.1776(3)	0.0039(2)	0.3167(3)	4.17
P1	0.0670(3)	-0.2351(2)	0.0442(3)	2.95
P2	0.2648(3)	-0.0127(2)	0.0728(3)	3.03
O1	-0.0255(6)	-0.1164(5)	-0.1361(7)	2.67
O2	-0.0884(6)	-0.0928(5)	-0.0666(7)	2.86
C1	0.172(2)	0.255(2)	0.492(2)	10.33
Cℓ2	0.223(2)	0.377(1)	0.484(2)	8.7
Cℓ3	0.305(3)	0.367(1)	0.606(5)	20.3
Cℓ4	0.1238(8)	0.2598(5)	0.6050(8)	20.4

* These values are equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 10

(Table continued)

Table 9 (continued)

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.133(1)	-0.2670(8)	0.198(1)	3.1(3)
C112	0.0663(9)	-0.3343(6)	0.2282(9)	3.8(3)
C113	0.118(1)	-0.3600(6)	0.3448(7)	5.0(3)
C114	0.237(1)	-0.3183(8)	0.432(1)	4.5(3)
C115	0.3033(9)	-0.2510(6)	0.4019(9)	4.9(3)
C116	0.251(1)	-0.2253(6)	0.2853(7)	4.2(3)
D	4.210(4)	$x^{1\ddagger}$	0.1848(5)	
E	3.026(9)	$y^{1\ddagger}$	-0.2967(4)	
F	5.267(9)	$z^{1\ddagger}$	0.3151(5)	
C121	0.0960(7)	-0.3181(5)	-0.0827(8)	3.1(3)
C122	0.0727(6)	-0.2976(5)	-0.2031(9)	3.9(3)
C123	0.0996(7)	-0.3538(6)	-0.2989(6)	4.6(3)
C124	0.1498(7)	-0.4305(5)	-0.2742(8)	5.0(3)
C125	0.1731(6)	-0.4510(5)	-0.1538(9)	4.4(3)
C126	0.1462(7)	-0.3948(6)	-0.0581(6)	3.9(3)
D	2.712(4)	x^1	0.1229(4)	
E	1.647(5)	y^1	-0.3743(4)	
F	3.889(5)	z^1	-0.1785(5)	
C131	-0.0850(5)	-0.3020(7)	-0.0251(9)	2.8(2)
C132	-0.1318(7)	-0.2561(5)	0.0515(9)	4.1(3)
C133	-0.2434(8)	-0.3101(7)	0.0128(8)	5.4(3)
C134	-0.3083(5)	-0.4099(7)	-0.1026(9)	5.7(3)

(Table continued)

Table 9 (continued)

Name	x	y	z	B
C135	-0.2614(7)	-0.4557(5)	-0.1792(9)	5.9(3)
C136	-0.1498(8)	-0.4018(7)	-0.1405(8)	4.4(3)
D	0.680(4)	x^1	-0.1966(4)	
E	0.445(6)	y^1	-0.3559(4)	
F	0.198(6)	z^1	-0.0638(5)	
C211	0.3531(6)	0.1322(5)	0.1712(9)	3.1(3)
C212	0.4363(8)	0.1728(7)	0.1425(9)	4.4(3)
C213	0.5123(6)	0.2797(7)	0.2237(9)	5.2(3)
C214	0.5051(6)	0.3459(5)	0.3337(9)	5.0(3)
C215	0.4219(8)	0.3053(7)	0.3625(9)	5.2(3)
C216	0.3459(6)	0.1985(7)	0.2812(9)	3.9(3)
D	0.598(5)	x^1	0.4291(4)	
E	0.871(6)	y^1	0.2391(4)	
F	4.332(6)	z^1	0.2525(5)	
C221	0.241(1)	-0.0358(5)	-0.1031(9)	3.2(3)
C222	0.1490(9)	-0.0154(6)	-0.194(1)	4.4(3)
C223	0.1290(8)	-0.0268(6)	-0.328(1)	5.8(3)
C224	0.201(1)	-0.0584(5)	-0.3712(9)	6.3(4)
C225	0.2940(9)	-0.0788(6)	-0.281(1)	6.1(3)
C226	0.3140(8)	-0.0675(6)	-0.147(1)	4.5(3)
D	2.202(5)	x^1	0.2215(5)	
E	1.800(7)	y^1	-0.0471(4)	
F	3.215(8)	z^1	-0.2372(6)	

(Table continued)

Table 9. (continued)

Name	x	y	z	B
C231	0.3710(7)	-0.0724(7)	0.1519(7)	3.3(3)
C232	0.3685(7)	-0.1722(6)	0.0755(8)	4.2(3)
C233	0.4474(8)	-0.2165(5)	0.143(1)	6.0(3)
C234	0.5289(7)	-0.1610(7)	0.2865(7)	6.0(3)
C235	0.5314(7)	-0.0611(6)	0.3629(8)	5.4(3)
C236	0.4524(8)	-0.0168(5)	0.296(1)	3.9(3)
D	2.879(5)	x[1]	0.4499(4)	
E	2.434(5)	y[1]	-0.1167(4)	
F	3.514(5)	z[1]	0.2192(6)	

ǂ These values represent the coordinates of the ring center of gravity.

(Table continued)

Table 9 continued

(b) Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	-0.019	-0.364	0.165	4.1
H113	0.070	-0.408	0.365	5.4
H114	0.274	-0.337	0.515	4.9
H115	0.388	-0.221	0.464	5.3
H116	0.299	-0.177	0.264	4.6
D	4.210			
E	3.026			
F	6.314			
H122	0.0371	-0.242	-0.221	4.3
H123	0.083	-0.339	-0.385	5.1
H124	0.169	-0.471	-0.343	5.5
H125	0.209	-0.506	-0.136	4.8
H126	0.163	-0.410	0.028	4.2
D	2.712			
E	1.647			
F	4.936			
H132	-0.085	-0.184	0.134	4.4
H133	-0.277	-0.277	0.068	5.9
H134	-0.[illegible]	-0.448	-0.130	6.3
H135	-0.[illegible]	-0.527	-0.262	6.5
H136	-0.116	-0.435	-0.196	4.8

(Table continued)

Table 9 (continued)

Name	x	y	z	B
D	0.680			
E	0.444			
F	1.245			
H212	0.441	0.125	0.063	4.8
H213	0.572	0.309	0.203	5.7
H214	0.560	0.423	0.392	5.5
H215	0.417	0.353	0.441	5.7
H216	0.286	0.169	0.302	4.3
D	0.598			
E	0.871			
F	5.380			
H222	0.097	0.007	-0.162	4.8
H223	0.062	-0.012	-0.392	6.3
H224	0.187	-0.067	-0.468	6.9
H225	0.346	-0.101	-0.312	6.7
H226	0.380	-0.082	-0.082	4.9
D	2.202			
E	1.800			
F	4.262			
H232	0.310	-0.212	-0.028	4.6
H233	0.446	-0.288	0.088	6.6
H234	0.586	-0.193	0.335	6.6

(Table continued)

Table 9 (continued)

Name	x	y	z	B
H235	0.590	-0.021	0.466	5.9
H236	0.454	0.055	0.350	4.3
D	2.879			
E	2.434			
F	6.561			

Table 10

Anisotropic Temperature Factors ($\mathring{A}^2 \times 10^3$)

Atom Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	33.4(7)	31.6(6)	31.0(7)	15.9(5)	16.6(5)	13.8(5)
P1	46(2)	35(2)	33(2)	20(2)	19(2)	15(2)
P2	38(2)	41(2)	35(2)	[illegible](2)	16(2)	16(2)
Cℓ1	73(2)	52(2)	34(2)	29(2)	25(2)	17(2)
O1	33(5)	45(5)	31(5)	22(4)	16(4)	11(4)
O2	32(5)	34(5)	38(5)	19(4)	16(4)	19(4)
C1	180(20)	120(20)	70(10)	50(20)	70(20)	100(10)
Cℓ2	100(10)	120(10)	120(20)	46(8)	70(10)	37(8)
Cℓ3	240(30)	160(10)	450(50)	80(10)	250(30)	90(20)
Cℓ4	420(10)	129(5)	207(7)	21(6)	203(8)	22(5)

Table 11

Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	P1	2.314(3)	2.316(3)*
Rh	P2	2.277(3)	2.281(3)*
Rh	Cℓ1	2.390(3)	2.402(3)*
Rh	O1	1.983(7)	
Rh	O2	2.198(7)	
Rh'	O1	2.778(7)	
Rh	O2'	2.069(7)	
P1	C111	1.815(7)	
P1	C121	1.829(7)	
P1	C131	1.829(7)	
P2	C211	1.833(7)	
P2	C221	1.821(8)	
P2	C231	1.832(7)	
O1	O2	1.44(1)	
C1	Cℓ2	1.70(3)	
C1	Cℓ3	1.80(3)	
C1	Cℓ4	1.70(3)	

* Distance corrected for riding

Table 12

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	100.3(1)
P1	Rh	Cℓ1	90.6(1)
P1	Rh	O1	87.5(2)
P1	Rh	O2	92.5(2)
P1	Rh	O2'	169.4(2)
P2	Rh	Cℓ1	95.7(1)
P2	Rh	O1	106.2(3)
P2	Rh	O2	143.4(2)
P2	Rh	O2'	89.2(2)
Cℓ1	Rh	O1	158.0(3)
Cℓ1	Rh	O2	118.4(2)
Cℓ1	Rh	O2'	93.4(2)
O1	Rh	O2	39.9(3)
O1	Rh	O2'	85.2(3)
O2	Rh	O2'	76.9(3)
Rh	P1	C111	121.3(3)
Rh	P1	C121	115.5(3)
Rh	P1	C131	107.4(3)
Rh	P2	C211	114.5(3)
Rh	P2	C221	110.7(3)
Rh	P2	C231	120.6(3)
Cℓ2	C1	Cℓ3	47. (1)

(Table continued)

Table 12 (continued)

Atom 1	Atom 2	Atom 3	Angle (A°)
Cℓ2	Cl	Cℓ4	116. (1)
Cℓ3	Cl	Cℓ4	100 (1)
O1	O2	Rh'	103.4(5)
O1	O2	Rh	61.7(4)
Rh	O2	Rh'	103.0(3)

Table 13

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	Rh'	3.340(2)
Rh	H222	2.98
O2	O2'	2.65(1)
H132	H222'	2.40
H216	O2'	2.62
H122	O1	2.25
H222	O1	2.33
H132	O2	2.88
H216	Cℓ1	2.56
H215	Cℓ3	2.91
O1	O1'	3.49(1)
O1	O2'	2.75(1)

Table 14

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance (Å)
H115	H236	$\bar{x}+1, \bar{y}, \bar{z}+1$	2.43
H223	H223	$\bar{x}, \bar{y}, z-1$	2.46
H115	H336	$\bar{x}+1, \bar{y}, \bar{z}+1$	2.43

Fig. 5

A General View of $[(O_2)RhC\ell(P(C_6H_5)_3)_2]_2$

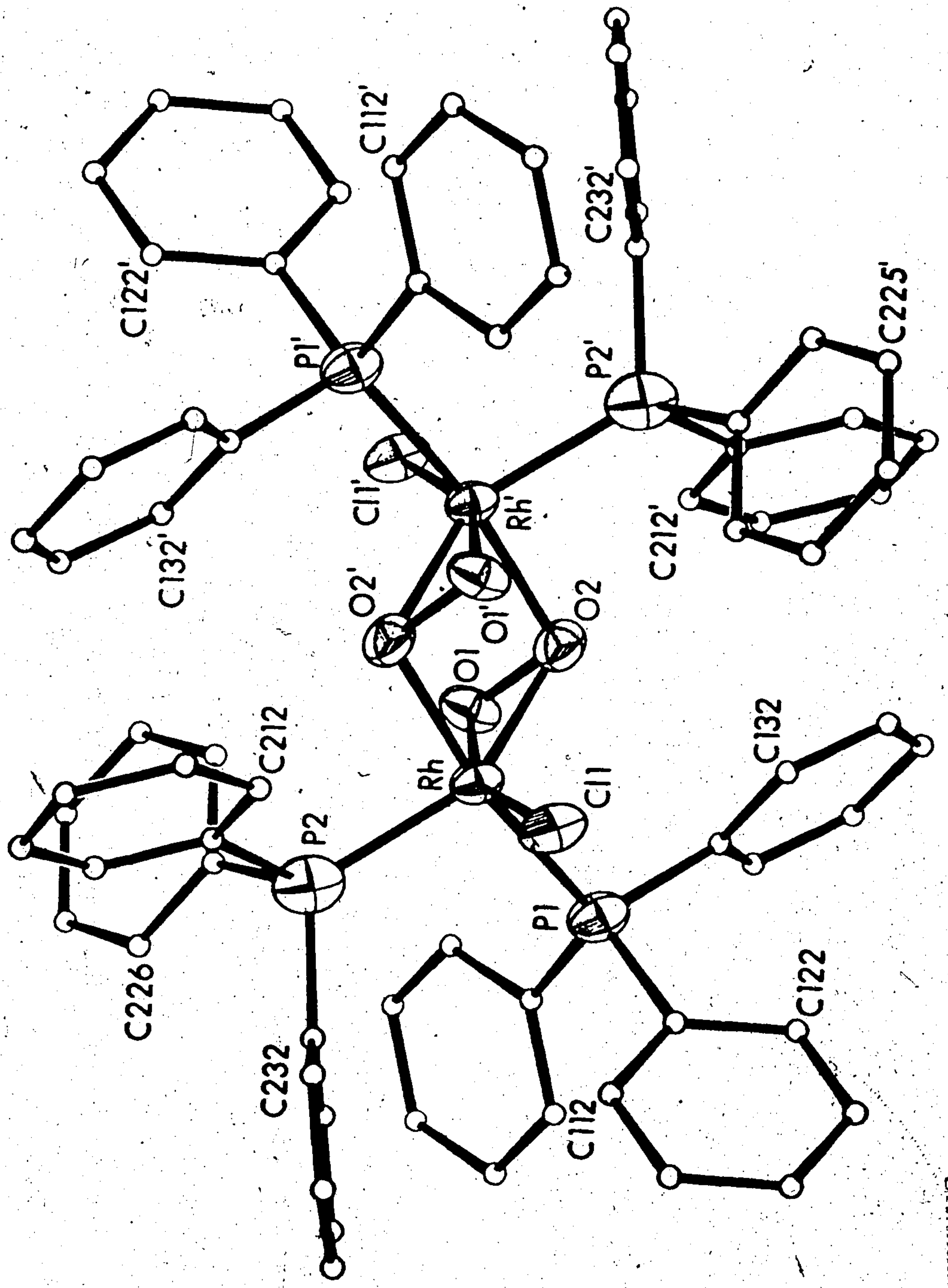


Fig. 6

Dioxygen Bridging Geometry

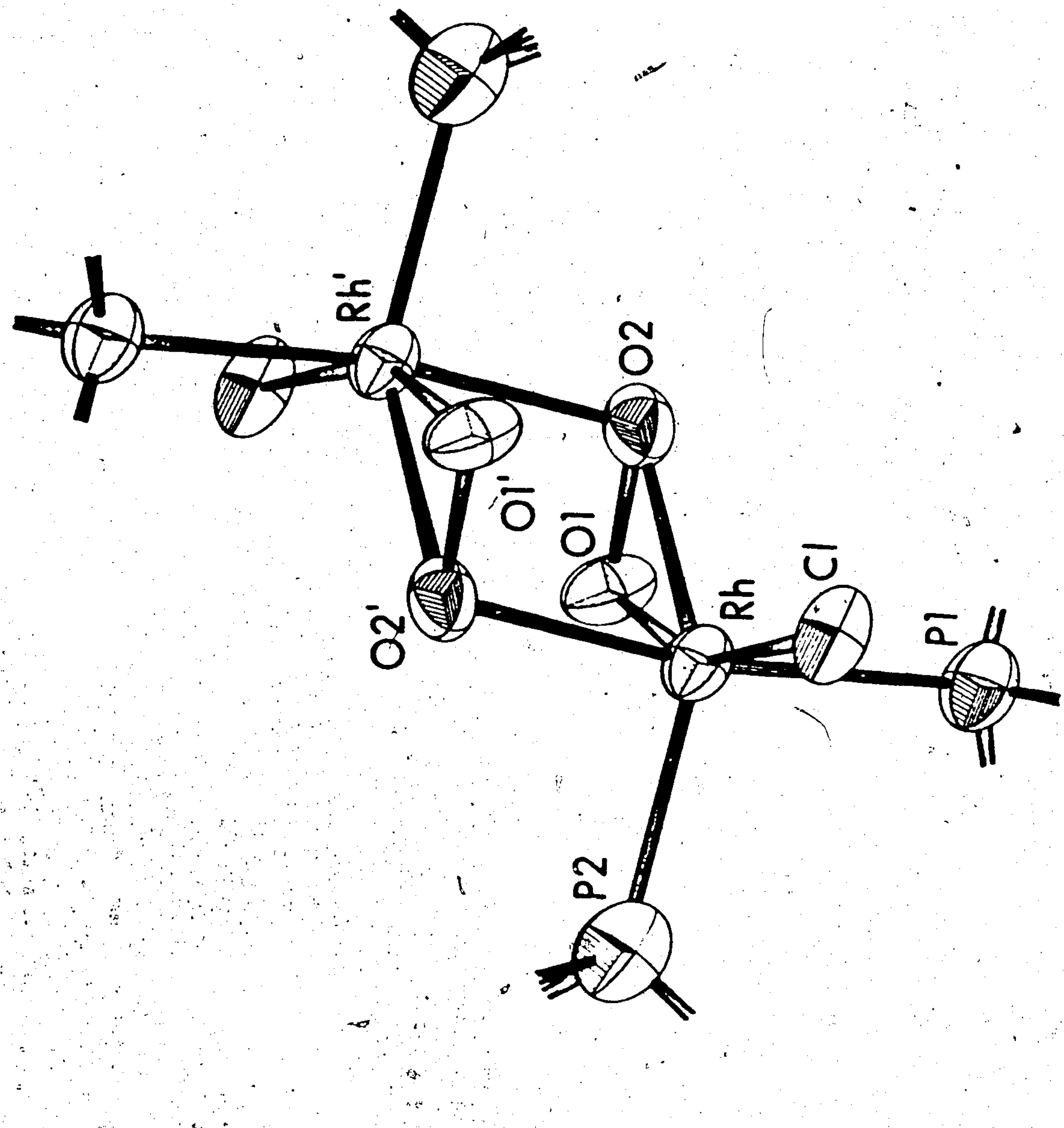
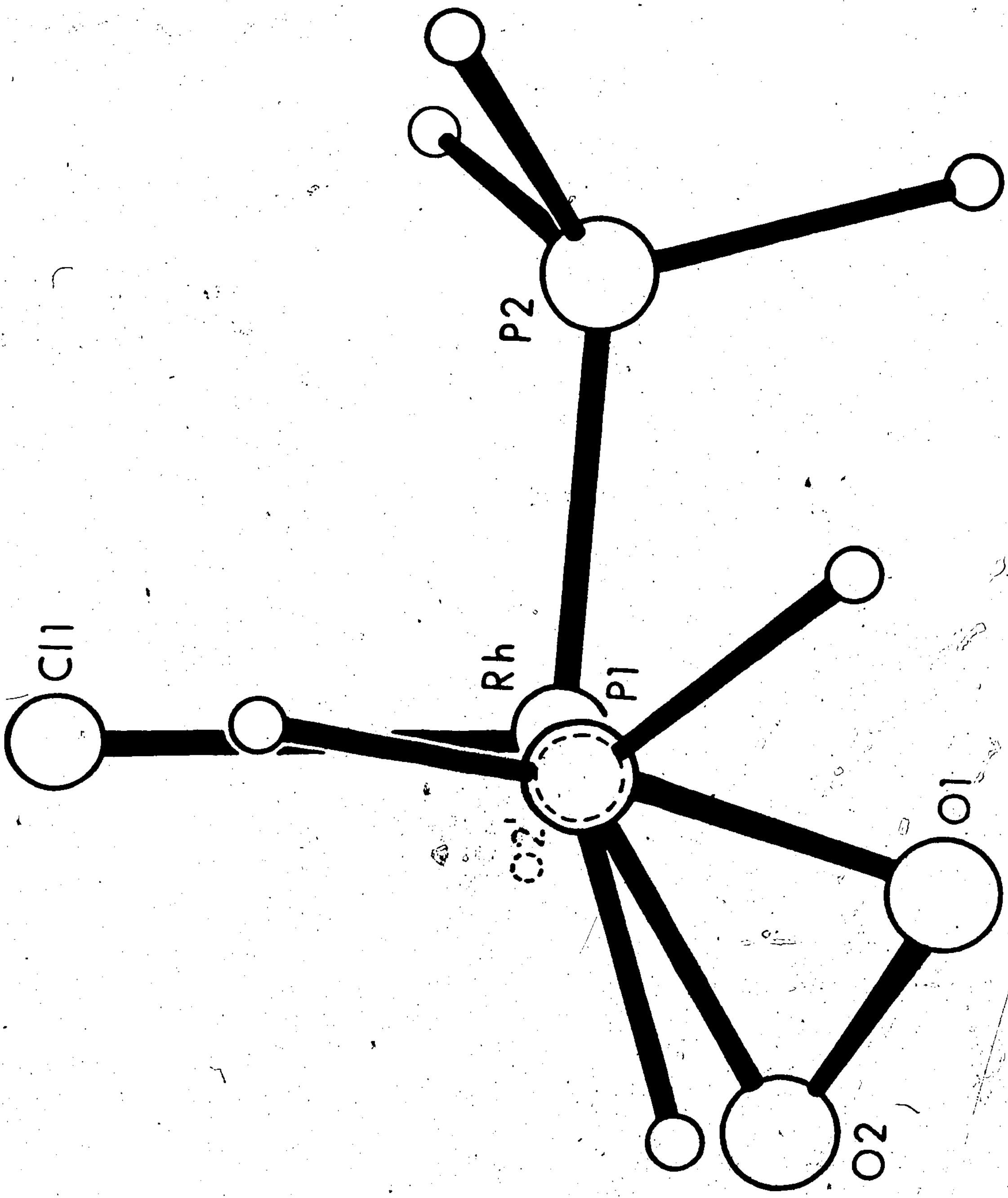


Fig. 7

Subunit Viewed down P1-O2' Direction



Discussion

The structure (Fig. 5) was found to contain dimeric units, situated at inversion centers in the unit cell. The methylene chloride molecule is situated at least 5.6 Å from the central coordination sphere and thus is in no way coordinated to the rhodium atoms. The overall geometry of each subunit can be described as a distorted trigonal bipyramid assuming that the coordinated dioxygen molecule is considered to occupy a single coordination site. The rhodium atoms obey the effective atomic number rule and are coordinatively saturated.

Five coordinate dioxygen species are not particularly unusual (Table 3), however the manner in which this compound achieves this geometry is most unexpected and quite novel. The three equatorial positions of the trigonal bipyramidal subunit are occupied by a triphenylphosphine, a chlorine atom and the coordinated dioxygen molecule in keeping with the similar iridium dioxygen complexes[17-19] (also containing equatorially coordinated dioxygen). The axial coordination sites are occupied by another triphenylphosphine and an oxygen atom from the dioxygen molecule coordinated to the rhodium related by the inversion center. Thus the coordinated dioxygen molecules act as bridging ligands between the rhodium atoms (Fig. 6), with one oxygen atom of each molecule being coordinated in the usual manner for a π-bonded diatomic ligand, whereas the other atom although posessing a similar geometric arrangement is also able, *via* a third bond to bridge the two rhodium atoms.

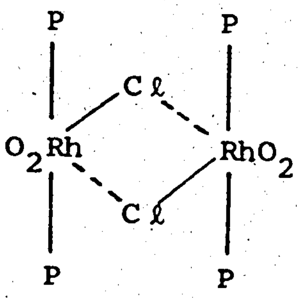
The previously known π-bonded dioxygen derivatives of Vaska's compound and its analogues [33] contain similar geometry but not the bridging bond, whilst O_2F_2 [81] and some of the dioxygen bridged cobalt complexes [97-100] contain fairly similar peroxo symmetry to the bridge without the π-geometry.

In the purely π-bonded dioxygen species dioxygen molecules are situated so that the metal-oxygen distances are equivalent (although some of these complexes [18,19] are disordered and thus any differences in these distances would have been impossible to detect). This is not the case in this complex as the two rhodium-oxygen bond lengths within the same subunit, (Rh-O1, 1.973(7); Rh-O2, 2.195(7) Å) are significantly different. The shorter bond is between the rhodium atom and the oxygen not participating in bridging. The rhodium-oxygen distances to the symmetry related subunit are: (Rh'-O1, 2.778(7); Rh'-O2, 2.069(7) Å). These values indicate that the dioxygen molecules are not perpendicular to the rhodium-rhodium vector as for example had been postulated originally by Vannerberg and Brosset [79] for the structure of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$. The rhodium-rhodium distance is 3.340(2) Å and thus is too long for a metal-metal bond [117,118]. Discussion of the rhodium-phosphorus and rhodium-chlorine bond lengths, which appear normal, is deferred until Chapter VI.

Using the conventional molecular orbital scheme for dioxygen in the coördinated state [46], the dioxygen molecule may be considered as having the initial configuration $\pi^{*2}\pi^{*0}$ instead of the usual paramagnetic ground state with two unpaired electrons $(\pi^{*1}\pi^{*1})$. The bonding within the fragment RhO1O2 could then be described (according to Griffith [64]) as involving a donation from the ligand to the metal from a fully occupied π-orbital accompanied by back donation from the metal to the empty dioxygen π^{*} orbital. This model has been widely used to explain a large variation in dioxygen bond lengths. The greater the amount of back donation, the longer the expected oxygen-oxygen bond length would be, assuming either: (1) a fairly constant ligand-metal donation, or (2) the normal synergic interaction [18]. Thus the iridium complexes [17,19] with variations in the oxygen-oxygen bond lengths of from 1.30(3) Å to 1.66(3) Å could be viewed as containing a superoxide ion (O_2^-) in the first case and a peroxide ion (O_2^{2-}) in the second. These increases in bond length would be expected from a simple bond-order calculation.

The retention of Griffith's model seems desirable for this complex and the bridging nature of the dioxygen ligand may be explained by observing that the filled π* orbital (of the dioxygen ligand) not taking part in overlap with the first rhodium atom would be perpendicular to the RhO1O2 plane and thus in a position favourable for the formation of a σ-bond to the neighbouring rhodium. The observed angles of 103.4(5)° for O1O2Rh′ and 103.0(3)° (RhO2Rh′) seem reasonable when the electron density plots for the molecular orbitals of dioxygen[49] are considered. This particular model could accommodate a wide range of O1O2Rh′ angles as it is possible for the filled π-orbitals of the dioxygen to also donate electrons to the second rhodium atom and the observed angle could be considered as a compromise between the two possible bonding extremes.

It is interesting that a *bis*-chloro bridged species (structure 1) does not form even though it might appear equally feasible.



1

The preference for the dioxygen bridge suggests that there is a particularly suitable energy relationship between the occupied π* orbital of the dioxygen molecule and the dz^2 orbital of the rhodium atom (the "z" axis being defined as the pseudothreefold rotation axis of the trigonal bipyramidal subunit). This is supported by the chemical behaviour of the complex as it is inert to either strong acid or base.

The bonding description does not allow a detailed discussion of the oxygen-oxygen bond length as π* donation to the neighbouring rhodium would decrease the oxygen-oxygen bond length whereas π as a donor would have an opposing effect. In addition the back donation from the metal to the empty π* orbital could vary. Comparisons with the similar complex $[(O_2)RhC\ell(P(C_6H_5)_3)_3]$ should prove meaningful and these are made in Chapter IV.

An alternate method of describing the structure of $[(O_2)RhC\ell(P(C_6H_5)_3)_2]_2$ would be to consider the rhodium as Rh(III) and the dioxygen molecule as a chelating peroxide ion, the bridges being formed from one of the lone pairs of one oxygen atom of each peroxide ion. This could then be viewed as partially analogous to the bent dioxygen cobalt species [65] containing only a π* donor bond as discussed in Chapter I.

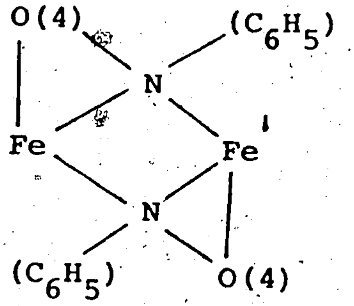
The steric requirements of triphenylphosphine have been discussed by Tolman [119]. The [illegible]n angle of 145 ± 2 for a single ligand suggests that a *cis* pair of triphenylphosphines (P1-Rh-P2, 100.2(1)°) would have to be interlocked. The hydrogen-hydrogen non-bonded contacts (Tables 13 and 14) are all longer than the sum of their van der Waals radii [120]. A number of other close intramolecular contacts were observed (Cℓ1-H216, 2.56; O1-H122, 2.25; O1-H222, 2.33; Rh-H222, 2.98 Å) with the closest intramolecular chlorine-hydrogen contact (Cℓ1-H224(x,y,z+1)) being 2.84 Å. The chlorine-hydrogen contacts are similar to those found in the structure of $RhC\ell(CS)(P(C_6H_5)_3)_2$ [121]. All contacts are not believed to represent any attraction, but rather to reflect the difficulty of accomodating two bulky ligands in a mutually *cis* arrangement.

The geometry of the methylene chloride molecule is in acceptable agreement with literature values [122,123] despite the deficiencies in the model. The molecule does not appear to be coordinated in any way to the rhodium complex.

The dimeric species reported here cannot represent the major species present in solution as indicated by its insolubility. When oxygen is passed through solutions of $RhC\ell(P(C_6H_5)_3)_3$ the formation of the dioxygen dimer from the $(O_2)RhC\ell(P(C_6H_5)_3)_2$ monomer would be expected to be a slow reaction in view of the highly specific geometry required.

A nitroso complex $[Fe(CO)_3(NO)(C_6H_5)]_2$ [125] (2)

published at the same time as the dioxygen dimer.[126] has certain similarities in structure.



2

The nitroso group is located with the nitrogen atom bonded in an analogous manner to the dioxygen dimer O2 atom. The geometry of the nitrosyl group is interesting as the iron-oxygen distances of 1.91(1) Å and 2.73(1) Å plus the two angles (Fe-N-Fe', 103.1(3)° and Fe-N-O(4), 104.6(5)°) closely resemble the equivalent values in the dioxygen complex. The geometries are thus extremely similar except for the expected differences in interatomic bond lengths and the equality of the two iron-nitrogen distances (Fe-N, 2.02(1); Fe'-N, 1.98(1) Å). No detailed bonding explanations were given. Other possibly similar dioxygen species are $Rh(P(C_6H_5)_3)_3O_2$ [127] which is diamagnetic, explosive and probably dimeric and $[(O_2)M(tert\text{-}BuNC)_2]_n$ [78], M = Ni, Pd. The latter polymeric species was postulated from highly unreliable data.

Further comparisons of the *bis*-phosphine dioxygen dimer with other similar complexes are included in Chapter IV and similarities to the parent complex $RhCl(P(C_6H_5)_3)_3$ are examined in Chapter VI.

CHAPTER IV

The Crystal and Molecular Structures of $[(O_2)RhC\ell(P(C_6H_5)_3)_3 \cdot 2CH_2C\ell_2]$

Experimental

Crystals of $(O_2)RhC\ell(P(C_6H_5)_3)_3$ were prepared according to the method described in Chapter II. They were examined under a microscope and found to be yellow needles, usually arranged in clusters. After considerable searching a single crystal was found and cut to the desired length of approximately 0.2 mm. This crystal was then mounted on the end of a thin glass fibre so that the needle axis was coincident with the rotation axis of the goniometer head.

Examination of preliminary Weissenberg and precession photographs indicated that the crystal possessed orthorhombic symmetry. The systematic absences (hk0, $h = 2n + 1$; h0ℓ, $\ell = 2n + 1$; 0kℓ, $k = 2n + 1$) were consistent with the unique choice of the space group *viz.* Pbca. The crystal was mounted on a Picker manual diffractometer so that the "b" axis (needle axis) was coincident with the diffractometer ϕ axis. Precise lattice parameters and their estimated standard deviations were determined as a, 24.817(4); b, 18.359(2); c, 23.200(4) Å from the setting angles of twelve accurately centered high angle reflections at [illegible] peaks showed good resolution of the Kα_1, Kα_2 doublet and only the α_1 peaks (λ, 1.54051 Å) were used. The density of the complex was determined by the flotation method in aqueous potassium iodide as ρ_{obs}, 1.411 g-cm^{-3} which is in excellent agreement with the calculated density of 1.416 g-cm^{-3} assuming eight formula units per unit cell. There are consequently no restrictions on the position or orientation of the formula unit in this space group since the number of general positions is eight.

A careful examination of peak profiles showed no obvious physical defects in the study crystal. Intensity data were collected with copper Kα X-radiation using the coupled $\omega/2\theta$ method with a 2° takeoff angle. The diffractometer was equipped with a graphite crystal monochromator (002 reflecting plane). Each data point was scanned from $(2\theta - 1)°$ to $(2\theta + 1)°$ with a scan speed of 2° per minute. Background counts were estimated from a linear interpolation of 30 second stationary counts taken at the limits of the scan. During the data collection, the intensities of six reflections were monitored at periodic intervals to allow for correction of crystal decomposition and to detect crystal misalignment. Data were only measured to 80° in 2θ as indicated by the preliminary photography. Data collection was terminated after 1755 reflections for this first crystal when the standard reflections had decreased in intensity by 10 - 20%.

The crystal faces were identified as the forms {100}, {010} and {001}, and the perpendicular distances between the opposite members of each form were measured as 0.010, 0.028 and 0.018 cm respectively. The variation in intensity of the 0k0 reflections with the setting angle ϕ was measured to provide experimental evidence for the correctness of subsequent absorption corrections. A second crystal of the same habit and with dimensions (0.008 x 0.009 x 0.032 cm), was used to collect the remaining 1970 reflections. The variation of I_{0k0} with ϕ was studied for this second crystal. All intense reflections with count rates in excess of 10^4 counts per second were remeasured under conditions such that the scattered X-rays did not exceed the linear response range of the scintillation counter.

Finally, representative reflections from the first crystal were remeasured with the second crystal to improve the merging of the two data sets. Both crystals appeared to have similar rates of decomposition (directly proportional to sin θ/λ and logarithmically related to time) and only decomposed when exposed to X-rays. Of the total 3745 reflections measured, 2073 were found to be statistically reliable using the criterion $I < 3$. Decomposition and absorption corrections were then applied (μ = 62.1 cm^{-1}) with the transmission factors varying from 0.517 to 0.637 in the first crystal and from

0.356 to 0.544 in the second. The data were then corrected for Lorentz and polarization effects and the derived structure amplitudes and their standard deviations calculated (p = 0.03) after the two data sets had been scaled.

Solution of Structure and Refinement

A Patterson map was calculated and the atomic coordinates of the rhodium atom found from the Harker line peaks[128] (Table 15). As the "y" and "z" coordinates were approximately 0.25, a large number of peaks were superimposed. Although some evidence of the chlorine was found, only the rhodium atom was included in the first cycle of refinement (R_1, 0.547). The positions of the chlorine atom Cℓ1 and the three phosphorus atoms were located from an electron density map calculated at this point. The rest of the molecule was found as outlined in Table 16.

The carbon rings were constrained to D_{6h} symmetry, with carbon-carbon bond lengths of 1.392 Å, to minimize the number of parameters. The temperature factors of all atoms were not refined until R_1 = 0.178 (Table 17) as unrealistic values were obtained before all atoms were included. The values used (Rh, Cℓ, P; 2.5; C, 5.0) were similar to the final equivalent isotropic temperature factors obtained for the dimeric species

(Chapter III). The atomic scattering factors for rhodium, chlorine, phosphorus and carbon atoms were those of the neutral atoms and included the real and imaginary terms for anomalous dispersion for the rhodium, chlorine and phosphorus atoms. These scattering factors were obtained from Cromer's coefficients [111]. Hydrogen atoms were included at their calculated positions with carbon-hydrogen bond lengths of 1.0 Å and isotropic thermal parameters set 10% larger than those of the carbon atoms to which they were attached. The hydrogen scattering factors were those of Mason and Robertson [113].

Refinement was considered complete when the maximum parameter shift was one seventh of the corresponding standard deviation. The standard deviation of an observation of unit weight was 1.79 at convergence, which is reasonable in view of the constraints imposed upon the model. A final electron density difference map was calculated and the largest positive and negative peaks (0.38 and -0.36 e.Å^{-3}; cf carbon ~3e.Å^{-3}) were located near the methylene chloride molecules.

Table 15

Assignment of Patterson Map Peaks

Peak Coordinates			Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)
u	v	w				
0.168,	0.500,	0.500	174	1/2-2x,1/2,1/2	159	0.168, 0.500, 0.500
-0.168,	0.500,	0.500	180	1/2+2x,1/2,1/2	159	-0.168, 0.500, 0.500
0.00,	0.00,	0.00		0,1/2+2y,0	159	0.0, -0.030, 0.0
..	..	..		0,1/2-2y,0	159	0.0, 0.030, 0.0
0.504,	0.00,	0.00	384	1/2,0,1/2+2z	159	0.500, 0.00, -0.026
..	..	..	(total)	1/2,0,1/2-2z	159	0.500, 0.00, 0.026
..	..	..		1/2,1/2+2y,1/2+2z	79	0.500, -0.030, -0.030
..	..	..		1/2,1/2-2y,1/2+2z	79	0.500, 0.030, -0.030
..	..	..		1/2,1/2+2y,1/2-2z	79	0.500, -0.030, 0.030
..	..	..		1/2,1/2-2y,1/2-2z	79	0.500, 0.030, 0.030
0.324,	0.500,	0.500	128	2x,1/2,2z	79	0.332, 0.500, 0.474
..	..	..		2x,1/2,$2\overline{z}$	79	0.332, 0.500, 0.526

(Table continued)

Table 15 continued

Peak Coordinates			Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)		
u	v	w						
..	..	..		$2x,2y,2z$	40	0.332,	0.470,	0.474
..	..	..		$2x,2y,2\bar{z}$	40	0.332,	0.470,	0.526
..	..	..		$2x,2\bar{y},2z$	40	0.332,	0.520,	0.474
..	..	..		$2x,2\bar{y},2z$	40	0.332,	0.530,	0.526

rhodium solution $x = 0.166$, $y = 0.235$, $z = 0.237$

Table 16

Structure Solution Sequence

Refinement Cycle	Atoms used in Refinement	R_1	Atoms found in Diff. Map
1	Rh	0.547	Cℓ1,P1,P2,P3
2	Rh,Cℓ1,P1,P2,P3	0.439	O1,O2,Cℓ2,Cℓ3,Cℓ4,Cℓ5,C111-C116, C121-C126,C311-C316
3	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C111-C116, C121-C126,C311-C316	0.406	
4	..	0.305	C131-C136,C211-C216,C221-C226 C231-C236,C321-C326,C331-C336, C1,C2
5	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C111-C116,C121-C126,C131-C136,C211-C216, C221-C226,C311-C316	0.243	
6	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C1,C2,C111-C116, C121-C126,C131-C136,C211-C216 C231-C236,C311-C316,C321-C326, C331-C336	0.178	

Table 17

Structure Refinement Sequence

Refinement Cycle	Model	R_1	R_2
6	All atoms included, isotropic temperature factors held constant	0.178	0.242
7	Temperature factors refined	0.111	0.134
8	Anomalous dispersion correction	0.092	0.109
9	Central atoms given anisotropic thermal parameters	0.073	0.087
10	Hydrogen atoms included	0.060	0.072
11	.. .. ..	0.053	0.064
12	.. .. ..	0.049	0.059

Results

Table 18 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes (electrons x 10). The final atomic coordinates of all atoms are included in Table 19 with the anisotropic thermal parameters (U_{ij}) of the central atoms listed in Table 20. Other tables give the interatomic distances (Table 21), interatomic angles (Table 22) and inter- and intramolecular non-bonded contacts (Tables 23 and 24 respectively) with the standard deviations (as calculated by ORFFE II) of the least significant digit included in parentheses. Bond lengths from the rhodium atom to the ligand atoms were also calculated to include a correction for thermal motion in which the second or lighter atom was assumed to ride on the heavier rhodium.

Fig. 8 shows a general view of the molecule with views down the P1-P3 and Rh-P2 directions (Figs. 9 and 10 respectively) being included.

Table 18

Observed and Calculated Structure Amplitudes

(electrons x 10)

H	K	FOBS	FCAL
L = 0**			
2	0	3692	4087
4	0	879	1020
6	0	1873	1816
8	0	2728	2880
10	0	4100	4236
12	0	1790	1830
14	0	1994	2098
2	1	4998	5474
4	1	524	505
6	1	3844	3690
8	1	4115	4327
10	1	3309	3468
12	1	1176	1289
14	1	613	662
16	1	1769	1706
20	1	749	481
0	2	7737	8371
2	2	3122	3278
4	2	395	373
6	2	1171	1145
8	2	3199	3310
10	2	1232	1040
12	2	3044	3003
14	2	483	474
2	3	2843	3131
4	3	5738	5984
6	3	1106	1164
8	3	1076	967
10	3	2483	2490
12	3	401	364
14	3	523	515
20	3	917	1218
0	4	3892	3774
2	4	1053	1007
4	4	3797	3907
6	4	2554	2646
8	4	513	495
10	4	445	420
12	4	2945	2933
16	4	654	724
2	5	2208	2283
4	5	2239	2279
6	5	653	691
8	5	1891	1967
10	5	1457	1550
12	5	1228	1280
14	5	671	677
0	6	5150	5031
2	6	603	605
4	6	1268	1326
6	6	1678	1607
8	6	1529	1502
10	6	377	269
12	6	3765	3657
14	6	2343	2399
18	6	535	727
2	7	2330	2419
4	7	4262	4268
6	7	1673	1646
8	7	1851	1899
10	7	2574	2548
14	7	1354	1391
16	7	1305	1196
0	8	1282	1302
2	8	1336	1401
4	8	1550	1520
6	8	700	678
8	8	1187	1201
10	8	550	492
12	8	2175	2222
14	8	1564	1549
2	9	1572	1614
4	9	2949	2905
6	9	355	199
10	9	720	741
12	9	624	606
16	9	729	762
2	10	751	710
4	10	413	225
6	10	867	872
8	10	859	802
14	10	532	363
2	11	574	611
4	11	581	704
8	11	1245	1192
10	11	849	725
12	11	674	643
14	11	423	551
0	12	1242	1197
4	12	526	294
6	12	1259	1281
2	13	825	840
4	13	1441	1456
8	13	1411	1352
0	14	616	675
2	14	1109	1077
4	14	860	784
6	14	1250	1328
4	15	615	595
L = 1**			
1	1	171	295
2	1	557	595
3	1	307	252
4	1	576	530
5	1	1347	1412
6	1	3164	3270
8	1	310	297
10	1	1175	1147
13	1	302	399
14	1	343	321
15	1	489	606
16	1	1183	1176
0	2	1476	1595
1	2	179	66
2	2	218	164
3	2	1229	1155
4	2	325	342
5	2	986	1007
6	2	808	786
7	2	2797	2965
8	2	1991	2147
9	2	317	278
12	2	747	721
14	2	812	883
15	2	466	592
16	2	677	718
1	3	831	749
2	3	1134	1143
3	3	1173	1126
5	3	2481	2470
6	3	614	584
7	3	1474	1566
8	3	456	483
9	3	513	656
10	3	1331	1357
12	3	723	605
13	3	396	484
14	3	366	269
15	3	387	355
16	3	525	597
17	3	585	639
20	3	796	838
0	4	1988	2072
1	4	1287	1355
2	4	726	691
3	4	462	575
4	4	561	554
5	4	1529	1577
6	4	614	652
7	4	1095	1146
8	4	1101	1077
9	4	341	260
10	4	304	323
11	4	540	675
12	4	1042	1025
15	4	617	716
18	4	488	499
1	5	247	137
3	5	1641	1717
4	5	1161	1206
5	5	345	344
6	5	364	371
8	5	620	654
9	5	1243	1255
10	5	542	617
11	5	313	375
12	5	507	533
14	5	373	316
0	6	983	1000
1	6	649	613
3	6	921	934
5	6	1701	1763
6	6	1659	1674
7	6	719	645
8	6	321	197
10	6	1883	1914
11	6	573	[illegible]
12	6	1653	1727
13	6	1027	1054
14	6	591	451
1	7	941	930
2	7	1724	1643
3	7	599	619
4	7	773	705
5	7	426	395
6	7	918	815
8	7	1241	1144
10	7	1217	1274
12	7	513	646
14	7	824	792
0	8	2772	2717
2	8	2191	2092
4	8	971	969
5	8	911	894
8	8	803	764
9	8	375	434
10	8	1811	1849
11	8	449	502
12	8	2776	2784
14	8	750	684
1	9	348	185
2	9	2018	2738
3	9	611	554
4	9	1598	1590
6	9	785	805
9	9	1371	1381
10	9	2234	2299
11	9	524	548
14	9	1574	1563
16	9	574	478
0	10	1878	1856
1	10	344	321
2	10	1482	1432
3	10	611	600
4	10	610	531
6	10	649	720
7	10	356	310
8	10	707	720
10	10	1115	1147
12	10	2669	2562
2	11	1378	1396
4	11	802	832
5	11	765	641
8	11	792	914
10	11	1116	1140
14	11	1155	1190
0	12	1328	1400
1	12	533	532
4	12	724	679
5	12	601	508
10	12	1707	1698
11	12	563	346
12	12	1017	1037
2	13	900	831
8	13	1374	1427
10	13	746	761
0	14	1542	2074
2	14	765	878
3	14	529	385
6	14	913	1007
2	15	1108	1066
L = 2**			
0	0	7101	8320
1	0	909	816
2	0	2296	2200
3	0	439	359
4	0	276	372
6	0	6927	7018
7	0	1578	1681
8	0	2659	2745
9	0	2468	2569
10	0	3953	3972
11	0	516	503
12	0	3312	3443
14	0	1499	1337
15	0	617	577
18	0	1273	1294
20	0	869	1062
1	1	168	106
2	1	4482	4480
3	1	937	958
4	1	732	709
5	1	1096	1127
6	1	1324	1376
7	1	1458	1427
8	1	1841	1854
9	1	1901	1965
10	1	4000	4059
14	1	2296	2294
15	1	579	646
16	1	1346	1292
20	1	1080	1135
0	2	5449	5490
1	2	221	180
2	2	1628	1630
3	2	1157	1171
4	2	739	494
5	2	573	423
6	2	2602	2476
7	2	664	743
8	2	547	487
9	2	835	746
10	2	2665	2699
11	2	1971	2169
12	2	2573	2732
13	2	583	525
14	2	1213	1175
15	2	278	741
1	3	333	255
2	3	4712	4639
3	3	546	565
4	3	1014	1084
5	3	1075	1130
6	3	471	515
7	3	834	966
8	3	1647	1559
10	3	1897	1964
11	3	667	738
12	3	814	825
13	3	1799	1890
14	3	949	1069
0	4	3398	3358
1	4	423	403
2	4	1991	1980
4	4	639	618
5	4	411	481
6	4	1382	1374
7	4	1724	1703
8	4	925	934
9	4	2211	2305
10	4	1073	1105
11	4	1673	1694
12	4	2035	2000
14	4	629	645
16	4	617	509
18	4	812	836
1	5	677	667
2	5	2247	2302
3	5	585	548
4	5	959	916
5	5	280	319
6	5	579	561
7	5	1051	1046
8	5	1092	1097
9	5	316	309
10	5	2384	2335
11	5	1075	1064
12	5	494	516
14	5	1174	1180
16	5	669	636
0	6	2359	2252
1	6	1245	1207
2	6	2575	2576
3	6	363	350
4	6	815	819
6	6	3536	3580
7	6	334	323
8	6	1345	1481
9	6	785	695
10	6	823	797
11	6	486	437
12	6	1388	1358
14	6	823	765
17	6	591	552
18	6	1117	1196
1	7	625	571
2	7	3768	3754
4	7	2766	2784
8	7	880	966
9	7	355	320
10	7	2545	2490
11	7	477	517
12	7	709	693
13	7	464	188
14	7	1603	1502
15	7	573	486
16	7	1113	1062
0	8	422	437
2	8	1743	1703
4	8	746	717
6	8	1359	1504
7	8	567	524
8	8	579	611
9	8	533	491
10	8	958	984
12	8	1436	1433
14	8	1268	1108
1	9	715	677
2	9	1382	1314
3	9	640	607
4	9	1715	1740
6	9	815	825
8	9	695	700
10	9	1181	1211
14	9	828	846
16	9	847	752
0	10	1619	1267
2	10	839	736
4	10	627	644
10	10	621	612
2	11	546	592
3	11	325	340
4	11	405	771
8	11	744	843
0	12	403	488
2	12	610	584
4	12	1814	1705
2	13	764	761
4	13	1146	1169
8	13	745	818
10	13	574	467
2	14	1226	992
4	14	1537	1521
9	14	482	449
L = 3**			
1	1	182	229
2	1	1569	1512
3	1	796	745
4	1	1628	1587
5	1	263	144
6	1	1300	1314
7	1	537	566
10	1	593	605
11	1	1042	999
0	2	1283	1238
1	2	1592	1546
2	2	252	289
3	2	1053	1053
4	2	4657	4627
5	2	2334	2307
6	2	1377	1405
7	2	886	850
8	2	1455	1394
10	2	397	358
11	2	403	351
12	2	1213	1247
13	2	1076	967
15	2	1052	1072
18	2	588	707
20	2	794	506
1	3	752	725
2	3	364	281
3	3	1994	1953
4	3	1716	1462
7	3	730	738
8	3	1430	1416
10	3	1688	1650
14	3	769	-798
15	3	400	413
20	3	531	585
0	4	276	262
1	4	519	505
2	4	970	1002
3	4	1030	1023
4	4	1507	1530
5	4	1590	1579
6	4	430	450
7	4	909	872
10	4	733	746
11	4	608	570
12	4	1359	1269
15	4	491	561
17	4	838	793
1	5	533	531
2	5	1145	1125
3	5	916	929
4	5	292	286
6	5	1004	573
7	5	1570	1500
10	5	632	590
11	5	1237	1250
12	5	813	805
0	6	2529	2610
1	6	1458	1425
2	6	1068	991
3	6	1285	[illegible]
5	6	838	829
6	6	574	520
7	6	766	719
10	6	1132	1115
12	6	1548	1512
13	6	622	669
17	6	784	729
2	7	1869	1857
3	7	621	543
4	7	416	369
5	7	278	328
7	7	372	349
8	7	421	478
9	7	1063	1035
10	7	2002	1944
11	7	562	654
12	7	393	404
14		1167	1202
11		554	594
0	8	3272	3267
1	8	1210	1196
2	8	1007	1001
3	8	[illegible]	370
4	8	[illegible]	1626
5	8	[illegible]	374
6	8	1081	1113
8	8	2440	2477
10	8	1143	1142
11	8	459	497
12	8	2140	2297
13	8	1447	1360
14	8	845	865
15	8	606	647
2	9	3214	3144
3	9	744	634
4	9	1104	1141
5	9	728	744
8	9	2043	2026

Table 18 continued

H	K	FOBS	FCAL
L = 3			
9	9	729	708
10	9	1798	1929
11	9	585	618
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16	9	521	625
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1	10	493	595
2	10	673	714
4	10	913	965
5	10	506	502
6	10	1350	1368
7	10	831	810
10	10	1306	1400
11	10	546	488
12	10	2111	2150
13	10	890	889
1	11	440	545
2	11	1239	1327
3	11	503	516
4	11	1116	1114
5	11	500	481
8	11	529	585
10	11	1269	1324
11	11	951	900
14	11	972	988
0	12	906	927
1	12	864	772
2	12	1037	1049
3	12	660	597
7	12	622	677
9	12	575	672
10	12	706	698
12	12	1765	1838
2	13	1065	1051
3	13	630	708
4	13	878	934
8	13	805	780
10	13	1283	1332
0	14	2202	2205
1	14	1541	1491
2	14	1019	1090
3	14	770	768
4	14	581	614
6	14	1001	1020
2	15	1649	1706
L = 4			
0	0	2847	2757
1	0	1072	1045
3	0	988	901
4	0	2796	2575
5	0	591	576
6	0	2346	2447
7	0	529	571
8	0	2274	2345
9	0	548	507
10	0	681	678
11	0	2571	2582
12	0	3443	3557
13	0	1117	[illegible]
14	0	1303	[illegible]
15	0	579	[illegible]
16	0	1094	[illegible]
17	0	866	[illegible]
18	0	1743	1704
20	0	1173	1282
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2	1	303	410
3	1	798	706
4	1	3134	3047
5	1	231	176
6	1	1627	1435
7	1	1235	1248
8	1	3126	3079
9	1	1464	1462
10	1	2144	2168
11	1	318	275
12	1	767	793
13	1	774	813
14	1	2147	2304
15	1	438	447
16	1	1760	1679
19	1	943	1026
20	1	1790	1842
0	2	3925	3849
1	2	2932	2958
2	2	789	828
3	2	658	622
4	2	2184	2300
5	2	598	629
6	2	1023	1000
7	2	670	675
8	2	1401	1453
9	2	1323	1305
10	2	1341	1351
11	2	1154	1127
12	2	2047	2026
14	2	500	496
15	2	505	482
16	2	1081	1086
18	2	1098	1263
20	2	1132	1106
1	3	1125	1065
2	3	1926	1867
3	3	764	720
4	3	516	484
5	3	396	327
6	3	727	773
7	3	944	1002
8	3	1298	1281
9	3	631	691
10	3	985	1026
12	3	741	681
13	3	521	605
14	3	950	921
16	3	544	629
0	4	2393	2290
1	4	1584	1498
4	4	751	676
5	4	1911	1914
6	4	860	890
7	4	374	354
8	4	682	741
9	4	627	489
10	4	1335	1314
11	4	1000	971
12	4	2128	2138
13	4	557	608
14	4	318	369
16	4	794	797
18	4	983	1087
1	5	1007	1027
2	5	576	448
3	5	441	549
4	5	2713	2743
5	5	769	787
8	5	1619	1787
9	5	319	373
10	5	1790	1746
12	5	485	444
13	5	340	394
14	5	1094	1071
15	5	855	943
16	5	933	745
0	6	4677	4072
1	6	1358	1324
2	6	1725	1721
4	6	739	713
5	6	264	163
6	6	875	883
7	6	1073	1040
8	6	297	272
9	6	816	836
10	6	1079	1129
11	6	1071	1062
12	6	1985	2104
13	6	505	543
[illegible]	[illegible]	954	990
[illegible]	[illegible]	327	571
[illegible]	[illegible]	813	526
[illegible]	[illegible]	1155	1093
[illegible]	[illegible]	382	353
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[illegible]	[illegible]	2608	2574
[illegible]	7	1823	1757
[illegible]	7	1256	1325
4	7	2901	2902
10	7	1430	1503
13	7	546	425
14	7	1008	1023
15	7	649	570
16	7	1493	1475
0	8	2871	2829
1	8	514	410
2	8	1241	1189
4	8	352	469
5	8	825	566
6	8	624	676
7	8	433	457
8	8	1162	1165
9	8	459	459
10	8	805	821
11	8	543	545
12	8	1682	1664
13	8	854	827
14	8	773	726
15	8	747	751
17	8	602	472
1	9	994	964
2	9	1309	1344
4	9	423	450
6	9	508	430
7	9	344	312
8	9	1304	1440
9	9	345	291
10	9	645	531
12	9	548	446
14	9	584	420
15	9	535	294
16	9	1644	1030
1	10	769	828
3	10	332	247
4	10	951	920
5	10	339	350
6	10	852	815
7	10	545	509
10	10	701	551
11	10	646	705
13	10	597	552
1	11	487	457
3	11	627	663
4	11	945	930
6	11	602	581
8	11	635	683
11	11	574	517
12	11	546	460
2	12	460	503
4	12	791	800
6	12	1147	1107
11	12	640	475
4	13	1523	1513
8	13	655	584
9	13	598	395
0	14	474	420
1	14	504	329
2	14	950	946
6	14	792	832
7	14	666	780
L = 5			
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2	1	2141	2052
3	1	1445	1363
4	1	675	974
5	1	1553	1539
6	1	1030	1035
7	1	1090	1070
9	1	574	606
10	1	1179	1156
12	1	371	363
14	1	480	437
17	1	501	657
0	2	3036	2999
1	2	817	750
2	2	6243	6260
3	2	3044	3080
4	2	2136	2167
5	2	1997	1995
6	2	2109	2119
7	2	275	295
8	2	544	574
10	2	680	615
11	2	836	915
12	2	1359	1380
13	2	820	965
15	2	647	653
1	3	1082	1067
2	3	1360	1341
3	3	1994	1985
4	3	1334	1292
5	3	426	412
6	3	1975	1915
7	3	527	508
8	3	1468	1509
9	3	457	535
10	3	869	759
11	3	752	758
13	3	377	411
14	3	605	620
15	3	478	389
0	4	1648	1641
1	4	2244	2238
3	4	374	380
4	4	380	343
5	4	294	332
6	4	334	294
7	4	1089	1020
8	4	572	596
9	4	554	536
10	4	410	273
13	4	1222	1368
14	4	725	757
17	4	742	690
1	5	1114	1037
3	5	1852	1830
4	5	946	656
5	5	954	858
7	5	521	441
9	5	512	484
10	5	915	865
12	5	585	569
15	5	626	535
6	6	2239	2269
7	6	1164	1146
4	6	1224	1211
6	6	894	865
8	6	1889	1875
10	6	963	939
12	6	1157	1132
14	6	695	725
17	6	508	440
18	6	687	533
1	7	365	429
2	7	2489	2464
3	7	912	894
4	7	836	914
5	7	374	391
6	7	356	230
9	7	1197	1144
10	7	1521	1550
11	7	585	652
12	7	744	762
14	7	740	544
0	8	3595	3664
1	8	2092	2002
2	8	1478	1396
3	8	1732	1688
4	8	2305	2305
5	8	618	514
6	8	1970	1968
7	8	1231	1115
8	8	1537	1506
9	8	367	262
10	8	747	649
11	8	867	974
12	8	1556	1533
13	8	818	753
1	9	1196	1107
2	9	2971	2867
3	9	1438	1434
4	9	2808	2509
5	9	1059	1065
6	9	770	757
8	9	1450	1457
9	9	844	818
10	9	2326	2365
11	9	634	747
14	9	1010	956
15	9	660	716
0	10	2054	2073
1	10	2193	2233
2	10	550	587
3	10	654	735
4	10	1131	1144
5	10	514	521
6	10	1825	1829
8	10	1530	1399
9	10	819	867
11	10	1020	876
12	10	1510	1541
2	11	1640	1700
3	11	491	392
4	11	1165	1156
6	11	557	545
7	11	565	385
8	11	932	885
9	11	953	920
10	11	1501	1506
0	12	1834	1832
1	12	1450	1360
4	12	671	671
6	12	1039	993
8	12	1006	1044
10	12	627	679
11	12	932	1033
2	13	1623	1734
4	13	959	912
8	13	1025	1011
9	13	824	840
0	14	1754	1749
1	14	867	817
2	14	977	883
4	14	1160	1374
L = 6			
0	0	2392	2336
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2	0	1367	1325
3	0	287	227
4	0	878	820
5	0	2145	2124
6	0	3898	3992
7	0	1527	1559
8	0	3078	3035
9	0	506	511
10	0	847	750
11	0	1474	1467
12	0	1442	1474
13	0	811	833
14	0	477	384
16	0	1235	1234
1	1	3455	3544
2	1	5290	5153
3	1	1254	1225
4	1	970	1040
5	1	561	484
7	1	1442	1470
8	1	1812	1764
9	1	1676	1651
10	1	1742	1611
13	1	697	808
14	1	2200	2108
15	1	1033	1082
16	1	1228	1248
0	2	443	390
1	2	2087	2105
3	2	1107	1066
4	2	860	871
5	2	545	498
6	2	1453	1389
8	2	2686	2582
9	2	765	737
10	2	577	634
11	2	1031	1018
12	2	1534	1560
13	2	698	701
14	2	420	297
16	2	1275	1229
18	2	1894	1843
1	3	1284	1220
3	3	1110	1094
7	3	346	300
8	3	509	413
9	3	1017	1016
10	3	1593	1535
11	3	1869	1904
12	3	1499	1490
13	3	610	539
14	3	1837	1914
15	3	566	639
0	4	1927	2005
1	4	371	354
2	4	455	390
3	4	437	437
4	4	2192	2137
5	4	292	302
6	4	257	215
7	4	1441	1396
8	4	676	695
9	4	1018	1000
10	4	1606	1564
11	4	1154	1152
12	4	1238	1390
13	4	594	1096
14	4	547	516
16	4	931	954
18	4	1338	1341
1	5	953	947
2	5	2297	2198
3	5	1277	1314
4	5	705	661
5	5	961	937
6	5	392	377
7	5	438	401
8	5	299	237
10	5	1575	1521
11	5	903	898
12	5	412	402
14	5	1932	1969
15	5	654	628
16	5	761	777
0	6	2031	1974
1	6	706	773
5	6	244	218
6	6	2020	2130
7	6	1234	1229
8	6	348	247
10	6	1622	1636
11	6	1354	1348
12	6	2146	2103
13	6	1324	1289
15	6	1171	1157
16	6	831	1040
1	7	1558	1545
2	7	1917	1865
4	7	974	1036
5	7	652	667
8	7	1067	1027
9	7	763	707
10	7	1543	1557
11	7	1824	1709
15	7	717	760
0	8	1395	1395
1	8	720	704
2	8	1346	1398
3	8	910	943
4	8	628	605
5	8	1177	1220
6	8	416	363
7	8	2388	2294
8	8	1340	1026
9	8	479	412
10	8	1106	1163
11	8	753	706
12	8	1008	900
13	8	682	557
14	8	762	784

Table 18 continued

H	K	FOBS	FCAL
L = 6**			
2	9	632	607
3	9	501	380
4	9	740	729
5	9	353	256
6	9	788	820
8	9	1190	1161
9	9	464	591
12	9	518	541
14	9	640	687
15	9	501	442
0	10	514	549
1	10	302	218
2	10	347	380
3	10	322	208
4	10	696	645
5	10	418	376
6	10	529	469
8	10	822	734
10	10	644	524
11	10	598	555
13	10	533	450
3	11	425	386
6	11	652	676
8	11	793	764
9	11	630	483
2	12	581	564
5	12	665	635
6	12	817	808
7	12	777	542
8	12	524	422
4	13	653	700
6	13	1152	1190
7	13	800	791
8	13	961	975
1	14	629	551
2	14	879	932
5	14	1120	1124
L = 7**			
1	1	954	1007
2	1	229	301
3	1	765	782
4	1	1056	1085
5	1	230	213
6	1	348	418
7	1	737	737
9	1	1294	1293
10	1	529	538
11	1	642	604
14	1	320	163
16	1	455	485
17	1	542	604
0	2	1195	1217
1	2	2113	2153
2	2	1086	1124
5	2	1628	1692
6	2	1791	1706
7	2	373	437
8	2	1209	1248
9	2	1084	1006
10	2	544	626
12	2	1064	1089
1	3	502	544
2	3	1254	1184
3	3	540	584
4	3	1621	1564
6	3	323	236
8	3	379	360
9	3	685	625
10	3	887	893
13	3	479	348
14	3	88[illegible]	891
18	3	664	572
0	[illegible]	[illegible]	2116
1			238
2			1224
3	4	251	208
4	4	1012	1005
7	4	548	596
8	4	1041	942
10	4	300	232
12	4	712	640
14	4	683	558
17	4	495	436
1	5	367	343
2	5	776	739
3	5	461	531
4	5	324	250
5	5	602	510
10	5	662	654
11	5	610	534
12	5	811	796
13	5	727	811
14	5	622	592
0	6	2461	2267
2	6	851	882
5	6	532	491
6	6	930	1308
8	6	1763	1696
9	6	478	421
11	6	571	567
12	6	583	553
13	6	467	236
14	6	821	661
1	7	286	237
2	7	1550	1528
3	7	983	968
5	7	811	761
6	7	449	398
7	7	1174	1162
8	7	1115	1028
9	7	1383	1310
10	7	1325	1374
12	7	695	780
13	7	673	628
16	7	596	601
0	8	1455	1749
1	8	1652	1679
2	8	473	387
3	8	764	803
4	8	1323	1241
5	8	770	687
6	8	2238	2182
7	8	462	464
8	8	1805	1840
9	8	761	820
11	8	1206	1113
12	8	855	831
13	8	772	879
1	9	790	778
2	9	2342	2410
3	9	1353	1383
4	9	1539	1524
5	9	488	562
6	9	701	730
7	9	458	457
8	9	1455	1425
9	9	1434	1438
10	9	2179	2173
13	9	851	895
14	9	704	671
0	10	1202	1329
1	10	1330	1252
2	10	541	538
3	10	458	487
4	10	1316	1334
6	10	1705	1725
8	10	1490	1341
9	10	734	790
11	10	2049	1964
12	10	755	839
13	10	1072	1093
1	11	870	805
2	11	1569	1659
3	11	1030	901
4	11	1169	1256
7	11	532	529
8	11	702	689
9	11	675	626
10	11	1018	1015
0	12	1222	1187
1	12	1233	1146
2	12	454	290
4	12	1123	1081
6	12	1345	1445
8	12	907	956
9	12	1011	1002
1	13	493	531
2	13	1371	1401
3	13	475	333
4	13	1590	1587
7	13	456	723
0	14	1073	1145
1	14	529	456
2	14	613	609
L = 8**			
0	0	3682	3701
1	0	2000	2031
2	0	1587	1550
3	0	888	813
4	0	2355	2339
5	0	2865	2862
6	0	1374	1335
7	0	1771	1776
8	0	1824	1754
9	0	1568	1615
11	0	1049	1101
12	0	2700	2756
13	0	1796	1865
16	0	1554	1479
18	0	1654	1476
1	1	1321	1360
2	1	2387	2343
3	1	2911	2848
4	1	1650	1587
5	1	2381	2365
7	1	851	872
8	1	1522	1553
9	1	1653	1654
10	1	1175	1162
11	1	795	829
12	1	986	987
13	1	540	515
14	1	1894	1798
15	1	1102	1038
16	1	645	684
17	1	774	672
18	1	633	612
0	2	1341	1261
1	2	2167	2143
3	2	688	650
4	2	2217	2236
5	2	342	124
6	2	633	570
7	2	1100	1130
8	2	1522	1447
9	2	706	705
10	2	519	400
11	2	887	934
12	2	1080	1027
13	2	1213	1267
15	2	[illegible]	375
16	2	857	850
18	2	1142	1232
1	3	618	543
2	3	2211	2150
3	3	1003	998
5	3	1682	1692
6	3	278	278
8	3	1370	1383
9	3	1717	1659
10	3	1033	1050
11	3	1549	1604
12	3	673	666
14	3	1433	1373
15	3	501	508
16	3	780	770
17	3	684	732
0	4	809	807
1	4	2127	2112
2	4	1971	1869
4	4	1498	1511
5	4	265	130
6	4	1028	1008
7	4	1013	982
8	4	1627	1540
9	4	403	386
10	4	1187	1161
11	4	1109	1014
12	4	829	807
14	4	468	360
15	4	707	763
16	4	1072	1109
18	4	1187	1089
1	5	627	634
2	5	1013	1061
3	5	1000	1032
5	5	1418	1286
6	5	815	770
8	5	1599	1483
9	5	1418	1330
10	5	1457	1442
11	5	607	622
14	5	1319	1305
16	5	886	1037
0	6	2375	2435
1	6	960	1005
2	6	788	723
4	6	2390	2348
5	6	757	781
6	6	2181	2031
7	6	1792	1818
8	6	896	899
9	6	915	834
10	6	711	780
11	6	767	752
12	6	1892	1887
13	6	1302	1297
15	6	617	562
16	6	959	1010
1	7	539	573
2	7	1240	1251
3	7	1375	1395
4	7	1094	1042
5	7	1045	1101
6	7	715	725
8	7	1646	1632
9	7	1397	1445
10	7	1118	1053
11	7	960	1042
12	7	644	700
14	7	1168	1163
15	7	[illegible]	572
16	7	1255	1201
0	8	737	779
1	8	1256	1239
2	8	544	387
3	8	325	268
4	8	739	776
5	8	1215	1241
6	8	1494	1471
7	8	1021	925
8	8	626	649
9	8	636	677
10	8	514	521
11	8	568	454
12	8	1246	1255
13	8	613	609
14	8	676	639
2	9	296	131
3	9	1431	1390
4	9	758	773
5	9	702	734
8	9	692	714
9	9	536	532
14	9	764	687
1	10	925	959
2	10	433	427
3	10	526	387
5	10	540	678
6	10	452	571
7	10	771	761
3	11	655	566
5	11	713	631
1	12	1263	1274
2	12	836	909
3	12	679	651
5	12	481	563
6	12	615	465
7	12	505	599
3	13	868	928
4	13	1082	1140
6	13	517	553
L = 9**			
1	1	326	339
2	1	1085	1069
3	1	770	788
4	1	1702	1672
5	1	1198	1223
6	1	643	598
7	1	464	388
8	1	449	449
10	1	551	489
11	1	555	497
12	1	316	212
14	1	541	607
18	1	594	651
0	2	782	811
1	2	1510	1567
2	2	1113	1037
4	2	639	703
5	2	489	486
7	2	624	631
8	2	852	839
11	2	450	426
14	2	1404	[illegible]
18	2	511	583
1	3	272	285
3	3	286	174
4	3	1300	1325
5	3	939	934
7	3	790	662
8	3	586	518
9	3	907	933
10	3	996	999
11	3	571	506
12	3	485	545
13	3	518	597
14	3	1029	1085
0	4	707	759
1	4	933	859
2	4	398	363
3	4	415	275
4	4	804	366
5	4	437	442
6	4	680	685
8	4	1207	1184
9	4	453	448
11	4	397	368
12	4	814	739
14	4	406	468
1	5	266	325
2	5	934	927
4	5	1083	1046
7	5	867	892
8	5	422	379
9	5	903	924
12	5	530	516
13	5	617	502
0	6	910	864
2	6	1345	1194
3	6	663	605
4	6	1347	1309
5	6	562	457
6	6	730	674
8	6	1104	1242
11	6	563	468
14	6	641	695
15	6	762	831
1	7	680	593
2	7	1354	1410
3	7	1796	1769
4	7	404	391
5	7	477	519
6	7	873	901
7	7	595	564
8	7	307	311
9	7	780	781
10	7	1832	1749
13	7	989	908
15	7	766	740
0	8	1285	1313
1	8	1206	1116
4	8	877	902
5	8	738	720
6	8	633	725
7	8	792	876
8	8	1671	1673
9	8	484	483
11	8	1482	1536
12	8	875	921
13	8	646	760
1	9	1109	1102
2	9	1517	1450
3	9	1133	1161
4	9	688	665
6	9	567	742
8	9	817	787
9	9	1006	959
10	9	1524	1570
13	9	1207	1258
0	10	1879	1904
1	10	1168	1118
3	10	921	878
4	10	665	842
5	10	688	698
6	10	1346	1318
8	10	889	820
9	10	625	584
11	10	1421	1412
12	10	575	481
1	11	729	717
2	11	759	757
3	11	626	682
4	11	625	641
8	11	515	586
9	11	692	752
10	11	627	671
4	12	1145	1090
5	12	584	545
6	12	1093	1175
2	13	866	915
3	13	914	891
4	13	1084	1162
L = 10**			
0	0	1006	988
1	0	1625	1644
2	0	486	493
3	0	320	310
4	0	1412	1303
5	0	719	796
6	0	3423	3515
7	0	2930	2945
8	0	2671	2634
9	0	1462	1533
10	0	804	784
11	0	1852	1962
12	0	1363	1319
13	0	1844	1805
15	0	844	775
1	1	2104	2069
2	1	3159	3223
3	1	2114	2142
4	1	1445	1315
5	1	1431	1476
6	1	581	641
8	1	1715	1713
9	1	2247	2252
10	1	1597	1574
11	1	1605	1601
13	1	775	646
14	1	1001	961
15	1	1236	1281
17	1	944	914
0	2	1394	1394
1	2	1291	1313
2	2	412	452
3	2	846	667
4	2	1538	1465
5	2	420	869
6	2	1194	1068
7	2	1761	1746
8	2	1445	1413
9	2	396	373
11	2	847	793

Table 18 continued

H	K	FOBS	FCAL
L = 10***			
12	2	810	776
13	2	841	834
15	2	708	709
1	3	1636	1620
2	3	1782	1795
3	3	1839	1900
4	3	1342	1312
5	3	1731	1678
8	3	1157	1053
9	3	1375	1380
10	3	1455	1443
11	3	571	610
12	3	715	744
13	3	441	372
14	3	1097	1020
15	3	847	811
16	3	492	420
0	4	1656	1632
1	4	1129	1166
2	4	267	254
4	4	1443	1537
5	4	1056	1096
6	4	1849	1805
7	4	1586	1633
8	4	1178	1136
12	4	706	656
13	4	750	698
16	4	532	501
1	5	1005	884
2	5	1525	1548
3	5	1290	1223
4	5	1579	1497
5	5	899	929
6	5	709	664
8	5	789	799
9	5	1045	1145
10	5	672	622
11	5	683	705
14	5	855	820
15	5	652	611
0	6	1773	1694
1	6	1722	1780
2	6	925	911
3	6	828	544
4	6	1317	1333
5	6	1928	1912
6	6	3108	3150
7	6	1913	1956
8	6	1716	1759
9	6	1951	1055
10	6	634	604
11	6	726	657
12	6	751	730
13	6	233	608
1	7	965	1050
2	7	2449	2361
3	7	2264	2266
4	7	1814	1785
5	7	345	276
6	7	419	463
7	7	620	582
8	7	1267	1324
9	7	1555	1421
10	7	1572	1700
11	7	1231	1213
14	7	687	669
0	8	2182	2101
1	8	1098	1117
2	8	429	521
4	8	448	406
5	8	1306	1269
6	8	1153	1259
7	8	1758	1722
8	8	958	984
9	8	558	582
13	8	498	343
2	9	493	510
3	9	1088	1118
8	9	615	546
9	9	739	650
10	9	848	842
11	9	848	869
0	10	428	463
1	10	1058	1107
5	10	1249	1396
6	10	875	886
7	10	588	529
2	11	571	444
3	11	825	773
4	11	656	555
7	11	639	620
0	12	916	919
1	12	835	903
2	12	739	775
3	12	718	777
5	12	888	969
L = 11***			
1	1	[illegible]	361

H	K	FOBS	FCAL
2	1	709	674
3	1	1105	1049
4	1	382	467
6	1	1095	1125
7	1	790	830
9	1	327	343
10	1	1021	1084
11	1	486	439
13	1	768	649
0	2	545	561
1	2	1165	1353
4	2	1422	1026
5	2	1924	1930
6	2	[illegible]	410
8	2	1232	1180
9	2	603	601
12	2	885	858
1	3	274	247
2	3	886	967
3	3	445	430
6	3	1261	1293
7	3	488	447
8	3	411	303
9	3	432	468
10	3	745	762
11	3	786	710
13	3	837	786
14	3	722	609
1	4	270	285
2	4	1134	1130
3	4	398	429
4	4	1164	1106
5	4	741	743
6	4	702	737
7	4	455	461
13	4	523	455
14	4	514	416
15	4	553	640
1	5	1185	1119
2	5	341	337
3	5	342	375
4	5	431	433
5	5	304	286
6	5	362	374
9	5	690	646
10	5	573	549
13	5	507	355
14	5	779	736
15	5	569	583
2	6	662	679
3	6	518	532
4	6	291	376
7	6	346	370
9	6	586	409
11	6	836	851
14	6	585	564
1	7	425	505
2	7	776	793
3	7	1153	1217
8	7	410	446
9	7	1087	1067
10	7	1180	1088
13	7	1025	994
0	8	648	628
1	8	756	710
3	8	572	509
4	8	756	799
5	8	1294	1255
7	8	909	879
8	8	1051	1024
9	8	696	747
11	8	1054	1138
12	8	862	913
13	8	652	655
1	9	690	670
2	9	1193	1199
3	9	1400	1457
9	9	1292	1227
10	9	642	718
11	9	558	529
0	10	603	744
1	10	495	520
2	10	586	521
3	10	836	861
5	10	1074	1120
6	10	508	609
7	10	1427	1416
8	10	879	935
1	11	677	583
2	11	487	502
3	11	601	650
0	12	532	541
1	12	546	545
2	12	851	842
4	12	909	342
5	12	657	649
L = 12***			
0	0	1013	1875
1	0	2344	2161

H	K	FOBS	FCAL
2	0	371	256
3	0	1251	1258
4	0	1969	1976
5	0	1840	1826
6	0	1503	1397
7	0	1966	1893
8	0	1666	1717
9	0	511	497
11	0	650	649
12	0	1954	1573
13	0	1247	1254
1	1	1337	1381
2	1	1927	1821
3	1	1770	1793
4	1	926	934
5	1	1233	1159
6	1	1205	1148
7	1	1046	1027
8	1	1160	1176
9	1	1616	1588
10	1	1684	1652
11	1	1157	1396
13	1	1135	1090
14	1	687	620
15	1	1564	1525
16	1	810	756
0	2	1565	1598
1	2	808	787
2	2	558	527
3	2	1038	1020
4	2	659	711
5	2	1319	1245
6	2	1125	1031
7	2	1495	1588
8	2	1699	1776
9	2	688	667
11	2	818	870
12	2	575	561
13	2	571	563
15	2	601	589
1	3	1169	1188
2	3	1364	1384
3	3	1863	1966
4	3	881	897
5	3	342	270
6	3	455	364
7	3	306	267
8	3	945	965
9	3	1519	1494
10	3	1355	1296
13	3	837	988
14	3	655	622
15	3	1042	995
0	4	2227	2237
1	4	667	639
2	4	1277	1213
3	4	1241	1262
4	4	932	848
5	4	1191	1181
6	4	1548	1516
7	4	1289	1252
8	4	878	921
9	4	439	396
11	4	982	908
12	4	583	509
15	4	672	732
1	5	1418	1452
2	5	1763	1745
3	5	1469	1450
4	5	1666	1659
5	5	311	393
8	5	765	837
9	5	1341	1261
10	5	590	551
13	5	624	588
14	5	576	647
0	6	1676	1650
1	6	1581	1552
2	6	475	497
3	6	527	403
4	6	1201	1045
5	6	1914	1940
6	6	1335	1507
7	6	1478	1418
8	6	552	605
9	6	545	611
10	6	1049	1072
12	6	1302	1303
13	6	1123	1076
1	7	464	440
2	7	1724	1671
3	7	1585	1552
4	7	1656	1615
5	7	878	878
6	7	644	579
7	7	744	748
8	7	1166	1285
9	7	1410	1360
10	7	1845	1815

H	K	FOBS	FCAL
11	7	712	770
13	7	667	555
0	8	1296	1206
1	8	1194	1084
4	8	752	908
5	8	1359	1412
6	8	1039	1028
7	8	1181	1198
8	8	851	856
11	8	861	798
2	9	935	890
3	9	694	864
4	9	815	888
7	9	603	523
9	9	561	678
0	10	528	589
1	10	497	471
2	10	540	505
6	10	822	883
4	11	723	726
6	11	540	407
0	12	441	314
L = 13***			
1	1	803	756
4	1	306	339
5	1	577	547
6	1	362	401
7	1	383	419
9	1	597	613
10	1	451	502
15	1	649	653
0	2	1372	1376
1	2	279	273
2	2	612	563
3	2	615	509
5	2	356	394
7	2	1472	1499
10	2	531	526
11	2	583	430
12	2	526	487
1	3	961	1034
2	3	1067	1063
3	3	490	573
4	3	285	317
5	3	655	622
8	3	644	608
9	3	712	676
10	3	402	370
12	3	559	550
1	4	307	240
2	4	700	724
3	4	431	441
4	4	794	752
5	4	894	900
7	4	484	431
9	4	707	718
3	5	305	356
5	5	415	431
9	5	419	369
10	5	573	415
12	5	539	448
13	5	488	400
0	6	536	263
1	6	578	520
2	6	554	518
4	6	553	516
5	6	799	812
7	6	863	909
9	6	1170	1200
11	6	467	236
1	7	620	565
3	7	1417	1263
5	7	450	515
9	7	884	808
10	7	747	656
11	7	793	794
12	7	693	452
0	8	731	705
1	8	908	817
2	8	425	406
5	8	1138	1020
7	8	1464	1459
9	8	919	1291
10	8	953	1008
1	9	758	876
2	9	737	691
3	9	1593	1705
5	9	942	956
9	9	1299	1262
1	10	616	472
5	10	981	1005
7	10	1265	1311
1	11	504	562
3	11	1016	1041
L = 14***			
0	0	2341	2231
1	0	1550	1569
2	0	472	447
3	0	844	856

H	K	FOBS	FCAL
5	0	2550	2448
6	0	584	567
7	0	2109	2026
8	0	1449	1489
11	0	675	552
12	0	1201	1151
1	1	1056	1068
2	1	1728	1707
3	1	1476	1579
4	1	347	287
6	1	709	741
7	1	1335	1372
9	1	1693	1606
10	1	1488	1467
11	1	516	529
13	1	1345	1346
0	2	2064	2015
1	2	982	1028
2	2	495	726
3	2	809	824
4	2	337	284
5	2	1632	1571
6	2	417	343
7	2	1649	1684
8	2	808	794
11	2	764	616
12	2	632	439
1	3	983	1061
2	3	545	529
3	3	1068	1107
4	3	705	668
7	3	490	595
8	3	491	453
9	3	1206	1259
10	3	849	873
13	3	1126	1065
0	4	855	930
2	4	645	726
3	4	982	1017
5	4	1160	1102
7	4	1212	1193
11	4	923	943
12	4	910	855
13	4	491	314
1	5	1267	1180
2	5	1321	1387
3	5	1727	1702
4	5	808	849
5	5	684	711
7	5	527	480
9	5	1215	1268
10	5	570	414
0	6	1008	985
1	6	642	622
3	6	479	504
5	6	1476	1498
6	6	804	788
7	6	1273	1106
11	6	1629	1580
1	7	674	611
2	7	1320	1453
3	7	1443	1508
4	7	770	739
5	7	505	536
7	7	442	406
8	7	852	789
9	7	947	800
10	7	609	623
0	8	889	787
1	8	952	945
5	8	1168	1113
6	8	925	991
7	8	496	519
8	8	681	685
9	8	578	508
4	9	543	500
L = 15***			
2	1	469	535
4	1	381	483
0	2	719	670
1	2	930	923
3	2	420	299
5	2	1211	1132
7	2	733	698
9	2	846	852
1	3	568	558
2	3	1011	1070
3	3	768	756
4	3	497	449
5	3	657	711
8	3	665	730
9	3	770	766
10	3	747	718
0	4	905	892
1	4	452	360
6	4	458	481
7	4	551	550
9	4	499	545
1	5	836	819

Table 18 continued

H	K	FOBS	FCAL
L = 15**			
2	5	665	653
3	5	640	539
0	6	1160	1154
1	6	492	490
3	6	831	845
5	6	758	830
7	6	731	461
9	6	869	808
1	7	597	468
2	7	698	642
3	7	1076	1041
9	7	833	835
0	8	927	923
1	8	514	517
3	8	733	628
5	8	1273	1270
7	8	1298	1349
1	9	732	785
2	9	882	949
3	9	1681	1721
4	9	450	495
L = 16**			
0	0	1380	1539
1	0	1430	1399
3	0	803	853
5	0	1407	1286
7	0	1709	1768
10	0	984	1110
11	0	1123	1111
1	1	979	929
2	1	617	668
3	1	1183	1107
6	1	438	452
7	1	677	695
9	1	1890	2010
10	1	457	459
0	2	1104	1082
1	2	891	851
3	2	1025	1015
5	2	1171	1132
6	2	513	560
7	2	1426	1497
10	2	768	794
11	2	1173	1161
1	3	717	815
3	3	493	533
5	3	467	414
7	3	897	897
9	3	965	911
10	3	742	682
2	4	480	471
3	4	552	503
5	4	969	999
6	4	585	616
7	4	593	709
3	5	1169	1282
7	5	951	1016
9	5	1232	1361
1	6	924	890
5	6	1342	1332
7	6	814	748
1	7	587	630
2	7	396	282
3	7	1308	1484
5	7	893	860
1	8	803	746
L = 17**			
3	1	663	674
6	1	580	507
0	2	700	714
1	2	835	895
5	2	800	813
6	2	491	578
1	3	839	822
2	3	419	362
3	3	769	698
9	3	971	1015
0	4	627	632
3	4	464	467
4	4	449	466
6	4	478	462
1	5	551	647
2	5	546	545
3	5	427	385
0	6	972	1030
3	6	418	444
5	6	634	531
1	7	533	437
2	7	837	858
L = 18**			
0	0	811	688
1	0	1634	1730
3	0	396	248
4	0	501	492
5	0	600	610
6	0	728	720
7	0	1235	1348
1	1	970	1013
3	1	1174	1184
4	1	830	693
5	1	530	496
1	2	1162	1106
3	2	436	405
6	2	715	719
7	2	1194	1259
1	3	873	900
3	3	991	1036
4	3	465	432
6	3	464	526
1	4	1373	1391
5	4	787	929
1	5	815	783
3	5	1217	1256
L = 19**			
1	1	608	672
1	2	563	586

Table 19

Atomic Coordinates and Isotropic Temperature Factors

Name	x	y	z	B
Rh	0.16618(4)	0.23480(5)	0.23730(4)	2.3*
Cℓ1	0.1727(1)	0.1049(2)	0.2386(1)	3.4*
P1	0.0722(1)	0.2154(2)	0.2424(1)	2.8*
P2	0.1877(1)	0.2637(2)	0.3333(1)	2.4*
P3	0.2531(2)	0.2252(2)	0.1938(1)	2.9*
Cℓ2	0.4111(3)	0.2504(5)	0.4869(4)	17.4*
Cℓ3	0.3976(3)	0.0987(4)	0.4933(3)	14.9*
C1	0.3687(9)	0.179(1)	0.506(1)	12.9*
Cℓ4	0.1302(2)	0.4769(3)	0.0778(3)	13.1*
Cℓ5	0.0451(4)	0.3844(4)	0.0444(3)	18.7*
C2	0.0846(9)	0.410(1)	0.1009(9)	11.2*
O1	0.1447(3)	0.2832(4)	0.1595(3)	3.4
O2	0.1534(3)	0.3341(4)	0.2041(3)	2.9

* These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors shown in table 20

(Table continued)

Table 19 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0411(7)	0.1660(5)	0.3022(5)	3.4(3)
C112	-0.0131(6)	0.1760(5)	0.3152(3)	6.4(4)
C113	-0.0363(6)	0.1386(6)	0.3612(5)	8.0(5)
C114	-0.0052(7)	0.0912(5)	0.3941(5)	6.1(4)
C115	0.0491(6)	0.0812(5)	0.3811(3)	5.6(4)
C116	0.0723(6)	0.1186(6)	0.3352(5)	4.1(4)
D	5.432(5)	$x^{1\ddagger}$	0.0180(3)	
E	0.372(8)	$y^{1\ddagger}$	0.1286(3)	
F	0.85(1)	$z^{1\ddagger}$	0.3482(3)	
C121	0.0546(4)	0.1579(5)	0.1814(3)	2.4(3)
C122	0.0437(4)	0.0840(5)	0.1880(3)	3.8(4)
C123	0.0327(4)	0.0413(4)	0.1398(5)	4.9(4)
C124	0.0326(4)	0.0725(5)	0.0851(3)	4.9(4)
C125	0.0436(4)	0.1464(5)	0.0786(3)	5.3(4)
C126	0.0546(4)	0.1891(4)	0.1267(5)	4.5(4)
D	0.208(5)	x^1	0.0436(2)	
E	1.666(5)	y^1	0.1152(3)	
F	2.528(6)	z^1	0.1332(3)	
C131	0.0302(4)	0.2949(5)	0.2324(3)	3.4(3)
C132	0.0465(3)	0.3625(6)	0.2533(2)	3.4(3)
C133	0.0142(4)	0.4235(4)	0.2448(4)	4.2(4)

(Table continued)

Table 19 continued

Name	x	y	z	B
C134	-0.0345(4)	0.4169(5)	0.2154(3)	5.5(4)
C135	-0.0508(3)	0.3493(6)	0.1945(2)	7.0(5)
C136	-0.0185(4)	0.2883(4)	0.2030(4)	6.4(4)
D	2.956(5)	x^1	-0.0022(3)	
E	2.644(5)	y^1	0.3559(4)	
F	2.183(7)	z^1	0.2239(2)	
C211	0.1364(3)	0.3164(6)	0.3707(3)	2.4(3)
C212	0.1371(3)	0.3921(6)	0.3727(3)	3.6(4)
C213	0.0948(4)	0.4298(3)	0.3985(4)	4.5(4)
C214	0.0518(3)	0.3916(6)	0.4224(3)	4.5(4)
C215	0.0511(3)	0.3158(6)	0.4204(3)	4.6(4)
C216	0.0934(4)	0.2782(3)	0.3945(4)	3.9(4)
D	0.035(5)	x^1	0.0941(2)	
E	0.499(5)	y^1	0.3540(3)	
F	5.764(7)	z^1	0.3965(2)	
C221	0.2445(3)	0.3293(4)	0.3348(3)	2.5(3)
C222	0.2447(4)	0.3828(5)	0.2922(3)	2.6(3)
C223	0.2830(4)	0.4381(4)	0.2937(4)	3.2(3)
C224	0.3211(3)	0.4400(4)	0.3377(3)	3.4(3)
C225	0.3209(4)	0.3866(5)	0.3803(3)	3.4(3)
C226	0.2825(4)	0.3312(4)	0.3788(4)	2.7(3)
D	0.594(5)	x^1	0.2827(2)	
E	2.300(6)	y^1	0.3846(3)	
F	5.206(7)	z^1	0.3363(2)	

(Table continued)

Table 19 continued

Name	x	y	z	B
C231	0.2074(4)	0.1967(5)	0.3875(4)	2.2(3)
C232	0.2318(4)	0.1319(5)	0.3706(3)	3.3(3)
C233	0.2492(4)	0.0823(4)	0.4121(5)	5.5(4)
C234	0.2421(4)	0.0976(5)	0.4704(4)	5.3(4)
C235	0.2176(4)	0.1625(5)	0.4872(3)	5.7(4)
C236	0.2003(4)	0.2120(4)	0.4457(5)	3.9(4)
D	2.677(6)	x^1	0.2247(2)	
E	1.545(6)	y^1	0.1472(3)	
F	5.464(7)	z^1	0.4289(3)	
C311	0.2469(7	0.1793(4)	0.1236(5)	2.7(3)
C312	0.1977(5)	0.1526(5)	0.1039(7)	3.3(3)
C313	0.1949(4)	0.1171(5)	0.0509(4)	4.5(4)
C314	0.2412(7)	0.1084(4)	0.0177(5)	3.9(4)
C315	0.2903(5)	0.1352(5)	0.0375(7)	5.4(4)
C316	0.2931(4)	0.1707(5)	0.0905(4)	4.5(4)
D	1.062(5)	x^1	0.2440(3)	
E	0.38(1)	y^1	0.1439(2)	
F	1.86(1)	z^1	0.0707(2)	
C321	0.3020(4)	0.1683(5)	0.2319(3)	2.5(3)
C322	0.3099(4)	0.0958(6)	0.2164(3)	4.2(4)
C323	0.3463(4)	0.0529(4)	0.2470(4)	5.7(4)
C324	0.3747(4)	0.0825(5)	0.2931(3)	5.5(4)
C325	0.3668(4)	0.1550(6)	0.3086(3)	4.8(4)

(Table continued)

Table 19 continued

Name	x	y	z	B
C236	0.3304(4)	0.1979(4)	0.2780(4)	3.9(4)
D	2.861(5)	x^1	0.3383(2)	
E	2.276(5)	y^1	0.1254(3)	
F	5.654(7)	z^1	0.2625(2)	
C331	0.2902(4)	0.3077(4)	0.1720(3)	3.1(3)
C332	0.3452(4)	0.3168(5)	0.1814(3)	4.9(4)
C333	0.3703(4)	0.3814(6)	0.1653(3)	6.1(4)
C334	0.3405(4)	0.4370(4)	0.1399(3)	5.0(4)
C335	0.2855(4)	0.4279(5)	0.1305(3)	4.0(4)
C336	0.2603(3)	0.3632(6)	0.1466(3)	3.0(3)
D	3.536(5)	x^1	0.3153(2)	
E	2.933(5)	y^1	0.3723(3)	
F	1.177(7)	z^1	0.1560(2)	

‡ Coordinates of center of gravity of ring.

(Table continued)

Table 19 continued

(b) Phenyl Hydrogen Atoms

Name	x	y	z	B
H112	-0.0353	0.2102	0.2915	7.0
H113	-0.0752	0.1460	0.3704	8.8
H114	-0.0219	0.0644	0.4271	6.7
H115	0.0713	0.0471	0.4048	6.2
H116	0.1112	0.1112	0.3259	4.5
D	5.432			
E	0.374			
F	1.890			
H122	0.0437	0.0615	0.2272	4.2
H123	0.0248	-0.0118	0.1444	5.4
H124	0.0247	0.0419	0.0505	5.4
H125	0.0436	0.1689	0.0393	5.8
H126	0.0625	0.2422	0.1221	4.9
D	0.208			
E	0.166			
F	3.576			
H132	0.0815	0.3669	0.2743	3.7
H133	0.0261	0.4719	0.2598	4.6
H134	-0.0576	0.4609	0.2094	6.0
H135	-0.0858	0.3449	0.1734	7.7
H136	-0.0303	0.2399	0.1880	7.0

(Table continued)

Table 19 continued

Name	x	y	z	B
D	2.956			
E	2.644			
F	3.230			
H212	0.1682	0.4194	0.3557	4.0
H213	0.0956	0.4842	0.4000	4.9
H214	0.0215	0.4188	0.4409	4.9
H215	0.0200	0.2886	0.4374	5.0
H216	0.0927	0.2238	0.3931	4.3
D	0.035			
E	0.499			
F	6.811			
H222	0.2172	0.3811	0.2607	2.9
H223	0.2830	0.4763	0.2630	3.5
H224	0.3485	0.4800	0.3385	3.7
H225	0.3483	0.3882	0.4118	3.7
H226	0.2826	0.2930	0.4095	3.0
D	0.594			
E	2.300			
F	6.253			
H232	0.2369	0.1208	0.3288	3.6
H233	0.2667	0.0358	0.4000	6.0
H234	0.2545	0.0622	0.5002	5.8
H235	0.2125	0.1736	0.5290	6.3

(Table continued)

Table 19 continued

Name	x	Y	z	B
H236	0.1827	0.2587	0.4577	4.3
D	2.677			
E	1.545			
F	6.511			
H312	0.1644	0.1589	0.1276	3.6
H313	0.1597	0.0979	0.0367	4.9
H314	0.2392	0.0829	-0.0202	4.3
H315	0.3236	0.1289	0.0138	5.9
H316	0.3284	0.1899	0.1048	4.9
D	1.062			
E	0.38			
F	2.90			
H322	0.2894	0.0745	0.1833	4.6
H323	0.3520	0.0009	0.2359	6.3
H324	0.4008	0.0518	0.3150	6.0
H325	0.3872	0.1763	0.3417	5.3
H326	0.3247	0.2499	0.2891	4.3
D	2.861			
E	2.276			
F	6.701			
H332	0.3666	0.2769	0.1998	5.4
H333	0.4098	0.3879	0.1721	6.7
H334	0.3586	0.4834	0.1283	5.5

(Table continued)

Table 19 continued

Name	x	Y	z	B
H335	0.2641	0.4678	0.1121	4.4
H336	0.2208	0.3568	0.1398	3.3
D	3.536			
E	2.933			
F	2.224			

Table 20

Anisotropic Temperature Factors ($\mathring{A}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	34.0(9)	24.8(9)	26.8(9)	0.9(7)	- 2.6(7)	3.0(6)
Cℓ1	51(3)	25(2)	55(2)	4(2)	1(2)	1(2)
P1	41(3)	30(3)	35(3)	2(2)	- 5(2)	2(2)
P2	36(3)	25(3)	30(2)	-2(2)	- 2(2)	5(2)
P3	43(3)	33(3)	33(2)	0(3)	0(2)	4(2)
Cℓ2	144(6)	186(7)	330(10)	36(6)	6(6)	4(7)
Cℓ3	182(7)	185(8)	198(7)	37(6)	40(5)	-43(5)
C1	140(20)	38(15)	312(30)	-7(16)	100(20)	-72(17)
Cℓ4	142(6)	115(6)	242(7)	20(5)	33(5)	14(5)
Cℓ5	327(11)	213(8)	172(6)	-54(7)	-119(7)	47(6)
C2	165(21)	123(19)	140(18)	-87(17)	- 66(16)	87(14)

Table 21

Selected Interatomic Distance

Atom 1	Atom	Distance (Å)	
Rh	Cℓ1	2.391(3)	2.401(3)*
Rh	P1	2.362(4)	2.365(4)*
Rh	P2	2.357(3)	2.357(3)*
Rh	P3	2.387(4)	2.391(4)*
Rh	O1	2.081(8)	
Rh	O2	2.005(8)	
P1	C111	1.828(7)	
P1	C121	1.819(7)	
P1	C131	1.809(7)	
P2	C211	1.836(7)	
P2	C221	1.836(7)	
P2	C231	1.818(7)	
P3	C311	1.840(7)	
P3	C321	1.829(7)	
P3	C331	1.842(7)	
O1	O2	1.413(9)	
C1	Cℓ2	1.74(2)	
C1	Cℓ3	1.67(2)	
C2	Cℓ4	1.75(2)	
C2	Cℓ5	1.70(2)	

* A riding correction was performed on these bondlengths with atom 2 assumed to ride on atom 1

Table 22

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
O1	Rh	O2	40.4(3)
O1	Rh	P1	90.0(2)
O1	Rh	P2	101.3(2)
O1	Rh	P3	92.8(2)
O1	Rh	Cℓ1	157.4(2)
O2	Rh	P1	81.7(2)
O2	Rh	P2	141.7(2)
O2	Rh	P3	84.1(2)
O2	Rh	Cℓ1	117.0(2)
P1	Rh	P2	102.7(1)
P1	Rh	P3	154.4(1)
P1	Rh	Cℓ1	85.1(1)
P2	Rh	P3	101.6(1)
P2	Rh	Cℓ1	101.3(1)
P3	Rh	Cℓ1	82.5(1)
Rh	P1	C111	122.0(4)
Rh	P1	C121	106.6(3)
Rh	P1	C131	116.2(4)
Rh	P2	C211	113.4(3)
Rh	P2	C221	110.1(3)
Rh	P2	C231	124.2(3)
Rh	P3	C311	109.4(4)

(Table continued)

Table 22 continued

Atom 1	Atom 2	Atom 3	Angle (°)
Rh	P3	C321	115.9(3)
Rh	P3	C331	120.4(4)
O1	O2	Rh	66.9(4)
O2	O1	Rh	72.7(5)
Rh	O1	C2	157(1)
O2	O1	C2	84(1)
O1	C2	Cℓ4	111(1)
O1	C2	Cℓ5	114(1)
O2	C2	Cℓ4	99(1)
O2	C2	Cℓ5	133(1)
Cℓ2	C1	Cℓ3	111(1)
Cℓ4	C2	Cℓ5	109(1)
P1	C111	C114	179.3(7)
P1	C121	C124	177.0(6)
P1	C131	C134	179.2(6)
P2	C211	C214	176.0(6)
P2	C221	C224	174.1(5)
P2	C231	C234	176.6(6)
P3	C311	C314	178.0(7)
P3	C321	C324	178.2(6)
P3	C331	C334	176.5(7)
C222	H222	O2	157.8
C223	H223	Cℓ1	140.5

(1/2-x, 1/2+y, z)

Table 23

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	H312	2.90
Cℓ1	H116	2.54
Cℓ1	H232	2.64
Cℓ1	H312	2.77
O11	H126	2.34
C21	H336	2.37
O2	H336	2.28
O2	H222	2.23
O2	H132	2.49
O2	C2	3.26(2)
O1	C2	3.08(2)
H332	H326	2.37

Table 24

Selected Intermolecular Contacts

Atom 1	Atom 4	Symmetry Operation (on atom 2)	Distance (Å)
Cℓ1	H223	1/2-x, 1/2+y-1, z	2.66
H122	H134	$\bar{x}$, 1/2+y-1, 1/2-z	2.39
H122	H133	$\bar{x}$, 1/2+y-1, 1/2-z	2.41
H136	H325	1/2+x-1, y, 1/2-z	2.45
H213	H324	1/2-x, 1/2+y, z	2.33
H225	H315	x, 1/2-y, 1/2+z	2.46

Fig. 8

A General View of $[(O_2)RhC\ell(P(C_6H_5)_3)_3\cdot 2CH_2C\ell_2]$

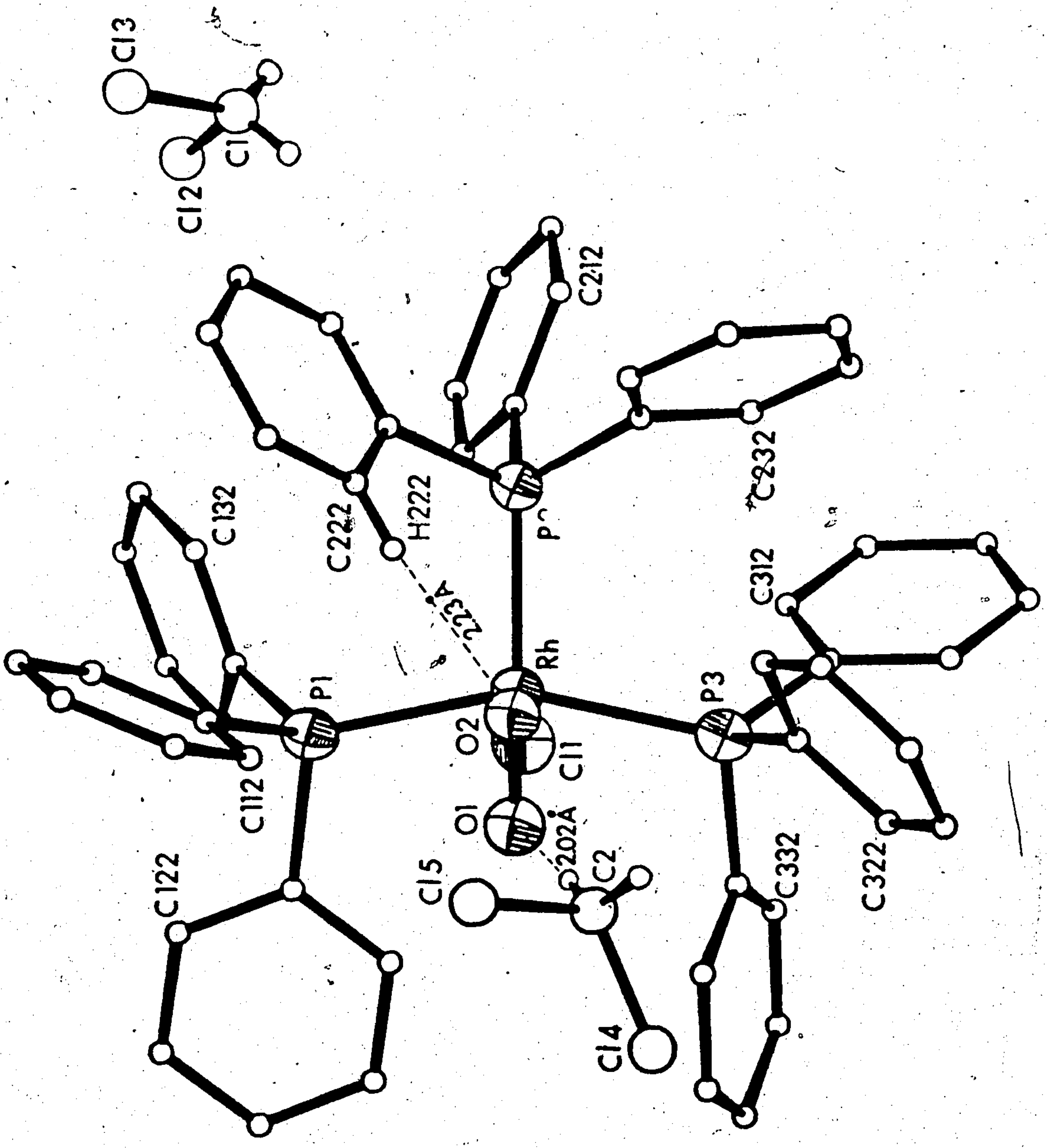


Fig. 9

Equatorial Plane Geometry

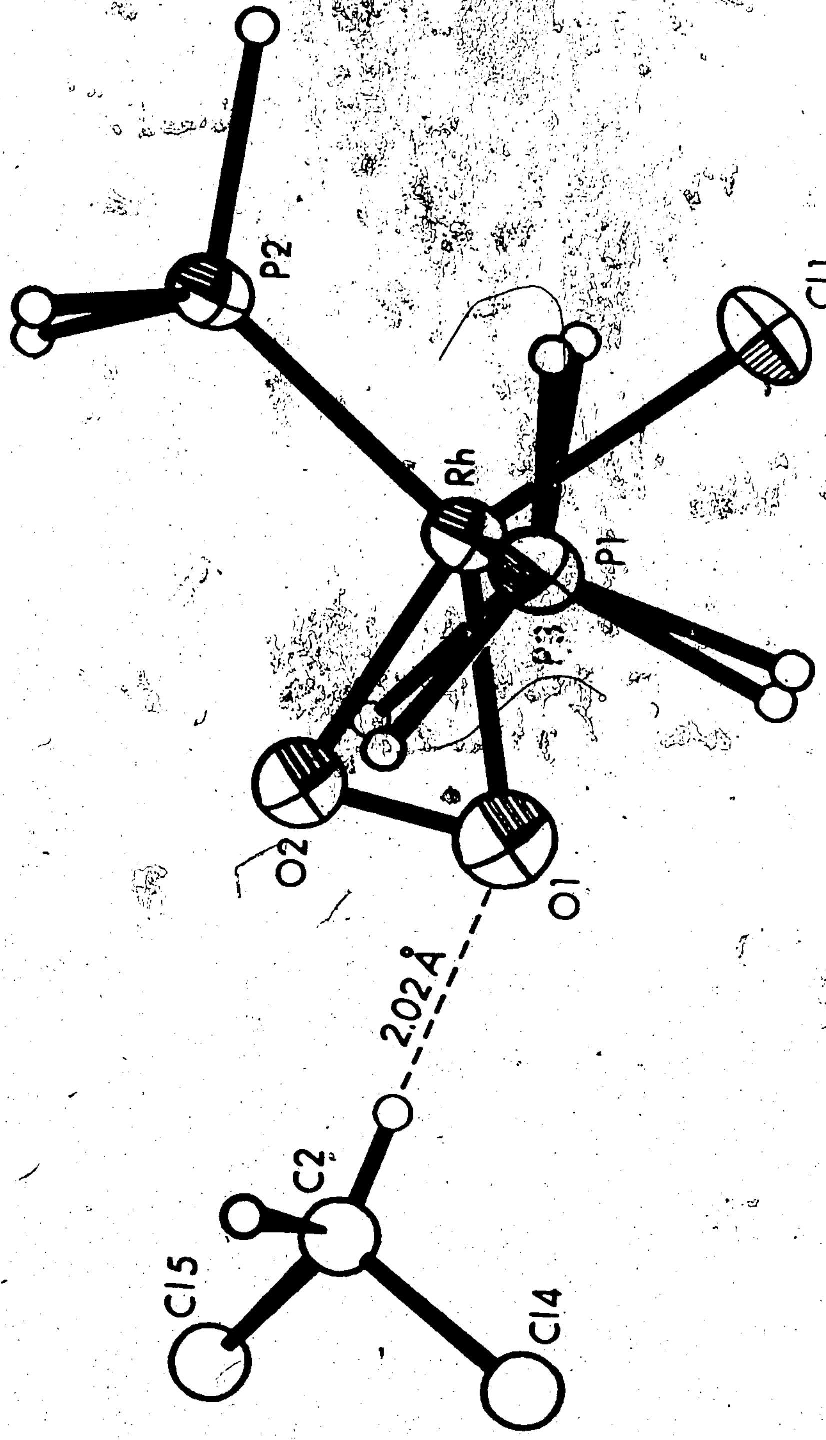
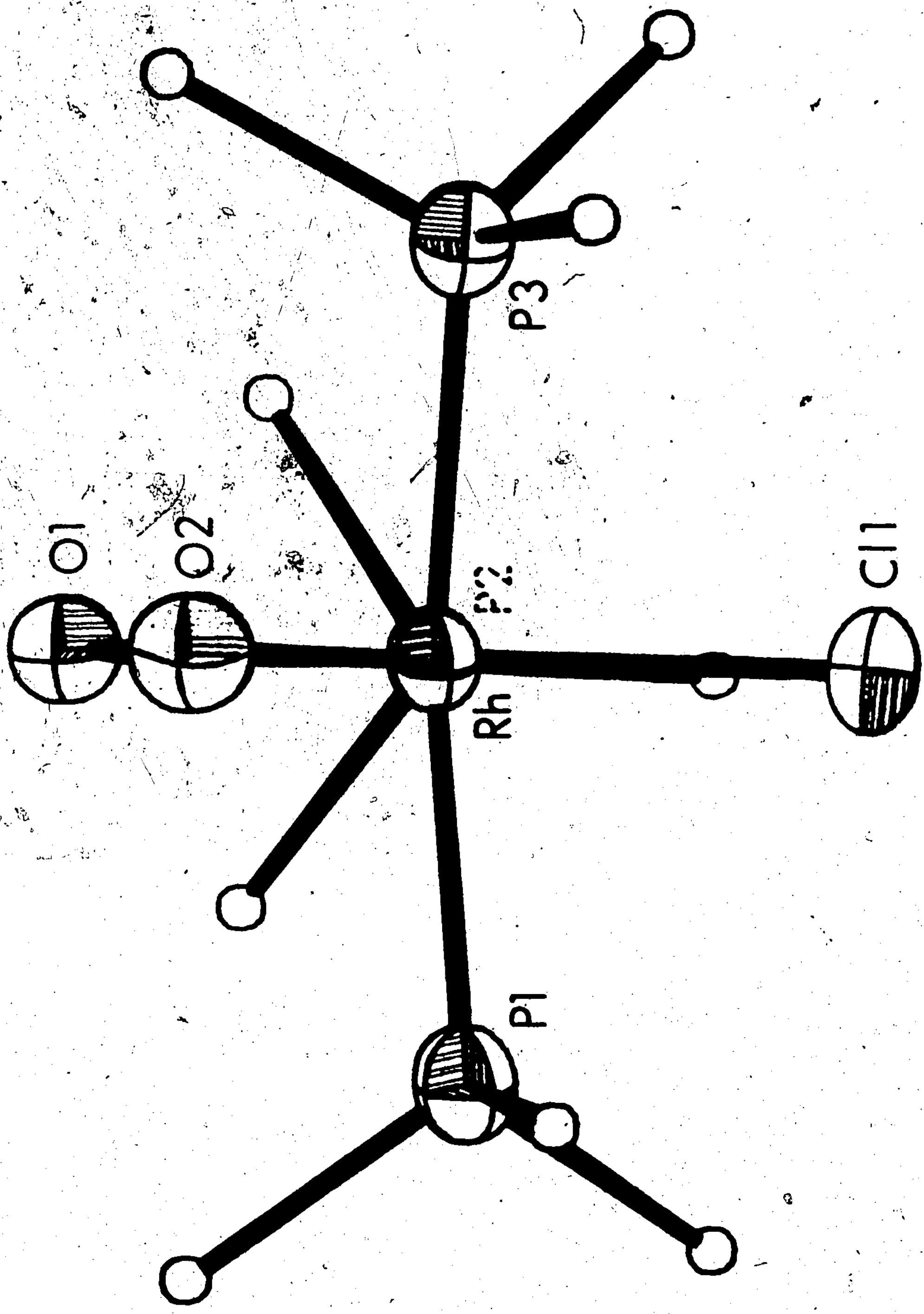


Fig. 10

Central Geometry Viewed down the Rh-P2 Bond



Discussion

The complex has a trigonal bipyramidal structure if dioxygen is treated as occupying a single coordination site (which is the preferred view in this thesis). Alternatively if dioxygen is treated as a bidentate ligand then the structure is approximately octahedral. In the trigonal bipyramidal description, the two axial sites are occupied by triphenylphosphine ligands while the equatorial sites (Fig. 10) contain the third phosphine ligand, the chlorine atom (Cℓ1) and the dioxygen molecule (with both oxygen atoms in the equatorial plane). The molecule is then coordinatively saturated (Fig. 8).

The rhodium-phosphorus bond lengths (Rh-P1, 2.365(4); Rh-P2, 2.357(3); Rh-P3, 2.391(3) Å) show significant variation. The chemically equivalent axial rhodium-phosphorus (P1 and P3) distances ($\Delta/\sigma \sim 3$) are interesting, however the actual difference is relatively small in absolute terms (0.026 Å) and can probably be ascribed to subtle inter and intramolecular interactions. Similarly statistically significant variations were observed in the structure of $[(\mathrm{Co}(2{=}\mathrm{phos})_2(\mathrm{O}_2)]^+$ [29] and no chemical significance was assigned. The rhodium-chlorine bond length of 2.401(3) Å is normal for the rhodium complexes discussed in this thesis (see Chapter VI for further discussion). The phosphorus-carbon bond lengths average 1.829 Å which is typical for triphenylphosphine complexes[17,18,129]. The distribution of these distances was consistent with a standard deviation of 0.010 Å (compared with typical values of ~0.007 Å from the least squares refinement) and [illegible] a small systematic error is indicated. No signi[illegible] variations were observed when the bond lengths were sorted as to phosphine ligand.

The dioxygen ligand is typical of the π-bonded type (classification (1) in the introduction) and the bonding is rationalized in a manner already discussed in Chapter III. Mason[130] has given a slightly different method of viewing such charge transfer as involving a transition similar to $\pi^4\pi^{*2} \rightarrow \pi^3\pi^{*3}$. Such a description was only meant to illustrate the effects of transfer of charge from the dioxygen bonding to antibonding orbitals by comparison with dioxygen excited states, and not to illustrate the manner of charge transfer. Parshall[131] considered similar species as involving octahedral co-ordination with two σ-bonds and no π-bonds being present, however such a description does not correlate the oxygen-oxygen bond length with irreversibility of oxygenation whilst the description of Ibers *et al.*,[18] (derived from Griffith's work)[64,132] does.

The oxygen-oxygen bond length is 1.413(9) Å and is not significantly different from that observed for the dimer, 1.438(9) Å. These distances correspond approximately to that expected for a peroxide[89] and the complex could be viewed as an octahedral rhodium (III) complex, although as mentioned in the introduction such a classification may be unrealistic. The rhodium-oxygen bond lengths (Rh-O1, 2.081(8); Rh-O2, 2.005(8) Å) appear to be significantly different and hence the ligand is not symmetrically attached. This may reflect differences in the *trans*-ligand (O1 is pseudo-*trans* to P2 and O2 is pseudo-*trans* to Cℓ1). A similar trend is observed in the compound $(O_2)IrC\ell(CO)(P(C_6H_5)_2(C_2H_5))_2$ [20] where the longer metal oxygen distance is pseudo-*trans* to the better π-bonding ligand (in this case carbon monoxide). Detection of this assymmetry in the structures $(O_2)IrX(CO)(P(C_6H_5)_3)_3$, X = Cℓ, I [17,19], is impossible due to the disorder of X and CO that occurs in these crystals.

There are two other features (both short hydrogen-oxygen contacts) that may contribute to the asymmetry of the rhodium-oxygen distances. The first and probably the most important is the contact of 2.02 Å between one methylene chloride hydrogen atom and O1. This is most clearly seen in Fig. 9. This contact is considerably shorter than the sum of the van der Waals radii (2.5 Å) [120] and it is tempting to describe this interaction as a hydrogen bond [133-138]. The orientation of the methylene chloride molecule is such that the calculated position of the hydrogen atom mentioned is approximately on the line joining C2-O1. This is illustrated by the near equivalence of the angles: Cℓ4-C2-O1, 111(1)°; Cℓ5-C2-O1, 114(1)°, which are in good agreement and expected for such an orientation. The second, somewhat longer, contact (O2-H222, 2.23 Å) is intramolecular and hence it is more difficult to decide whether it is attractive or repulsive in nature, however the hydrogen atom is directed towards the oxygen with the ring having the most bending of any phenyl group in the structure (P2-C221-C224, 174.1(5)°) and very low temperature factors. Thus this interaction could possibly be attractive.

The two dioxygen derivatives described in this thesis both demonstrate that coordinated dioxygen is still basic. In the *bis*-phosphine dimer (Chapter III) the coordinated dioxygen forms a donor bond to another rhodium atom, while in the *tris*-phosphine complex the dioxygen molecule is involved in at least one hydrogen bond.

It is probable that neither of these compounds represent the major dioxygen complex formed in solution by the addition of oxygen to $RhC\ell(P(C_6H_5)_3)_3$. Rather they result from the conditions of crystallisation. The course of events is likely to be that shown below where triphenylphosphine is represented by P.

$$RhP_3C\ell + O_2 \rightleftharpoons RhP_3C\ell O_2 \qquad [1]$$

$$RhP_3C\ell O_2 \rightleftharpoons RhP_2C\ell O_2 + P \qquad [2]$$

$$2RhP_2C\ell O_2 \rightleftharpoons [RhP_2C\ell O_2]_2 \qquad [3]$$

$$[RhP_2C\ell O_2]_2 \rightleftharpoons [RhP_2C\ell O_2]_{2\,(s)} \qquad [4]$$

$$P + 1/2\ O_2 \overset{\text{catalyst}}{\rightleftharpoons} PO \qquad [5]$$

The equilibrium [2] favours $RhP_2C\ell O_2$ and only when the phosphine concentration is high does $RhP_3C\ell O_2$ form in sufficient quantity to crystallize. The dimer $[RhP_2C\ell O_2]_2$ has a very low solubility and hence cannot account for the moderately high concentrations of rhodium in solution. It is probable that reaction [3] is extremely slow in view of the steric factors involved in the formation of the dimer. Hence fresh solutions, formed by the addition of dioxygen to $RhP_3C\ell$, correspond to $RhP_2C\ell(O_2)$ in agreement with the earlier osmometric studies [3,37] and this species is thermodynamically more stable than $RhP_3C\ell(O_2)$ and kinetically stable with respect to its dimer. Reaction [5] is similar to other reactions [43] producing triphenylphosphine oxide and may explain why free triphenylphosphine is only observed in very low concentrations, whilst the oxide is usually observed in solutions having osmometric molecular weights of ~600 [37].

CHAPTER V

The Crystal and Molecular Structures of the Orange Form of $RhCl(P(C_6H_5)_3)_3$

Experimental

Orange crystals of $RhCl(P(C_6H_5)_3)_3$ were found to have a "lathe" like habit and were arranged in clusters. A suitable crystal was cut from one of these clusters and after examination under a polarizing microscope, it was mounted on the end of a thin glass fibre so that the needle axis was coincident with the goniometer axis.

Examination of preliminary Weissenberg and precession photographs indicated that the compound crystallized in the orthorhombic crystal system (Laué symmetry mmm). Absences were found that satisfied the following set of conditions (hkℓ, no restrictions; 0kℓ, k + ℓ = 2n + 1; h0ℓ, h = 2n + 1; hk0, no restrictions). This combination of absences is consistent with the space-groups $Pna2_1$ or Pnam.

The crystal was oriented on a Picker manual diffractometer with the "b" axis coincident with the ϕ axis of the instrument. Several high intensity peaks were scanned for any sign of splitting due to twinning of the crystal (a Laué photograph had been taken earlier as an initial check of the optical examination) and no evidence of twinning was observed.

Lattice parameters were then calculated using diffractometer 2θ values for 13 high angle reflections. The 2θ values were obtained with the independent ω/2θ method and utilized the positive and negative 2θ values. The crude lattice parameters from the photographic study were then subjected to a least squares refinement to give the best fit between the observed and calculated 2θ angles. The high angle reflections were chosen so that there was a large variation in the ϕ and χ angles and in all cases the α_1/α_2 splitting was resolved sufficiently to allow the α_1 peak (λ, 1.54051 Å) to be centered. Lattice parameters were a, 19.4 (3); b, 12.689(2); c, 18.202(3) Å; α = β = γ, 90°. The density of the compound was measured by flotation in aqueous potassium iodide solution as 1.363 $g\text{-}cm^{-3}$. The density calculated for four molecules in the unit cell is 1.367 $g\text{-}cm^{-3}$.

Intensity data were collected on a Picker manual diffractometer using copper Kα X-radiation, a 2° takeoff angle and a graphite crystal monochromator (002 reflecting plane). The coupled 2θ/ω method was used with 1 minute scans from (2θ-1)° to (2θ+1)°, 20 second stationary background counts being taken at the limits of the scan. The diffractometer settings were calculated with the programme MIXG2. Data were only collected to 90° in 2θ because of the rapid decrease in the intensities with increasing 2θ, as observed in the photographic study. During the data collection eight standard reflections were measured at eight hour intervals as an indication of any crystal decomposition (no evidence of which was found) and all reflections having a count rate in excess of 10^4 counts-sec^{-1} were noted. A total of 2212 reflections were measured and of this number 1412 were found to be statistically reliable using the criterion $I < 3\sigma$ for rejection. After the data collection the high intensity peaks i.e. those exceeding the linear response range of the detector, were recollected at lower voltages and scaled into the data by comparison with less intense peaks recollected in the same manner. The 0k0 reflections (at $\chi = 90°$) were measured at 10° intervals in ϕ to provide experimental confirmation of the correctness of any absorption correction.

The crystal faces were identified as members of the forms {1,0,0}, {0,1,0}, {0,0,1} and {1,1,0}. The dimensions of the crystal as measured under a microscope were $\sim$0.22 x 0.13 x 0.05 mm. Reflection data were corrected for Lorentz, polarization and absorption effects. Transmission factors varied from 0.805 to 0.550 (μ(CuKα), 47.6 cm^{-1}). Finally the structure amplitudes and their standard deviations were calculated using an uncertainty factor [10] of 0.03.

Structure Solution and Refinement

A three dimensional Patterson map was calculated and carefully examined to resolve the choice of space group. In this case the structural possibilities are: (1) $Pna2_1$ with each molecule occupying a general position and with no constraints on coordinates, (2) Pnam with each molecule occupying a special position and having a mirror plane parallel to the "xy" plane. Special positions involving $\bar{1}$ were not considered a serious option for this molecule.

These two possibilities give rise to the same rhodium-rhodium vectors (1/2 ± 2x, 1/2, 1/2; 1/2, 1/2 ± 2y, 0; ± 2x, ± 2y, 1/2) but in principle they should be resolvable from vectors involving the lighter heavy atoms (phosphorus and chlorine). In this structure three of the heavy ligand atoms have "z" coordinates approximately equal to that of the rhodium and the fourth atom (later shown to be the chlorine atom) has a "z" coordinate definitely different from the "z" coordinate of the rhodium atom albeit by a relatively small amount (Table 25). Thus spacegroup $Pna2_1$ is clearly indicated as the correct spacegroup but the heavy atom fragment (RhP_3Cl) is approximately planar and perpendicular to the "z" axis. The "z" coordinate of the rhodium atom was assigned a value of 0.250 to define the origin of the unit cell in this direction.

This pseudo mirror plane in the fragment of the molecule used for phasing the structure amplitudes produced a pseudo mirror in the electron density map calculated at this stage i.e. the map represented the electron density of the molecule and superimposed upon this was the electron density of the mirror image although not with equal weight. Solution of the structure was slow and required several electron density difference maps to locate all of the atoms. The second image disappeared as the number of atoms in the model increased. The sequence of events in solving the structure is outlined in Table 26.

Subsequent refinements of the model were routine except for incomplete refinement of the phenyl groups due to an error that was specific to rigid bodies in non-centrosymmetric spacegroups in the least squares refinement programme. Once this error had been detected and corrected the structure converged satisfactorily (Table 27). Structure factors for rhodium, chlorine, phosphorus and carbon were calculated using neutral atom scattering factors derived from Cromer's coefficients [111] and included for rhodium, phosphorus and chlorine the real and imaginary terms for anomalous dispersion. The scattering factors of Mason and Robertson [113] were used for the hydrogen atoms. Throughout the calculations the six carbon atoms of each phenyl group were treated as rigid bodies of D_{6h} symmetry with carbon-carbon bond lengths of 1.392 Å. Hydrogen atoms were included at their calculated positions (carbon-hydrogen bond length, 1.0 Å) with isotropic thermal parameters set at 10% higher than those of the carbon atoms to which they were attached. Due to the shortage of data the number of parameters was a serious concern during the refinement process and the rigid body model for the phenyl groups enabled the number of parameters to be minimized. Anisotropic thermal parameters were introduced for the rhodium, phosphorus and chlorine atoms only.

At convergence (shift/sigma = 0.12) the standard deviation of an observation of unit weight was 1.55 which is certainly acceptable in view of the constraints placed on the model. A final electron density difference map showed no systematic residual peaks with the largest positive and negative peaks being 0.44 and -0.36 e.Å^{-3} respectively (cf. carbon ~3 e.Å^{-3}). These peaks were situated in the vicinity of the 11 and 12 phenyl groups. The correlation matrix was also printed out in this final cycle (R_1 = 0.047; R_2 = 0.053) and high correlations were observed between some carbon temperature factors, however all coordinate correlations were less than 0.2.

Although the space group Pna2_1 contains both enantiomers the solutions x, y, z and x, y, $\bar{z}$ (or $\bar{x}$, y, z or x, $\bar{y}$, z) are not equivalent when anomalous scattering is included in the calculation of the structure factors. Since the space group is polar the 'incorrect' solution would have systematic coordinate errors [135] and hence errors in geometry. For this data set the solution x, y, $\bar{z}$ can be rejected on the basis of a Hamilton R factor ratio test [114] with a confidence level of greater than 99.5%

The atomic coordinates were then entered into the programme ORFFE II with their respective standard deviations and the interatomic distances and angles (with their corresponding standard deviations) calculated. Rhodium-phosphorus and rhodium-chlorine bond lengths were also calculated including an allowance for thermal motion. In this correction the lighter atom (phosphorus or chlorine) was assumed to ride on the heavier atom (rhodium). This correction was only appreciable for the rhodium-chlorine bond length.

Table 25

Assignment of Patterson Peaks

Peak Coordinates u, v, w	Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)
0.373, 0.504, 0.494	304	$1/2-2x_a,1/2,1/2$	198	0.374, 0.500, 0.500
0.500, 0.440, 0.000	295	$1/2,1/2-2y_a,0$	198	0.500, 0.442, 0.000
0.125, 0.060, 0.494	158	$2x_a,2y_a,1/2$	99	0.126, 0.058, 0.500
0.012, 0.103, 0.456	73	$x_a+x_b,y_a+y_b,1/2-z_a+z_b$	37	0.012, 0.102, 0.459
0.385, 0.399, 0.050	68	$1/2-x_a+x_b,1/2-y_a-y_b,z_a-z_b$	37	0.386, 0.398, 0.041
0.116, 0.046, 0.050	66	$x_a-x_b,-y_a+y_b,z_a-z_b$	37	0.114, 0.044, 0.041
0.382, 0.460, 0.456	60	$1/2-x_a+x_b,1/2+y_a-y_b,1/2-z_a+z_b$	37	0.386, 0.456, 0.459
0.397, 0.540, 0.494	56	$1/2+2x_b,1/2,1/2$	28	0.398, 0.500, 0.500
0.500, 0.354, 0.000	53	$1/2,1/2-2y_b,0$	28	0.500, 0.354, 0.000

Assignment Results a = Rh (0.063, 0.029, 0.250)

b = Cl (-0.051, 0.073, 0.209)

Table 26

Refinement Cycle	Atoms used in Phasing	R_1	New Atoms Located in Corresponding Difference Map
1	Rh, $C\ell$	0.425	P1,P2,P3
2	Rh,$C\ell$,P1,P2,P3	0.349	C_{111}-C_{116}, C_{131}-C_{136}, C_{211}-C_{216}
3	..	0.304	C_{321}-C_{326}, C_{331}-C_{336}
4	Rh,$C\ell$,P1,P2,P3		
	C_{111}-C_{116}, C_{131}-C_{136}	0.254	C_{121}-C_{126}, C_{221}-C_{226},
5	C_{211}-C_{216}, C_{321}-C_{326},	0.202	C_{231}-C_{236}, C_{311}-C_{316}
	C_{331}-C_{336}		
6	all atoms except	0.139	
7	hydrogen included		

Table 27

Refinement Sequence for $RhC\ell(P(C_6H_5)_3)_3$

Refinement Cycle	Model	R_1	R_2
7	all atoms isotropic	0.092	0.106
8	anomalous dispersion correction applied	0.090	0.104
9	central atoms anisotropic	0.076	0.088
10	.. .. ..	0.069	0.082
11	hydrogen atoms included	0.065	0.076
12	model x, y, $\bar{z}$ tested	0.081	0.097
13	programme error located	0.051	0.057
14[a]	.. .. ..	0.047	0.053
15	model x, y, $\bar{z}$ retested	0.052	0.064

[a] Test of convergence in cycle 14

Maximum coordinate shift as measured in terms of the corresponding standard deviation 0.05

Maximum thermal parameter shift as measured in terms of the corresponding standard deviation 0.12

Results

Table 28 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes. The atomic coordinates of all atoms are included in Table 29 with the anisotropic thermal parameters (U_{ij}) of the central atoms being listed in Table 30. Other tables include interatomic distances (Table 31) and interatomic angles (Table 32) with the inter- and intramolecular non-bonded contacts listed in Tables 33 and 34 respectively.

Fig. 11 shows the central coordination geometry viewed perpendicular to the P1-P2-P3 plane. Fig. 12 shows a similar segment of the molecule viewed down the P1-P3 direction whilst Fig. 13 represents a general view of the molecule.

Table 28

Observed and Calculated Structure Amplitudes (electrons x 10)

H	K	FOBS	FCAL
L = 0			
2	0	1889	1936
4	0	1206	1276
6	0	1613	1567
8	0	2720	2730
10	0	1962	1976
12	0	454	480
14	0	539	542
16	0	651	671
1	1	2358	2400
2	1	392	398
4	1	1915	1891
6	1	989	1004
7	1	1303	1297
9	1	1753	1791
10	1	542	546
13	1	480	491
15	1	411	431
17	1	1008	1017
0	2	480	481
2	2	167	179
3	2	1089	966
4	2	197	246
5	2	1056	1017
6	2	414	418
7	2	778	789
8	2	929	921
9	2	415	491
10	2	632	690
11	2	664	673
13	2	528	489
16	2	631	675
1	3	2081	2039
2	3	253	263
3	3	1113	1157
4	3	939	915
5	3	489	494
7	3	1448	1451
8	3	352	373
9	3	1409	1424
11	3	308	317
12	3	532	588
15	3	348	361
17	3	603	628
0	4	485	451
2	4	1038	1046
4	4	848	846
5	4	499	486
6	4	852	832
7	4	201	229
8	4	1693	1676
10	4	687	665
11	4	449	440
12	4	732	716
13	4	638	494
14	4	292	321
16	4	605	576
1	5	1296	1299
2	5	720	694
4	5	736	763
5	5	370	390
6	5	526	572
7	5	576	656
9	5	795	825
12	5	656	630
13	5	376	391
15	5	427	363
16	5	370	380
1	6	316	276
3	6	1362	1352
4	6	618	600
5	6	1500	1537
9	6	346	382
10	6	327	329
11	6	416	427
12	6	353	307
13	6	367	336
15	6	248	295
1	7	230	210
2	7	843	843
3	7	262	240
4	7	1446	1498
5	7	862	545
6	7	582	622
7	7	459	505
8	7	227	295
10	7	346	345
11	7	376	365
12	7	796	806
14	7	565	518
0	8	373	320
3	8	848	849
5	8	1077	1051
6	8	486	531
7	8	222	206
11	8	579	581
12	8	236	205
2	9	333	314
4	9	1077	1069
6	9	298	273
10	9	311	353
11	9	351	395
2	10	262	231
3	10	980	916
5	10	950	1010
9	10	462	475
1	11	624	500
2	11	542	571
4	11	1317	1295
L = 1			
2	0	2327	2394
4	0	788	777
6	0	1086	1115
10	0	1474	1444
12	0	635	568
16	0	445	459
0	1	552	546
1	1	1372	1301
3	1	539	531
4	1	441	413
5	1	957	932
6	1	409	461
7	1	721	677
8	1	1025	1003
9	1	1082	1046
10	1	423	444
11	1	1105	1087
12	1	218	193
13	1	234	212
17	1	351	374
1	2	678	469
2	2	482	515
3	2	306	295
4	2	614	605
5	2	1694	1685
6	2	422	449
7	2	1445	1425
8	2	511	581
9	2	195	205
10	2	550	535
11	2	352	329
12	2	644	674
13	2	373	363
14	2	438	358
17	2	374	331
0	3	2047	2039
1	3	1533	1549
2	3	1051	1049
3	3	342	321
4	3	1296	1204
5	3	1136	1116
6	3	1813	1440
7	3	524	517
8	3	567	618
10	3	881	902
11	3	629	641
12	3	478	498
13	3	551	535
15	3	681	679
16	3	554	540
1	4	1099	1106
2	4	1925	1949
3	4	305	330
4	4	670	639
5	4	325	348
6	4	1100	1110
7	4	465	468
8	4	480	330
9	4	731	741
10	4	1331	1356
11	4	980	920
12	4	1110	1086
14	4	427	395
15	4	458	488
16	4	270	348
0	5	1056	1055
1	5	576	[illegible]
2	5	1021	[illegible]
3	5	1161	[illegible]
4	5	172	[illegible]
5	5	600	[illegible]
6	5	762	752
7	5	593	605
8	5	757	730
9	5	437	468
10	5	581	688
11	5	1318	1328
13	5	595	648
14	5	357	394
16	5	628	625
1	6	1456	1503
2	6	912	912
3	6	1105	1129
4	6	345	394
5	6	690	725
6	6	778	746
7	6	1039	1057
9	6	646	671
10	6	376	416
14	6	356	364
15	6	828	764
0	7	494	539
1	7	272	295
2	7	741	796
3	7	643	617
4	7	247	290
5	7	221	251
6	7	844	846
7	7	1075	1082
8	7	637	613
9	7	435	421
10	7	480	580
14	7	798	781
1	8	426	387
2	8	343	377
3	8	702	692
4	8	347	354
5	8	475	526
6	8	375	329
7	8	639	646
8	8	621	643
9	8	546	572
11	8	402	382
2	9	263	289
6	9	811	817
8	9	406	426
9	9	428	361
10	9	549	546
5	10	618	587
6	10	421	407
7	10	649	667
9	10	255	242
0	11	405	350
1	11	253	156
2	11	610	616
3	11	408	435
5	11	356	394
L = 2			
0	0	4699	5262
2	0	1272	1263
4	0	858	843
6	0	1044	1037
8	0	1470	1499
10	0	989	973
12	0	342	367
14	0	901	821
16	0	616	622
1	1	2331	2378
2	1	530	557
3	1	1295	1284
4	1	2415	2421
6	1	505	529
7	1	1492	1471
8	1	455	434
9	1	1237	1228
10	1	509	493
11	1	564	490
12	1	250	258
13	1	329	340
15	1	541	551
16	1	267	223
17	1	1026	989
0	2	1176	1160
1	2	168	152
2	2	924	987
3	2	2199	2147
4	2	225	217
5	2	650	635
6	2	704	742
7	2	798	715
8	2	1423	1423
9	2	389	358
10	2	924	938
11	2	566	573
12	2	287	257
13	2	414	379
14	2	388	408
15	2	343	316
16	2	803	877
1	3	664	705
2	3	733	767
4	3	1606	1641
5	3	374	400
6	3	546	512
7	3	879	903
8	3	490	482
9	3	1499	1528
10	3	435	479
11	3	342	332
12	3	686	688
14	3	461	497
15	3	478	464
17	3	658	699
0	4	571	580
1	4	534	536
2	4	455	489
3	4	580	574
4	4	254	243
5	4	1092	1101
6	4	731	724
7	4	775	719
8	4	1169	1156
9	4	580	530
10	4	688	684
11	4	275	275
12	4	345	348
13	4	592	549
16	4	484	441
1	5	822	828
2	5	687	711
3	5	413	397
4	5	785	754
5	5	575	542
6	5	472	428
7	5	483	583
9	5	545	547
10	5	322	318
12	5	478	442
13	5	318	374
15	5	315	363
0	6	757	751
1	6	555	537
2	6	219	193
3	6	994	997
5	6	1300	1290
6	6	287	260
8	6	361	352
9	6	386	376
11	6	522	565
12	6	276	313
13	6	353	314
14	6	264	256
1	7	486	483
2	7	626	646
4	7	1126	1121
5	7	546	540
6	7	984	888
7	7	346	302
8	7	267	246
12	7	872	813
14	7	578	600
0	8	628	614
2	8	221	218
3	8	848	898
4	8	253	173
5	8	798	790
6	8	516	524
7	8	297	242
8	8	279	282
10	8	315	212
11	8	733	738
2	9	363	343
3	9	268	250
4	9	665	645
6	9	370	375
10	9	346	415
3	10	652	672
4	10	245	195
5	10	770	758
7	10	271	217
1	11	532	584
2	11	519	548
3	11	256	270
4	11	1142	1093
L = 3			
2	0	2205	2236
4	0	1935	1965
6	0	1102	1114
8	0	871	827
10	0	1387	1356
12	0	460	439
14	0	294	286
16	0	360	350
0	1	1239	1264
1	1	1288	1299
2	1	798	676
3	1	1758	1661
4	1	1411	1395
5	1	1052	1027
6	1	367	347
7	1	1148	1114
8	1	604	628
9	1	306	381
11	1	985	921
14	1	450	449
17	1	389	430
1	2	1370	1335
2	2	904	930
3	2	1356	1342
4	2	682	669
5	2	854	821
6	2	707	683
7	2	1048	984
8	2	441	425
9	2	1027	1035
10	2	705	721
11	2	541	557
12	2	813	843
13	2	320	280
14	2	576	579
16	2	267	288
17	2	432	367
0	3	1678	1696
1	3	1268	1227
2	3	182	171
3	3	1070	1101
4	3	671	672
5	3	758	717
6	3	880	879
7	3	297	348
8	3	685	683
9	3	674	664
10	3	1040	962
11	3	1028	997
12	3	582	579
13	3	607	602
14	3	307	309
15	3	394	398
16	3	485	453
1	4	1272	1282
2	4	1014	1007
3	4	708	712
4	4	1062	1070
5	4	419	396
6	4	510	483
7	4	390	427
8	4	214	241
9	4	582	548
10	4	985	995
11	4	577	628
12	4	877	875
14	4	330	378
15	4	484	457
16	4	287	250
0	5	1482	1490
1	5	876	861
2	5	1164	1180
3	5	683	614
4	5	341	363
5	5	1254	1307
6	5	986	988
7	5	229	248
8	5	953	927
9	5	513	584
10	5	569	688
11	5	843	866
13	5	475	456
14	5	553	541
15	5	343	311
1	6	1553	1593
2	6	811	824
3	6	872	901
4	6	616	587
5	6	591	567
6	6	772	812
7	6	873	989
9	6	651	659
10	6	432	463
13	6	491	498
14	6	354	386
0	7	1024	1039
1	7	233	220
2	7	1152	1140
3	7	572	539
4	7	645	682
7	7	746	760
8	7	746	748
10	7	397	461
12	7	231	149
13	7	313	316
1	8	506	497
3	8	296	296
6	8	382	379
7	8	724	731
8	8	308	310
9	8	486	509
11	8	622	570
0	9	295	309
2	9	485	367
4	9	221	182

Table 28 continued

H	K	FOBS	FCAL
00L = 3			
6	9	651	647
7	9	262	248
8	9	492	519
9	9	331	307
10	9	602	626
1	10	420	435
5	10	587	597
6	10	387	348
7	10	946	911
0	11	502	506
1	11	211	115
2	11	510	512
3	11	368	345
00L = 4			
0	0	1059	1096
2	0	1000	954
4	0	1048	1039
8	0	1422	1467
10	0	707	675
12	0	516	569
14	0	550	479
16	0	803	851
1	1	2140	2121
2	1	743	740
3	1	578	646
4	1	649	667
5	1	294	220
6	1	257	249
7	1	1130	1120
9	1	1215	1206
10	1	661	654
11	1	298	306
12	1	515	520
13	1	626	633
15	1	530	570
16	1	371	354
17	1	861	875
0	2	2391	2361
1	2	403	394
2	2	640	670
3	2	764	766
4	2	242	210
6	2	647	614
7	2	557	517
8	2	1455	1474
9	2	809	820
10	2	992	979
11	2	452	414
13	2	558	612
15	2	416	393
16	2	851	842
1	3	1515	1506
2	3	576	569
3	3	226	232
4	3	736	726
5	3	425	450
6	3	476	485
7	3	674	644
8	3	392	428
9	3	1364	1390
11	3	319	315
12	3	472	439
14	3	719	633
15	3	420	386
0	4	1213	1233
1	4	284	298
2	4	330	305
3	4	451	425
4	4	747	712
5	4	666	636
6	4	617	632
7	4	482	488
8	4	1149	1176
9	4	369	335
10	4	741	727
13	4	688	673
14	4	264	290
16	4	325	367
1	5	559	582
2	5	785	820
3	5	369	374
4	5	1403	1365
5	5	396	405
6	5	644	685
7	5	897	905
9	5	781	768
10	5	433	399
11	5	308	335
12	5	423	455
13	5	405	379
15	5	271	358
0	6	847	843
1	6	500	490
2	6	534	531
3	6	1139	1169
4	6	290	291
5	6	1206	1245
6	6	291	299
8	6	595	590
9	6	315	295
11	6	398	310
13	6	440	449
1	7	430	420
2	7	597	553
3	7	216	239
4	7	625	843
5	7	421	412
6	7	940	904
8	7	394	278
10	7	316	367
11	7	311	258
12	7	736	736
0	8	628	614
1	8	224	146
2	8	221	197
3	8	[illegible]	642
4	8	[illegible]	451
5	8	[illegible]	735
6	8	[illegible]	415
10	8	265	309
11	8	816	792
1	9	234	227
2	9	323	320
3	9	226	209
4	9	840	893
6	9	454	505
8	9	265	257
9	9	236	213
10	9	318	315
3	10	794	788
4	10	283	276
5	10	825	827
7	10	361	338
1	11	426	402
2	11	418	455
3	11	316	335
00L = 5			
2	0	1748	1746
4	0	1710	1703
6	0	1066	1051
8	0	1049	996
10	0	980	972
12	0	268	367
14	0	265	133
0	1	648	621
1	1	889	895
2	1	821	864
3	1	1402	1452
4	1	458	478
5	1	1215	1218
6	1	835	836
7	1	1244	1263
8	1	463	483
9	1	373	368
10	1	231	240
11	1	887	885
13	1	432	477
14	1	372	379
15	1	350	375
1	2	749	768
2	2	689	578
3	2	426	408
4	2	838	768
5	2	837	760
6	2	976	919
7	2	747	[illegible]
8	2	458	435
9	2	859	542
10	2	932	912
11	2	407	389
12	2	[illegible]	775
14	2	487	463
15	2	264	246
16	2	434	414
0	3	1100	[illegible]
1	3	307	[illegible]
2	3	700	750
3	3	589	574
4	3	515	518
6	3	540	501
7	3	307	429
8	3	608	564
9	3	597	559
10	3	950	886
11	3	980	903
12	3	421	381
13	3	535	537
15	3	493	524
16	3	465	471
1	4	509	460
2	4	951	919
3	4	884	922
4	4	394	439
5	4	190	129
6	4	588	530
7	4	970	935
8	4	211	193
9	4	809	826
10	4	786	829
11	4	502	482
12	4	909	855
14	4	282	313
15	4	605	582
0	5	671	662
1	5	612	623
2	5	1066	1069
3	5	517	533
4	5	353	379
5	5	861	879
6	5	922	927
7	5	243	218
8	5	744	761
9	5	305	308
10	5	306	319
11	5	867	893
14	5	613	578
1	6	1159	1176
2	6	963	929
3	6	830	824
4	6	256	289
5	6	537	539
6	6	558	627
7	6	1076	1068
9	6	527	494
10	6	399	332
13	6	436	467
14	6	299	255
0	7	620	625
2	7	839	878
3	7	280	315
4	7	342	341
6	7	676	645
7	7	557	527
8	7	596	608
10	7	399	352
13	7	356	333
1	8	481	458
3	8	294	245
4	8	289	235
5	8	261	296
6	8	316	298
7	8	509	554
9	8	401	431
11	8	588	563
0	9	411	448
1	9	395	336
2	9	435	460
6	9	782	763
8	9	541	536
1	10	421	419
3	10	372	314
5	10	430	416
7	10	890	852
0	11	512	542
2	11	495	488
00L = 6			
0	0	2578	2629
2	0	999	963
4	0	903	950
6	0	900	884
8	0	1473	1474
10	0	756	739
12	0	889	898
14	0	790	830
16	0	646	599
1	1	1487	1499
2	1	218	197
3	1	537	555
4	1	341	234
5	1	550	596
7	1	767	787
8	1	230	240
9	1	1377	1427
10	1	627	626
11	1	357	318
12	1	404	404
13	1	644	639
15	1	307	303
0	2	1239	1229
1	2	849	817
2	2	929	928
3	2	803	845
4	2	295	333
5	2	957	982
7	2	305	[illegible]
8	2	943	918
9	2	647	689
10	2	896	902
11	2	411	406
12	2	295	184
13	2	612	585
15	2	340	301
16	2	611	617
1	3	1064	1081
2	3	338	298
3	3	781	802
4	3	190	202
5	3	305	331
6	3	337	331
7	3	770	799
9	3	782	773
11	3	503	471
12	3	304	396
14	3	541	533
15	3	406	390
0	4	1427	1452
1	4	346	347
2	4	657	713
3	4	262	201
4	4	811	811
5	4	546	558
6	4	721	683
7	4	260	288
8	4	1090	1123
10	4	740	729
11	4	279	304
13	4	503	492
14	4	335	327
15	4	269	276
1	5	999	949
2	5	844	859
4	5	1496	1460
5	5	310	289
6	5	843	795
7	5	1001	992
9	5	1009	1017
12	5	572	558
13	5	344	455
14	5	305	351
0	6	1008	1075
1	6	429	430
2	6	580	575
3	6	1318	1348
5	6	1274	1276
6	6	313	288
8	6	562	495
9	6	626	387
10	6	255	275
11	6	537	526
13	6	628	577
1	7	573	573
2	7	782	764
3	7	390	414
4	7	1156	1212
5	7	482	448
6	7	964	937
7	7	226	212
10	7	387	423
12	7	725	686
0	8	417	353
2	8	283	267
3	8	386	395
4	8	432	424
5	8	603	615
6	8	242	268
11	8	487	512
1	9	353	352
2	9	220	227
4	9	639	636
6	9	461	469
8	9	391	336
1	10	264	308
2	10	301	265
3	10	920	890
5	10	938	914
00L = 7			
2	0	1032	1092
4	0	1513	1472
6	0	541	516
8	0	671	678
10	0	1081	1116
12	0	842	790
0	1	446	471
1	1	1112	1101
2	1	611	343
3	1	1700	1644
4	1	342	366
5	1	1143	1171
6	1	928	901
7	1	900	905
8	1	369	382
9	1	632	628
11	1	916	957
12	1	293	270
13	1	521	590
14	1	344	337
1	2	730	700
2	2	1057	1059
3	2	754	773
4	2	971	1044
5	2	806	815
6	2	740	776
7	2	637	678
8	2	358	447
9	2	588	591
10	2	761	768
12	2	676	719
14	2	504	513
15	2	290	252
0	3	814	813
1	3	516	502
2	3	788	647
3	3	305	293
5	3	275	246
6	3	290	294
7	3	364	400
8	3	343	354
9	3	376	466
10	3	307	361
11	3	886	899
12	3	263	233
13	3	427	366
14	3	330	296
15	3	473	472
1	4	238	184
2	4	1022	991
4	4	362	391
5	4	307	248
6	4	545	540
7	4	348	368
9	4	269	379
10	4	916	935
11	4	379	388
12	4	603	578
0	5	862	844
1	5	596	612
2	5	904	874
3	5	1068	1093
5	5	571	570
6	5	524	564
8	5	673	684
9	5	520	494
10	5	372	386
11	5	871	895
14	5	617	596
1	6	1870	1882
2	6	560	560
3	6	437	408
4	6	481	420
5	6	643	480
6	6	497	518
7	6	1034	1023
9	6	560	519
10	6	323	318
12	6	297	252
13	6	545	527
0	7	905	847
2	7	720	720
3	7	226	238
5	7	232	241
6	7	652	643
7	7	236	265
8	7	500	561
9	7	238	218
10	7	523	454
1	8	359	302
4	8	360	339
6	8	374	[illegible]
7	8	557	547
8	8	241	224
9	8	354	358
0	9	305	319
1	9	252	251
2	9	300	303
3	9	264	261
6	9	705	732
8	9	523	540
1	10	696	681
3	10	553	534
5	10	369	405
00L = 8			
0	0	1670	1654
2	0	587	560
4	0	376	385
6	0	686	665
8	0	1067	1062
10	0	395	418
12	0	984	918
16	0	580	529

Table 28 continued

H	K	FOBS	FCAL
L = 8***			
1	1	1316	1309
2	1	340	320
3	1	263	197
4	1	582	549
5	1	460	476
7	1	894	952
8	1	309	316
9	1	959	987
10	1	464	457
12	1	443	416
13	1	410	424
15	1	465	464
0	2	1205	1184
1	2	343	361
2	2	560	542
3	2	604	610
5	2	582	570
6	2	545	554
7	2	443	430
8	2	856	860
9	2	566	574
10	2	613	595
11	2	329	235
13	2	430	458
14	2	261	230
1	3	493	500
2	3	203	160
3	3	320	264
4	3	809	873
5	3	328	368
6	3	593	590
7	3	770	720
9	3	821	707
10	3	245	150
12	3	443	397
14	3	517	502
0	4	894	861
2	4	886	813
3	4	501	466
4	4	440	487
5	4	784	764
6	4	469	503
7	4	468	429
8	4	1041	1119
9	4	255	198
10	4	436	309
13	4	630	653
14	4	301	201
1	5	894	910
2	5	445	464
4	5	1015	1071
5	5	311	262
6	5	462	447
7	5	600	604
8	5	265	214
9	5	810	794
10	5	307	391
12	5	720	670
0	6	842	816
2	6	564	520
3	6	1313	1203
5	6	1197	1153
6	6	506	559
9	6	341	351
10	6	413	477
14	6	717	605
1	7	569	503
2	7	518	438
4	7	1071	1032
5	7	401	405
6	7	549	618
9	7	478	431
10	7	201	272
0	8	470	510
3	8	306	443
5	8	864	635
9	8	243	214
1	9	330	252
2	9	314	262
4	9	552	570
6	9	418	390
2	10	209	340
3	10	570	611
L = 9***			
2	0	1672	1630
4	0	1601	1632
6	0	1110	1106
8	0	420	450
10	0	1019	976
12	0	815	827
14	0	307	430
0	1	936	979
1	1	904	920
3	1	1012	1095
4	1	350	301
5	1	863	868
6	1	400	442
7	1	667	707
8	1	415	384
9	1	387	394
11	1	670	730
13	1	587	592
1	2	334	282
2	2	757	729
3	2	402	401
4	2	597	634
5	2	434	583
6	2	706	824
7	2	436	474
8	2	394	376
10	2	520	532
12	2	543	579
13	2	391	336
14	2	569	497
0	3	752	807
1	3	659	642
3	3	621	622
5	3	992	973
7	3	709	722
9	3	321	306
10	3	326	324
11	3	812	810
13	3	469	463
1	4	291	250
2	4	724	755
3	4	257	234
4	4	595	525
5	4	223	240
6	4	624	595
7	4	267	262
10	4	826	870
11	4	302	293
12	4	353	362
0	5	633	633
2	5	713	703
3	5	700	676
5	5	263	572
6	5	543	595
7	5	260	263
8	5	964	510
9	5	493	465
10	5	395	447
11	5	521	543
1	6	269	579
2	6	348	341
3	6	643	670
5	6	400	507
6	6	271	205
7	6	675	643
9	6	599	581
11	6	332	291
0	7	806	561
2	7	748	730
5	7	270	214
6	7	690	698
8	7	490	334
10	7	447	392
1	8	348	342
3	8	305	342
5	8	322	355
7	8	601	584
0	9	403	400
2	9	407	366
L = 10***			
0	0	1152	1130
2	0	430	361
4	0	226	245
6	0	762	821
8	0	921	914
10	0	343	399
12	0	649	643
14	0	445	440
1	1	918	957
2	1	691	711
4	1	466	465
5	1	553	600
6	1	370	357
7	1	657	630
8	1	420	402
9	1	617	629
10	1	404	502
11	1	301	317
12	1	555	569
13	1	207	310
0	2	807	915
2	2	528	841
5	2	529	567
6	2	455	511
8	2	867	872
9	2	376	463
10	2	324	362
11	2	302	340
12	2	253	198
13	2	368	372
1	3	669	711
2	3	361	389
3	3	320	311
4	3	631	645
5	3	235	180
6	3	410	377
7	3	539	501
9	3	774	751
12	3	497	454
0	4	767	661
1	4	302	252
2	4	437	433
3	4	568	610
4	4	399	367
5	4	756	798
6	4	357	245
7	4	414	407
[illegible]	[illegible]	707	802
[illegible]	[illegible]	370	384
[illegible]	[illegible]	723	783
2	[illegible]	370	582
4	5	917	938
6	5	401	360
7	5	804	819
8	5	232	164
9	5	565	536
10	5	562	569
12	5	753	751
0	6	746	785
1	6	400	401
2	6	419	504
3	6	990	943
5	6	812	773
8	6	388	377
10	6	401	400
1	7	292	335
3	7	266	259
4	7	713	650
6	7	264	292
0	8	269	310
3	8	651	613
4	8	273	230
5	8	501	493
6	8	257	271
2	9	316	333
L = 11***			
0	0	652	0
2	0	861	840
4	0	1090	1162
6	0	845	859
8	0	418	427
10	0	795	811
12	0	655	671
0	1	536	583
1	1	569	568
3	1	1017	1046
4	1	253	261
5	1	729	720
6	1	236	220
7	1	706	700
8	1	283	349
9	1	424	411
10	1	272	230
11	1	766	783
13	1	569	530
2	2	704	600
4	2	656	642
5	2	293	287
6	2	743	730
7	2	287	236
8	2	247	230
10	2	424	488
12	2	626	617
13	2	281	266
0	3	440	434
1	3	456	491
3	3	617	590
5	3	648	682
7	3	492	473
11	3	575	570
1	4	301	350
2	4	712	760
3	4	306	347
4	4	662	662
6	4	444	400
7	4	297	316
9	4	321	231
10	4	601	550
0	5	421	415
1	5	290	281
2	5	505	541
3	5	813	420
4	5	273	209
5	5	425	371
6	5	541	583
8	5	374	335
9	5	273	322
1	6	731	750
2	6	321	359
3	6	586	596
5	6	579	530
7	6	610	541
9	6	439	470
0	7	473	442
2	7	631	712
4	7	247	241
6	7	583	574
1	8	565	548
3	8	410	354
4	8	332	356
L = 12***			
0	0	1111	1130
2	0	580	633
4	0	352	298
6	0	646	620
8	0	974	967
10	0	352	369
1	1	649	635
2	1	396	420
4	1	401	516
5	1	261	289
7	1	591	576
9	1	647	637
10	1	407	418
0	2	632	622
3	2	484	478
5	2	505	507
7	2	286	340
8	2	588	596
9	2	368	439
10	2	406	443
11	2	252	200
1	3	646	677
2	3	273	348
3	3	357	415
4	3	665	668
6	3	421	403
7	3	385	370
8	3	358	378
9	3	567	620
0	4	906	900
2	4	546	609
3	4	516	545
4	4	369	395
5	4	556	574
7	4	398	449
8	4	672	654
9	4	247	117
10	4	383	388
1	5	768	729
2	5	293	244
4	5	936	896
6	5	490	541
7	5	560	560
9	5	635	634
0	6	457	446
3	6	606	650
4	6	261	113
5	6	765	745
6	6	276	225
8	6	383	294
2	7	422	417
4	7	560	553
6	7	373	362
0	8	332	325
L = 13***			
2	0	1062	1045
4	0	1007	1260
6	0	724	717
8	0	372	382
10	0	635	501
0	1	465	470
1	1	445	390
2	1	406	418
3	1	925	934
5	1	546	513
6	1	370	353
7	1	387	452
8	1	336	327
9	1	600	587
11	1	715	690
1	2	290	290
2	2	494	514
4	2	399	328
5	2	279	236
6	2	301	285
10	2	473	470
0	3	360	351
1	3	493	526
3	3	385	427
5	3	381	368
7	3	906	487
2	4	764	747
3	4	297	358
4	4	518	522
5	4	282	327
6	4	454	471
7	4	270	247
0	5	312	385
1	5	443	439
2	5	479	465
3	5	548	524
5	5	330	399
6	5	512	465
8	5	384	359
1	6	525	563
2	6	272	280
3	6	360	313
5	6	451	413
0	7	520	516
2	7	486	561
3	7	279	206
L = 14***			
0	0	899	865
2	0	610	635
4	0	673	694
8	0	831	857
1	1	652	681
2	1	331	326
4	1	457	457
5	1	497	495
6	1	239	224
7	1	411	508
9	1	695	667
0	2	525	545
1	2	263	248
2	2	396	390
3	2	369	349
5	2	329	335
7	2	331	290
8	2	453	433
9	2	237	241
1	3	567	584
2	3	334	325
3	3	391	382
4	3	449	432
6	3	263	357
7	3	313	290
8	3	240	250
0	4	823	820
2	4	630	709
3	4	504	509
5	4	302	320
6	4	485	386
7	4	309	268
1	5	633	693
3	5	244	136
4	5	657	686
0	6	283	264
3	6	645	556
L = 15***			
2	0	990	639
4	0	1118	1172
6	0	426	448
0	1	394	380
1	1	233	145
2	1	253	348
3	1	647	680
5	1	682	620
6	1	245	337
7	1	326	342
1	2	326	370
2	2	280	275
4	2	311	335
6	2	266	243
7	2	265	243
3	3	357	336
5	3	354	393
2	4	421	377
3	4	272	260
4	4	313	498
6	5	374	271
1	5	286	323
L = 16***			
0	0	590	617
2	0	230	219
1	1	343	371
4	1	246	207
0	2	547	610
2	2	295	224
3	2	395	428
1	3	364	365

Table 29

Atomic Coordinates and Isotropic Temperature Factors for the Unique Contents of the Unit Cell

Name	x	y	z	B *
Rh	0.06304(5)	0.02892(9)	0.2500(0)	2.38
Cℓ	-0.0508(2)	0.0726(3)	0.2088(3)	3.88
P1	0.0800(2)	0.2085(3)	0.2555(4)	2.91
P2	0.1723(2)	-0.0199(3)	0.2607(4)	2.81
P3	0.0154(2)	-0.1362(3)	0.2757(2)	2.71

* These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors given in table 30

(Table continued)

Table 29 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0247(6)	0.273(1)	0.3240(6)	3.0(4)
C112	0.0372(5)	0.377(1)	0.3439(5)	7.6(7)
C113	-0.0054(7)	0.4268(7)	0.3945(8)	8.4(7)
C114	-0.0605(6)	0.373(1)	0.4253(6)	5.8(5)
C115	-0.0730(5)	0.268(1)	0.4054(5)	4.8(4)
C116	-0.0305(7)	0.2184(7)	0.3548(8)	4.0(4)
D	0.318(8)	$x^{1\ddagger}$	-0.0179(4)	
E	0.669(8)	$y^{1\ddagger}$	0.3226(7)	
F	5.783(9)	$z^{1\ddagger}$	0.3746(4)	
C121	0.0606(6)	0.278(1)	0.1699(6)	3.4(4)
C122	0.0657(6)	0.2186(7)	0.1059(8)	3.9(4)
C123	0.0549(7)	0.266(1)	0.0379(6)	6.2(5)
C124	0.0389(6)	0.373(1)	0.0339(6)	5.7(5)
C125	0.0338(6)	0.4322(7)	0.0979(8)	6.4(6)
C126	0.0446(7)	0.385(1)	0.1659(6)	5.6(6)
D	6.061(7)	x^1	0.0497(4)	
E	1.632(8)	y^1	0.3254(6)	
F	3.599(8)	z^1	0.1019(5)	
C131	0.1620(8)	0.2692(8)	0.2818(9)	2.6(4)
C132	0.201(1)	0.3252(9)	0.2308(6)	3.2(4)
C133	0.2614(8)	0.3746(8)	0.253(1)	5.3(4)

(Table continued)

Table 29 continued

Name	x	y	z	B
C134	0.2830(8)	0.3680(8)	0.3254(9)	4.6(5)
C135	0.244(1)	0.3119(9)	0.3763(6)	6.1(5)
C136	0.1837(8)	0.2625(8)	0.355(1)	5.7(5)
D	0.979(6)	x^1	0.2225(4)	
E	1.97(1)	y^1	0.3186(5)	
F	5.34(1)	z^1	0.3036(4)	
C211	0.2396(6)	0.0833(8)	0.220(1)	2.9(4)
C212	0.232(1)	0.0852(8)	0.1451(7)	3.8(4)
C213	0.282(1)	0.1424(8)	0.1081(8)	5.7(5)
C214	0.3401(6)	0.1777(8)	0.146(1)	4.8(5)
C215	0.348(1)	0.1559(8)	0.2201(7)	3.1(4)
C216	0.298(1)	0.0987(8)	0.2571(8)	3.5(3)
D	1.017(6)	x^1	0.2899(4)	
E	2.01(1)	y^1	0.1205(5)	
F	4.58(1)	z^1	0.1826(4)	
C221	0.1885(8)	-0.1394(8)	0.2047(9)	2.9(4)
C222	0.1481(7)	-0.1499(9)	0.1420(6)	4.4(5)
C223	0.1593(9)	-0.233(1)	0.0939(5)	6.3(5)
C224	0.2109(8)	-0.3064(8)	0.1085(9)	6.5(5)
C225	0.2513(7)	-0.2959(9)	0.1712(6)	5.9(5)
C226	0.2401(9)	-0.212(1)	0.2193(5)	5.0(5)
D	2.548(7)	x^1	0.1997(4)	
E	2.239(9)	y^1	-0.2229(6)	
F	4.305(9)	z^1	0.1566(4)	

(Table continued)

Table 29 continued

Name	x	y	z	B
C231	0.204(2)	-0.044(1)	0.356(1)	3.7(4)
C232	0.268(1)	-0.087(1)	0.372(1)	7.3(6)
C233	0.2879(6)	-0.104(1)	0.445(2)	7.8(6)
C234	0.244(2)	-0.076(1)	0.502(1)	6.5(6)
C235	0.180(1)	-0.032(1)	0.486(1)	7.2(6)
C236	0.1601(6)	-0.016(1)	0.413(2)	5.1(5)
D	1.986(8)	x^1	0.2240(5)	
E	1.51(2)	y^1	-0.0599(6)	
F	5.91(2)	z^1	0.4289(5)	
C311	-0.0533(6)	-0.1085(9)	0.3436(8)	2.9(4)
C312	-0.0379(5)	-0.0402(8)	0.4012(5)	3.5(4)
C313	-0.0876(8)	-0.0167(8)	0.4537(7)	4.5(4)
C314	-0.1527(6)	-0.0613(9)	0.4486(8)	4.8(5)
C315	-0.1682(5)	-0.1295(8)	0.3911(5)	4.2(4)
C316	-0.1185(8)	-0.1531(8)	0.3385(7)	3.6(4)
D	0.887(7)	x^1	-0.1030(4)	
E	0.51(1)	y^1	-0.0849(5)	
F	5.94(1)	z^1	0.3961(4)	
C321	0.0649(6)	-0.2422(8)	0.3208(8)	3.6(4)
C322	0.0965(9)	-0.320(1)	0.2785(4)	3.6(4)
C323	0.1365(6)	-0.3968(8)	0.3121(8)	4.8(5)
C324	0.1449(6)	-0.3965(8)	0.3886(8)	4.7(5)

(Table continued)

Table 29 continued

Name	x	y	z	B
C325	0.1133(9)	-0.319(1)	0.4304(4)	6.2(5)
C326	0.0733(6)	-0.2419(8)	0.3968(8)	4.6(4)
D	2.521(7)	x^1	0.1049(3)	
E	1.691(9)	y^1	-0.3194(5)	
F	5.239(9)	z^1	0.3544(4)	
C331	-0.0278(6)	-0.212(1)	0.2037(6)	3.9(4)
C332	-0.0329(6)	-0.1672(7)	0.1340(9)	5.0(5)
C333	-0.0650(7)	-0.222(1)	0.0775(6)	8.0(6)
C334	-0.0921(6)	-0.3[illegible]2(1)	0.0906(6)	7.7(6)
C335	-0.0870(6)	-0.3669(7)	0.1603(9)	5.5(5)
C336	-0.0549(7)	-0.312(1)	0.2168(6)	4.4(4)
D	3.566(7)	x^1	-0.0599(4)	
E	1.851(8)	y^1	-0.2671(7)	
F	3.725(9)	z^1	0.1471(5)	

‡ These values are the coordinates of the ring center of gravity.

(Table continued)

Table 29 continued

(b) Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	0.077	0.416	0.322	8.3
H113	0.004	0.501	0.410	9.4
H114	-0.091	0.408	0.462	6.5
H115	-0.112	0.229	0.427	5.2
H116	-0.039	0.144	0.340	4.2
D	0.318			
E	0.669			
F	6.830			
H122	0.077	0.142	0.109	4.2
H123	0.059	0.223	-0.008	6.7
H124	0.031	0.407	-0.015	6.4
H125	0.022	0.509	0.095	6.9
H126	0.041	0.427	0.212	6.3
D	6.061			
E	1.632			
F	4.646			
H132	0.186	0.331	0.179	3.5
H133	0.290	0.416	0.218	5.9
H134	0.326	0.403	0.343	5.9
H135	0.259	0.305	0.429	6.6
H136	0.155	0.221	0.391	6.3

(Table continued)

Table 29 continued

Name	x	y	z	B
D	0.979			
E	1.97			
F	6.39			
H212	0.190	0.060	0.118	4.0
H213	0.277	0.158	0.054	6.0
H214	0.376	0.219	0.119	5.2
H215	0.390	0.181	0.247	3.3
H216	0.303	0.083	0.310	4.0
D	1.017			
E	2.01			
F	5.62			
H222	0.111	-0.097	0.132	4.8
H223	0.130	-0.241	0.049	6.7
H224	0.219	-0.366	0.074	7.1
H225	0.288	-0.349	0.181	6.9
H226	0.269	-0.205	0.264	5.5
D	2.548			
E	2.239			
F	5.350			
H232	0.300	-0.107	0.331	7.5
H233	0.334	-0.135	0.457	8.6
H234	0.257	-0.087	0.554	7.1

(Table continued)

Table 29 continued

Name	x	y	z	B
H235	0.148	-0.012	0.527	7.6
H236	0.114	0.015	0.402	5.6
D	1.986			
E	1.51			
F	6.96			
H312	0.009	-0.008	0.405	3.8
H313	-0.077	0.032	0.495	4.7
H314	-0.188	-0.045	0.486	5.1
H315	-0.215	-0.162	0.387	4.8
H316	-0.130	-0.202	0.297	4.0
D	0.887			
E	0.51			
F	6.99			
H322	0.091	-0.321	0.224	4.0
H323	0.160	-0.453	0.283	5.2
H324	0.173	-0.451	0.414	5.2
H325	0.119	-0.318	0.486	6.7
H326	0.050	-0.186	0.427	5.1
D	2.521			
E	1.691			
F	6.286			

(Table continued)

Table 29 continued

Name	x	y	z	B
H332	-0.013	-0.096	0.124	5.6
H333	-0.069	-0.191	0.027	9.0
H334	-0.115	-0.363	0.050	8.5
H335	-0.107	-0.439	0.170	6.4
H336	-0.051	-0.343	0.267	4.7
D	3.566			
E	1.851			
F	4.772			

Table 30

Anisotropic Temperature Factors ($\mathring{A}^2 \times 10^3$)

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	24.6(6)	27.3(6)	38.6(7)	-0.4(6)	0(1)	0(1)
Cℓ	30(3)	48(3)	69(3)	1(2)	-11(3)	6(2)
P1	32(3)	34(2)	45(3)	-1(2)	-3(4)	-5(4)
P2	26(2)	35(2)	46(4)	0(2)	3(3)	-3(4)
P3	34(3)	25(2)	44(4)	-3(2)	0(3)	0(2)

Table 31

Selected Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	Cℓ	2.404(4)	2.416(4)*
Rh	P1	2.304(4)	2.307(4)*
Rh	P2	2.225(4)	2.228(4)*
Rh	P3	2.338(4)	2.341(4)*
P1	C111	1.84(1)	
P1	C121	1.83(1)	
P1	C131	1.836(9)	
P2	C211	1.841(9)	
P2	C221	1.85(1)	
P2	C231	1.87(1)	
P3	C311	1.856(9)	
P3	C321	1.847(9)	
P3	C331	1.83(1)	

* value corrected for riding

Table 32

Selected Interatomic Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.7(1)
P1	Rh	P3	159.1(2)
P1	Rh	Cℓ	85.3(1)
P1	Rh	H222	122.9
P2	Rh	P3	96.4(2)
P2	Rh	Cℓ	166.7(2)
P2	Rh	H222	66.1
P3	Rh	Cℓ	84.5(1)
P3	Rh	H122	77.1
Cℓ	Rh	H122	101.3
Rh	P1	C111	112.5(5)
Rh	P1	C121	114.3(5)
Rh	P1	C131	123.4(4)
Rh	P2	C211	119.0(4)
Rh	P2	C221	109.9(5)
Rh	P2	C231	116.4(5)
Rh	P3	C311	104.4(4)
Rh	P3	C321	122.3(4)
Rh	P3	C331	120.6(5)
P1	C111	C114	178.7(8)
P1	C121	C124	175.1(8)
P1	C131	C134	177.3(6)

(Table continued)

Table 32

Selected Interatomic Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.7(1)
P1	Rh	P3	159.1(2)
P1	Rh	Cℓ	85.3(1)
P1	Rh	H222	122.9
P2	Rh	P3	96.4(2)
P2	Rh	Cℓ	166.7(2)
P2	Rh	H222	66.1
P3	Rh	Cℓ	84.5(1)
P3	Rh	H122	77.1
Cℓ	Rh	H122	101.3
Rh	P1	C111	112.5(5)
Rh	P1	C121	114.3(5)
Rh	P1	C131	123.4(4)
Rh	P2	C211	119.0(4)
Rh	P2	C221	109.9(5)
Rh	P2	C231	116.4(5)
Rh	P3	C311	104.4(4)
Rh	P3	C321	122.3(4)
Rh	P3	C331	120.6(5)
P1	C111	C114	178.7(8)
P1	C121	C124	175.1(8)
P1	C131	C134	177.3(6)

(Table continued)

Table 32 continued

Atom 1	Atom 2	Atom 3	Angle (°)
P2	C211	C214	174.6(7)
P2	C221	C224	174.3(8)
P2	C231	C234	176.4(9)
P3	C311	C314	177.6(7)
P3	C321	C324	177.4(7)
P3	C331	C334	178.1(9)
C111	P1	C121	104.1(5)
C111	P1	C131	98.5(6)
C121	P1	C131	101.5(6)
C211	P2	C221	97.2(6)
C211	P2	C231	103.5(6)
C221	P2	C231	108.9(6)
C311	P3	C321	102.6(5)
C311	P3	C331	104.2(6)
C321	P3	C331	100.2(6)

Table 33

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance (Å)
H112	H323	$x,y+1,z$	2.41
H113	H124	$\overline{x},\overline{y}+1,1/2+z$	1.92
H123	H326	$\overline{x},\overline{y},1/2+z-1$	2.48
H212	H314	$\overline{x},\overline{y},1/2+z-1$	2.40
H213	H325	$1/2-x,1/2+y,1/2+z-1$	2.41
H214	H325	$1/2-x,1/2+y,1/2+z-1$	2.47

Table 34

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom	Distance (Å)
Rh	H222	2.84
Rh	H236	2.94
Rh	H122	2.96
Rh	H116	2.96
P1	Cℓ	3.190(6)
P3	Cℓ	3.188(6)
P1	P2	3.411(5)
P2	P3	3.404(6)
H112	H126	2.12
H226	H232	1.84
H236	H312	2.07
C131	C211	3.22(1)
C133	C215	3.30(1)
C221	C322	3.20(1)
C226	C322	3.29(1)
C236	C326	3.34(1)

Fig. 11

View Perpendicular to the P1-P2-P3 Plane

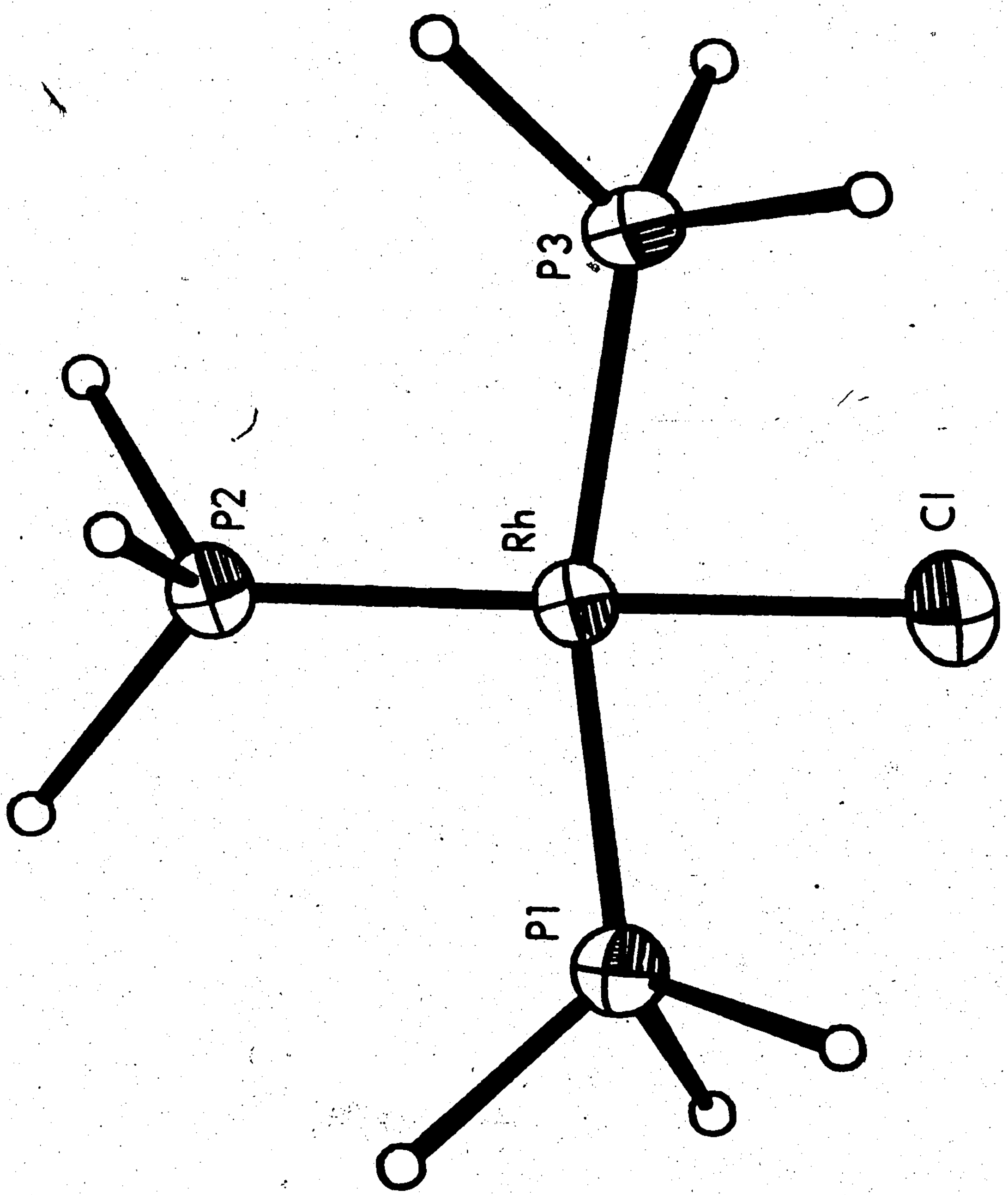


Fig. 12

Central Geometry Viewed down P1-P3 Direction

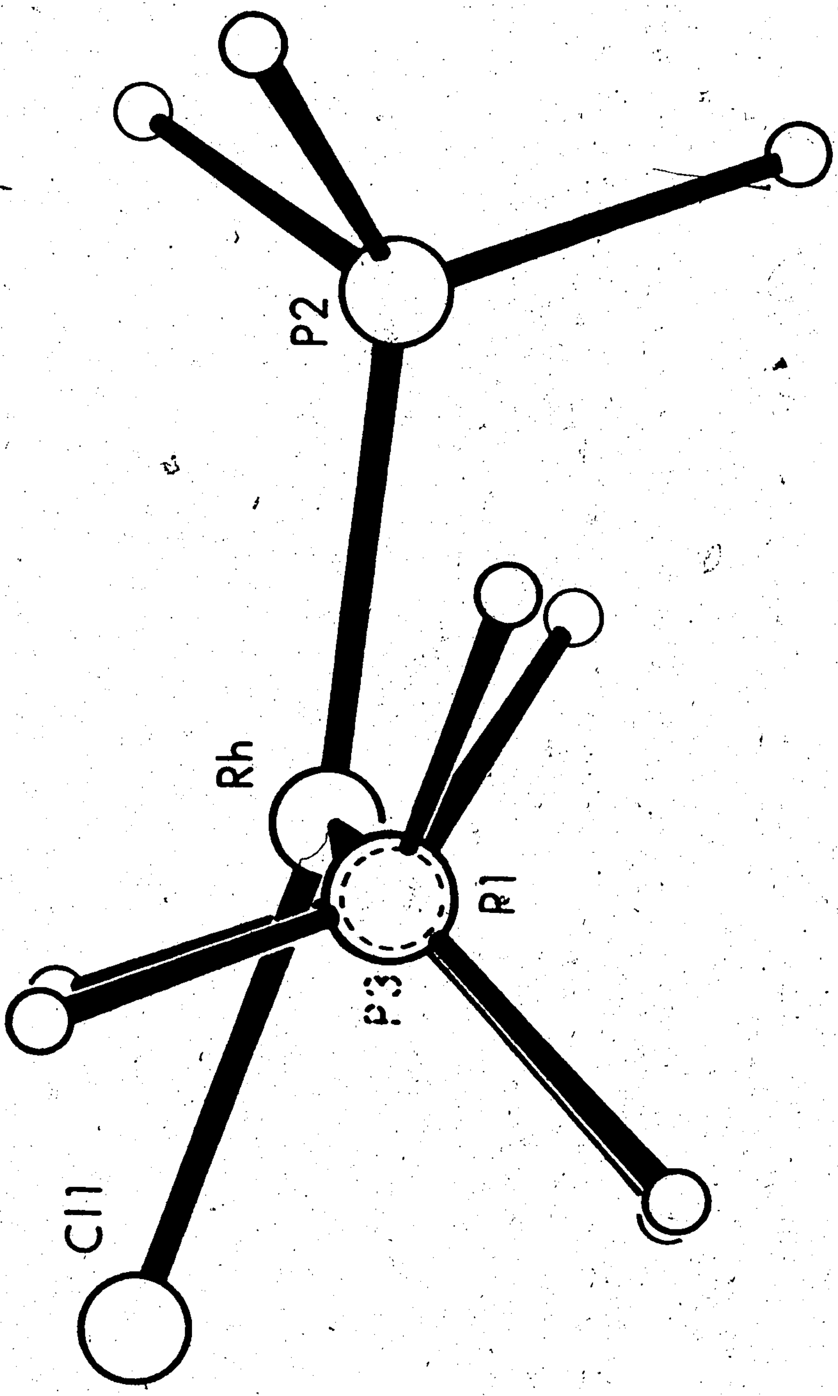
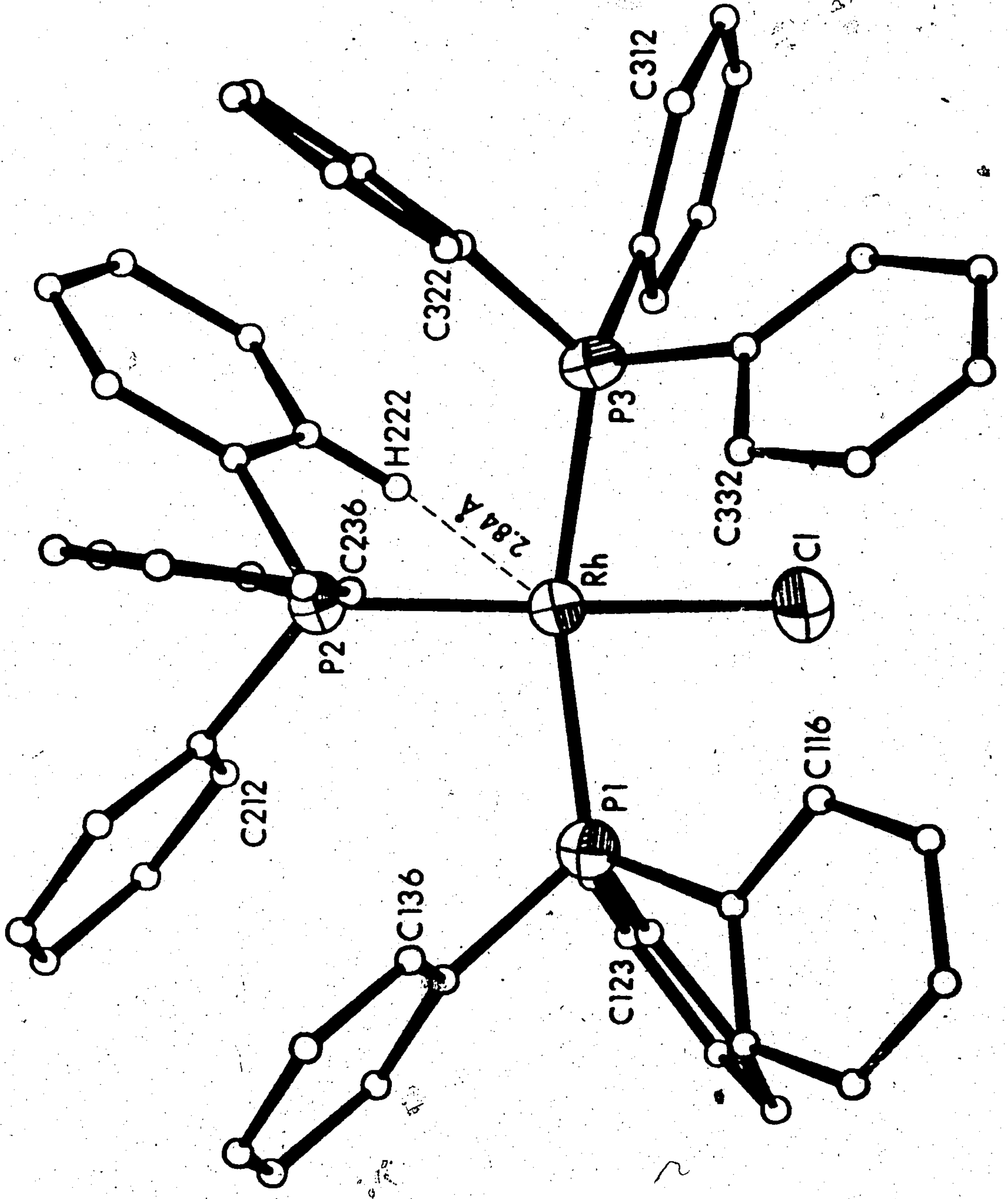


Fig. 13

A General View of $[RhCl(P(C_6H_5)_3)_3]$ (Orange Form)



Discussion

To a first approximation the coordination of the rhodium atom (Fig. 11) is square planar but there is a marked distortion towards tetrahedral geometry as emphasized by Fig. 12 and the angles Cℓ-Rh-P2 and P1-Rh-P3 of 166.7(2)° and 159.1(2)° respectively. The latter angle cannot be interpreted simply as being due to the distortion towards a tetrahedral geometry since it contains a significant contribution from a bending of P1-Rh-P3 within the mean molecular plane of the complex. The distortions from square planar coordination are explained by the bulkiness of the triphenylphosphine ligands *(vide infra)*.

The phosphorus atoms can be grouped chemically into two categories, (1) one pair mutually *trans* and *cis* to the chlorine atom, and (2) the unique phosphorus *trans* to chlorine. For this latter phosphorus, the rhodium-phosphorus bond length is 2.228(4) Å which is significantly shorter than the other two bond lengths (Rh-P1, 2.307(4), Rh-P3, 2.341(4) Å) between rhodium and the mutually *trans* phosphorus atoms (Δ/σ: 14 and 19 respectively). This pattern of rhodium-phosphorus bond lengths is consistent with the π-acidity and thus *trans* effect of phosphorus being greater than that of chlorine [137-141]. The difference between the chemically equivalent rhodium-phosphorus bond lengths appears to be statistically significant (Δ/σ,6) and may reflect differences in intra ligand contacts. The difference may not be significant in that the standard deviations as derived must underestimate the true values if systematic errors are present.

The average phosphorus-carbon bond length in this structure is 1.844 Å and is somewhat longer than the value observed for triphenylphosphine [129] and its typical metal complexes [17,18] (~1.83Å). This increase appears to be correlated to the short rhodium-phosphorus bonds. If the phosphorus-carbon bond lengths are sorted according to the phosphorus atom then the bonds involving P1 and P3 average 1.838 Å while those involving P2 average 1.855 Å. An analysis of the six phosphorus-carbon bonds involving P1 and P3 shows that they are consistent with a standard deviation of 0.010 Å which is in remarkable agreement with the standard deviations derived *via* the least squares refinement and ORFFE II. The P2-carbon distances show a maximum deviation from their mean 1.6σ. The difference between the group averages is interesting but not acceptable as statistically significant by normal conservative crystallographic criteria. It was this feature which lead to the redetermination of the structure of the red form (Chapter VI) since it might provide independent evidence of the observed trend and averaging the values of both structures might produce a significant variation in distances.

The rhodium-chlorine bond length agrees well with those observed for the dioxygen derivatives described in Chapters III and IV but appears to be rather longer than the values as reported by Mason *et al.*,[138] for the red form of $RhC\ell(P(C_6H_5)_3)_3$, (2.373(8), 2.381[140] Å) and $RhC\ell(C_2F_4)(P(C_6H_5)_3)_2$, (2.375(8) Å). This topic is discussed in more detail in Chapter VI.

The final structural detail to be discussed is the close rhodium-H222 contact of 2.84 Å which is evident in Fig. 13. This close contact could result from (1) natural attraction of the hydrogen for the rhodium atom, or (2) a repulsion elsewhere in the molecule[139]. Table 33 contains all important intramolecular non-bonded contacts. In this Table if one ignores contacts between carbon atoms of the type (M11),(M21),(M31) then there are surprisingly few contacts between phenyl groups that are significantly less than the sum of the van der Waals radii. These contacts are: H112-H126, 2.12 Å: H226-H232, 1.84 Å; H236-H312, 2.07 Å; C131-C211, 3.22(1) Å; C133-C215, 3.30(1) Å; C221-C322, 3.20(1) Å; C226-C322, 3.29 Å; C236-C326, 3.34 Å. From these contacts it is obvious that phenyl group 22 is repelled by H232 and C322 into close contact with the rhodium atom i.e. the short rhodium hydrogen contact cannot be treated as representing an attractive force. Rather it represents a balance of repulsive forces. There is also a larger number of repulsions involving the atoms of the phenyl groups attached to P3 relative to the number of repulsions involving the atoms of the phenyl rings attached to P1. Thus one could explain the slight increase of bond length for Rh-P3 when compared to Rh-P1. It is highly doubtful that the interligand repulsions lead to the apparently abnormal phosphorus-carbon bond lengths in this structure. This view is discussed further in Chapter VI. Intermolecular contacts are listed in Table 32. Only one of these contacts is abnormally short *viz.* H113 at x,y,z to H124 at $\bar{x}$, 1-y, 1/2+z of 1.92 Å. All other contacts are equal to or greater than the sum of the van der Waals radii and further discussion is not warranted.

CHAPTER VI

The Crystal and Molecular Structures of the Red Form of $RhC\ell(P(C_6H_5)_3)_3$.

Experimental

Dark red crystals of the compound were examined under a polarizing microscope and found to be chunky, capped prisms, with no sign of twinning being evident. A crystal was mounted on the end of a thin glass fibre and a Laué photograph taken. Again no crystal defects were noticed and the crystal appeared to be suitable for a diffraction study. Preliminary Weissenberg and precession photographs indicated that the compound crystallized in the orthorhombic crystal system (Laué symmetry mmm). The systematic absences ($0k\ell$, $k + \ell = 2n + 1$; $h0\ell$, $h = 2n + 1$) were consistent with the spacegroups $Pna2_1$ or Pnam.

Precise lattice parameters were obtained from a least squares refinement using 2θ values of 18 accurately centered high angle reflections ($CuK\alpha_1$ 1.54051 Å) as: a, 32.96(1); b, 12.271(2); C, 11.013(1) Å. All reflections used showed resolvable splitting of the α_1/α_2 peaks. The density of the compound was measured by flotation in aqueous potassium iodide solution as $\rho_{obs} = 1.382$ g-cm^3, a value in good agreement with that calculated using precise lattice parameters, $\rho_{calc} =$

1.379 g-cm^{-3} (for 4 molecules per unit cell).

Intensity data were collected on a Picker manual diffractometer with the crystal "b" axis aligned coincident with the diffractometer ϕ axis. Copper k$\bar{\alpha}$ X-radiation was used with a graphite monochromator (002 reflecting plane) and a 2° takeoff angle. Diffractometer settings were calculated using the programme MIXG2 and the high intensity axial peaks were scanned at expanded chart speeds to detect twinning or unusual reflection shape. No unusual effects were found. Each reflection was scanned from $(2\theta - 1)°$ to $(2\theta + 1)°$ in 1 minute and 20 second stationary background counts were taken at the limits of the coupled $\omega/2\theta$ scan. The total background counts were calculated from a linear interpolation of the two stationary counts. Data were only measured to 90° in 2θ because of the rapid decrease in intensities with increasing 2θ as observed in the preliminary photographic study. During the data collection 5 reflections were measured at 8 hour intervals to check against crystal misalignment and/or decomposition. No significant changes in these intensities were found throughout the entire data collection. A total of 2221 reflections were measured and of this number 1469 were statistically reliable using the criterion $I < 3\sigma$ for rejection. Reflections having a maximum count rate in excess of 10^4 counts-sec^{-1} (and thus greater than the linear response of the scintillation counter) were recollected at the end of the initial data collection at reduced voltages and scaled into the data by comparison with the other reflections of lower intensity, recollected under the same conditions. The 0k0 reflections were measured at 10° intervals in ϕ to provide experimental verification of absorption corrections.

The crystal faces were identified as members of the forms {100}, {210}, {201} and the crystal was removed from the diffractometer. The crystal dimensions (0.17 x 0.21 x 0.14 mm) were measured under a calibrated microscope. These values were used to make an absorption correction ($\mu_{K\bar{\alpha}} = 47.6\ \mathrm{cm}^{-1}$) and the data for different ϕ values after correction for absorption were consistent within 5%. Transmission factors varied from 0.683 to 0.566. Reflection data were corrected for Lorentz and polarization effects and the structure amplitudes with their respective standard deviations calculated using an uncertainty factor of 0.03. Only the significant data were used in the structure solution and refinement.

Solution of Structure and Refinement

A Patterson map was calculated and the molecule was assumed to have the more general space group $Pna2_1$

for reasons outlined in Chapter V. The Harker lines gave peaks representing the rhodium-rhodium intermolecular vectors and the rhodium "x" and "y" coordinates were obtained. The "z" coordinate of the rhodium atom was set at 0.25 to fix the origin in this direction. The atomic coordinates of the chlorine atom were found from the intramolecular vectors and checked with the Harker line peaks for this atom (see Table 35). The remaining atoms were identified in a series of electron density difference maps as indicated in Table 36.

The rigid body description for the carbon atoms of the phenyl groups was used to minimize the number of parameters. The atomic scattering factors for the rhodium, chlorine, phosphorus and carbon atoms were for neutral species. These were derived from Cromer's coefficients [111] and included (for rhodium, chlorine and phosphorus) the real and imaginary terms for anomalous dispersion. Hydrogen atoms were added to the refinement at their calculated positions with carbon-hydrogen bond lengths of 1.0 Å and isotropic temperature factors 10% greater than those of the carbon atoms to which they were attached. Hydrogen scattering factors were those of Mason and Robertson [113].

Refinement of the completed structure was routine (Table 37) except for problems caused by an error in the refinement programme that was specific to noncentrosymmetric space groups. Elimination of this error allowed the structure to refine to convergence. As mentioned in Chapter V two solutions must be tested for this spacegroup when anomalous scattering is considered. When the molecule was reflected through the "xy" plane a Hamilton test showed that the new model was preferred at better than the 99.5% confidence level.

At convergence (estimated standard deviation of an observation of unit weight = 1.595; maximum shift/ $\sigma = 0.02$; $R_1 = 0.042$; $R_2 = 0.045$) a final electron density difference map was calculated and the correlation matrix printed. Examination of the electron density map showed the largest positive and negative peaks (0.38 e.Å^{-3} and -0.20 e.Å^{-3}; cf. carbon ~3e.Å^{-3}) to be situated near phenyl groups. The correlation matrix showed high correlations between some phenyl carbon temperature factors, but all coordinate interactions were less than 0.18.

All interatomic bond lengths, inter- and intramolecular contacts (with their angles and standard deviations) to a distance of 3.5 Å were calculated using FE II. Bond lengths involving the rhodium atom were also calculated to include a correction for thermal motion assuming the lighter atoms to ride on the heavier rhodium atom.

Table 35

Assignment of Patterson Map Peaks

Peak Coordinates u v w	Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)
0.504, 0.204, 0.000	295	$1/2, 1/2-2y_a, 0$	198	0.500, 0.256, 0.000
0.270, 0.504, 0.494	285	$1/2-2x_a, 1/2, 1/2$	198	0.274, 0.500, 0.500
0.225, 0.240, 0.494	167	$2x_a, 2y_a, 1/2$	99	0.226, 0.244, 0.500
0.347, 0.504, 0.494	78	$1/2-2x_b, 1/2, 1/2$	28	0.346, 0.500, 0.500
0.504, 0.312, 0.000	60	$1/2, 1/2-2y_b, 0$	28	0.500, 0.322, 0.000
0.148, 0.176, 0.494	40	$2x_b, 2y_b, 1/2$	14	0.154, 0.178. 0.500
0.036, 0.020, 0.182	43	$x_a-x_b, y_a-y_b, z_a-z_b$	37	0.036, 0.033, 0.184
0.309, 0.480, 0.312	34	$1/2-x_a-x_b, 1/2-y_a+y_b, 1/2-z_a+z_b$	37	0.310, 0.467, 0.316
0.462, 0.288, 0.182	31	$1/2-x_a+x_b, 1/2-y_a-y_b, z_a-z_b$	37	0.464, 0.289, 0.184
0.193, 0.216, 0.312	29	$x_a+x_b, y_a+y_b, 1/2-z_a+z_b$	37	0.190, 0.211, 0.316

Assignment Results	x	y	z
a = Rh	0.113	0.122	-0.250
b = Cℓ	0.077	0.089	-0.434

Table 36

Structure Solution Sequence

Refinement Cycle	Atoms used in Phasing	R_1	Atoms Located in Diff. Map
1	Rh,Cℓ	0.427	P1,P2,P3
2	Rh,Cℓ,P1,P2,P3	0.326	
3	.. ..	0.281	C111-C116,C131-C136,C221-C226, C331-C336
4	Rh,Cℓ,P1,P2,P3,C111-C116, C131-C136,C221-C226,C331-C336	0.262	
5	.. ..	0.245	C121-C126,C211-C216,C231-C236, C311-C316,C321-C326

Table 37

Refinement Sequence for Model

Refinement Cycle		R_1	R_2
6	All atoms except hydrogens included, temperature factors held constant (B:Rh, 2.5; Cℓ, 2.5; P, 3.0; C, 5.0)	0.201	0.220
7	.. ..	0.172	0.193
8	temperature factors refined	0.147	0.164
9	.. ..	0.112	0.129
10	anomalous dispersion correction applied	0.097	0.107
11	central atoms given anisotropic temperature factors	0.079	0.086
12	hydrogen atoms included	0.072	0.078
13	error in refinement programme corrected	0.047	0.056
14	origin molecule reflected through "xy" plane	0.044	0.047
15	.. ..	0.042	0.044

Results

The observed and calculated structure amplitudes ($|F_o|$ and $|F_c|$ respectively) are listed in Table 38. Table 39 gives the atomic coordinates of all atoms with the anisotropic thermal parameters of the central atoms being included in Table 40. The interatomic angles and distances are given in Tables 41 and 42 respectively with the inter- and intramolecular non-bonded contacts being listed in Tables 43 and 44. The standard deviations of the least significant digit are included in parentheses.

Fig. 14 shows the general geometry of the molecule whilst Figs. 15 and 16 show views down the P1-P3 direction and perpendicular to the P1-P2-P3 plane.

Table 38

Observed and Calculated Structure Amplitudes(electronsx10)

H	K	FOBS	FCAL
L = 0***			
2	0	364	361
4	0	2344	2418
6	0	393	394
8	0	980	987
10	0	1248	1267
12	0	422	457
14	0	468	497
16	0	744	720
18	0	851	777
20	0	903	1071
22	0	1282	1366
24	0	563	529
26	0	1191	1224
28	0	702	667
30	0	452	485
1	1	1531	1531
2	1	1660	1670
3	1	1508	1588
4	1	669	694
5	1	748	791
6	1	779	662
7	1	2682	2709
8	1	2049	2015
9	1	681	669
10	1	240	229
11	1	827	833
12	1	880	876
13	1	1006	1025
14	1	466	398
15	1	212	218
16	1	351	362
17	1	1065	1112
18	1	658	614
19	1	677	715
20	1	976	1011
21	1	497	495
22	1	546	548
23	1	470	499
24	1	823	830
25	1	706	697
28	1	324	294
30	1	584	587
0	2	464	470
1	2	189	209
2	2	538	568
3	2	345	376
5	2	1145	1137
6	2	2736	2758
7	2	1670	1636
8	2	953	956
9	2	203	136
10	2	257	145
11	2	1140	1135
12	2	777	751
13	2	884	877
14	2	223	207
15	2	754	784
16	2	333	317
17	2	749	742
19	2	977	935
20	2	227	277
21	2	791	775
23	2	666	686
29	2	361	295
1	3	2957	3019
2	3	1812	1804
3	3	1680	1639
5	3	630	661
6	3	441	469
7	3	575	596
8	3	1287	1266
9	3	493	493
10	3	624	618
11	3	275	141
12	3	571	553
13	3	381	384
15	3	364	371
16	3	773	844
17	3	484	480
19	3	870	808
20	3	570	559
21	3	262	337
23	3	254	276
24	3	398	421
25	3	279	315
26	3	391	401
27	3	364	351
0	4	1549	1550
1	4	415	424
2	4	365	386
3	4	303	318
4	4	2986	3102
5	4	1410	1431
6	4	265	341
7	4	617	605
8	4	1155	1135
9	4	1020	995
10	4	329	345
11	4	390	360
12	4	465	468
13	4	807	785
14	4	880	889
15	4	364	392
17	4	675	721
18	4	1024	1105
22	4	794	786
25	4	431	412
26	4	569	502
27	4	222	386
28	4	256	232
1	5	1430	1374
2	5	1424	1364
3	5	944	985
4	5	314	350
5	5	1629	1704
6	5	1256	1321
7	5	634	666
9	5	1051	1037
11	5	353	325
12	5	837	771
13	5	377	401
14	5	348	288
15	5	[illegible]	251
16	5	865	933
17	5	463	480
19	5	236	235
20	5	843	825
21	5	839	881
23	5	340	321
24	5	367	469
25	5	279	302
26	5	307	316
27	5	823	774
0	6	368	371
1	6	611	651
2	6	663	653
3	6	1043	1099
4	6	187	223
5	6	556	561
6	6	567	600
7	6	1317	1334
8	6	514	528
10	6	411	449
11	6	1246	1235
12	6	278	283
13	6	402	383
14	6	302	294
15	6	1042	1051
16	6	370	377
17	6	484	481
19	6	728	750
21	6	303	257
23	6	578	568
25	6	582	594
2	7	928	960
3	7	422	446
4	7	1114	1162
5	7	780	828
6	7	838	785
7	7	638	568
8	7	965	919
9	7	328	294
10	7	703	766
12	7	419	466
13	7	326	365
14	7	686	663
15	7	600	627
17	7	286	323
20	7	315	335
23	7	461	429
0	8	967	941
2	8	365	337
4	8	857	888
6	8	642	687
7	8	307	304
8	8	504	452
10	8	501	469
11	8	716	760
14	8	330	335
18	8	390	417
19	8	282	223
4	9	313	285
5	9	447	403
6	9	770	765
7	9	262	255
9	9	1032	1065
10	9	616	638
12	9	324	338
13	9	665	666
14	9	302	219
16	9	629	612
0	10	295	230
1	10	235	192
3	10	402	407
5	10	352	356
7	10	827	848
9	10	595	600
10	10	360	436
11	10	1471	1484
2	11	702	743
3	11	288	314
4	11	325	315
6	11	781	731
L = 1**			
2	0	3852	4048
4	0	1482	1503
6	0	548	450
8	0	1284	1276
10	0	790	807
12	0	639	594
14	0	415	425
16	0	428	480
18	0	897	871
20	0	1563	1596
22	0	536	555
24	0	1303	1287
26	0	507	530
28	0	552	588
30	0	581	644
0	1	2106	2148
1	1	1380	1401
2	1	647	655
3	1	1023	982
4	1	617	630
5	1	343	335
6	1	1414	1432
7	1	2074	2034
8	1	672	678
9	1	1347	1362
10	1	907	912
11	1	1325	1343
12	1	741	769
13	1	264	300
14	1	830	863
15	1	893	965
17	1	701	691
18	1	958	938
19	1	809	803
20	1	493	569
21	1	568	585
22	1	786	788
23	1	609	613
25	1	319	348
26	1	502	452
27	1	372	397
28	1	560	589
29	1	470	477
1	2	410	427
2	2	577	564
3	2	553	562
4	2	675	658
5	2	989	953
6	2	439	408
7	2	733	730
9	2	1183	1170
10	2	622	610
11	2	514	543
12	2	405	433
13	2	1132	1119
14	2	767	761
15	2	1340	1347
16	2	388	390
17	2	789	806
18	2	224	232
19	2	1108	1088
20	2	291	326
21	2	674	665
23	2	585	582
25	2	251	233
26	2	318	309
27	2	437	447
29	2	280	177
0	3	971	981
1	3	1069	1062
2	3	989	1008
3	3	723	683
5	3	1606	1590
6	3	972	980
7	3	784	780
8	3	482	479
10	3	707	663
11	3	723	731
12	3	500	487
13	3	395	408
14	3	900	878
15	3	396	460
16	3	247	290
17	3	548	555
18	3	815	823
19	3	427	421
21	3	667	656
22	3	648	669
23	3	371	358
24	3	297	323
25	3	381	373
28	3	323	357
1	4	355	403
2	4	1507	1489
3	4	762	744
4	4	465	465
5	4	301	278
6	4	1142	1158
7	4	1456	1466
8	4	1325	1317
9	4	497	498
10	4	941	932
11	4	551	540
12	4	858	893
13	4	284	313
14	4	405	477
15	4	527	499
16	4	1006	1041
17	4	369	395
20	4	917	889
21	4	264	301
23	4	412	414
24	4	635	660
25	4	276	227
27	4	365	376
28	4	639	654
0	5	1125	1130
1	5	1289	1243
2	5	284	308
3	5	1291	1294
4	5	1140	1144
5	5	303	276
7	5	863	881
8	5	747	756
9	5	684	644
10	5	408	409
11	5	1113	1126
12	5	898	933
13	5	197	130
14	5	968	1003
15	5	690	668
16	5	310	332
17	5	301	244
18	5	964	1004
19	5	436	404
20	5	228	228
21	5	401	455
22	5	512	515
23	5	588	587
24	5	351	363
25	5	654	675
1	6	943	939
2	6	890	804
3	6	602	617
4	6	845	862
5	6	1258	1302
7	6	308	319
8	6	275	268
9	6	920	911
10	6	908	895
11	6	226	207
12	6	311	346
13	6	1219	1235
14	6	351	326
17	6	978	974
19	6	355	326
20	6	301	297
21	6	708	669
22	6	269	274
23	6	471	472
0	7	656	663
1	7	512	477
2	7	228	166
3	7	506	511
4	7	762	754
6	7	870	896
7	7	354	363
8	7	527	549
10	7	908	906
11	7	303	317

Table 38 continued

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
**L =		1****		12	1	720	727	9	4	475	465	4	8	623	636	4	2	675	730
12	7	710	721	13	1	1538	1548	10	4	837	802	5	8	255	233	5	2	871	844
13	7	311	330	14	1	732	735	11	4	570	561	6	8	613	589	6	2	1053	1061
14	7	509	501	15	1	540	673	12	4	1091	1075	8	8	518	488	7	2	825	781
16	7	343	350	16	1	509	529	14	4	1249	1236	9	8	313	281	8	2	233	213
18	7	472	489	17	1	1041	1020	15	4	336	264	10	8	432	456	9	2	1432	1444
19	7	314	327	19	1	600	618	16	4	480	455	11	8	634	624	10	2	699	675
21	7	299	273	20	1	756	778	17	4	438	415	14	8	427	425	11	2	359	380
22	7	509	537	21	1	548	560	18	4	1008	1010	17	8	427	389	12	2	233	225
1	8	285	299	23	1	387	402	19	4	305	289	18	8	608	584	13	2	1382	1369
2	8	717	711	24	1	602	553	20	4	391	421	19	8	256	260	15	2	433	448
4	8	697	707	25	1	423	487	21	4	407	395	1	9	389	328	16	2	442	432
6	8	699	733	26	1	407	382	22	4	682	722	2	9	579	562	17	2	568	559
7	8	224	238	27	1	411	401	26	4	612	603	3	9	479	443	18	2	377	436
8	8	377	389	28	1	357	410	27	4	330	356	4	9	500	501	19	2	902	665
9	8	505	461	0	2	618	603	1	5	811	804	6	9	666	655	20	2	284	315
10	8	238	259	1	2	1087	1044	2	5	775	807	7	9	462	377	21	2	415	376
11	8	303	287	2	2	1945	1868	3	5	1009	1023	8	9	296	312	23	2	758	761
12	8	597	601	3	2	709	720	5	5	770	768	9	9	738	687	26	2	393	374
13	8	385	380	4	2	328	320	6	5	1329	1340	10	9	385	366	27	2	684	693
16	8	277	286	5	2	1488	1450	7	5	406	348	12	9	306	328	0	3	416	413
17	8	262	237	6	2	318	299	9	5	1340	1308	13	9	639	645	1	3	525	524
20	8	607	618	7	2	1318	1304	10	5	1230	1159	14	9	285	275	2	3	246	192
21	8	270	263	8	2	705	709	11	5	304	273	15	9	408	367	3	3	816	842
0	9	383	378	9	2	817	819	12	5	757	732	16	9	400	403	4	3	580	579
1	9	274	174	10	2	282	255	13	5	971	946	17	9	434	434	5	3	207	213
2	9	331	345	11	2	1687	1637	14	5	737	748	1	10	612	590	6	3	807	812
4	9	556	551	12	2	1044	1002	16	5	835	849	3	10	496	456	7	3	1080	1052
6	9	402	386	13	2	538	529	17	5	576	603	5	10	596	573	8	3	1137	1120
7	9	645	670	14	2	302	292	19	5	385	419	7	10	730	729	9	3	269	259
8	9	520	546	15	2	838	874	20	5	438	501	9	10	320	299	10	3	868	905
10	9	330	365	17	2	1104	1166	21	5	742	761	11	10	1183	1158	11	3	618	614
11	9	785	808	18	2	490	460	22	5	310	329	1	11	314	264	12	3	802	800
13	9	318	275	19	2	450	423	23	5	518	503	2	11	762	727	13	3	413	386
14	9	620	593	20	2	252	257	24	5	333	353	**L =		3****		14	3	876	887
16	9	488	471	21	2	939	959	25	5	251	215	2	0	2036	1985	15	3	802	826
17	9	530	514	23	2	307	247	0	6	972	946	4	0	801	800	17	3	317	330
1	10	328	313	24	2	378	403	1	6	1024	984	6	0	1066	1049	18	3	881	795
3	10	446	410	25	2	616	605	2	6	548	481	8	0	1415	1396	19	3	351	391
5	10	448	475	29	2	608	598	3	6	1385	1339	10	0	1690	1694	20	3	718	762
7	10	577	556	1	3	885	841	4	6	500	507	12	0	1352	1365	21	3	461	439
9	10	1205	1216	2	3	1078	1077	5	6	515	522	14	0	1232	1262	23	3	389	388
10	10	255	255	3	3	595	605	6	6	266	207	16	0	613	613	24	3	493	534
11	10	246	158	4	3	775	786	7	6	1263	1263	18	0	574	616	25	3	509	441
13	10	1244	1216	5	3	630	637	8	6	788	740	20	0	1101	1098	1	4	265	242
0	11	577	580	6	3	848	840	9	6	355	314	24	0	900	827	2	4	260	260
2	11	313	246	7	3	170	151	11	6	772	788	26	0	383	309	3	4	376	401
4	11	789	796	8	3	339	311	12	6	473	483	28	0	523	470	4	4	378	373
5	11	388	365	9	3	913	896	14	6	217	170	0	1	383	394	5	4	741	715
**L =		2****		10	3	1100	1108	15	6	1062	1065	1	1	549	559	6	4	1309	1278
0	0	2599	2608	11	3	416	409	16	6	256	319	2	1	387	394	8	4	709	653
2	0	393	369	12	3	578	611	19	6	901	933	3	1	1015	987	9	4	629	608
4	0	664	663	13	3	477	491	20	6	431	426	4	1	1086	1136	10	4	1410	1442
6	0	1447	1461	14	3	215	248	21	6	295	290	5	1	1020	1024	11	4	287	251
8	0	1593	1609	15	3	463	447	22	6	250	235	6	1	932	900	12	4	957	966
10	0	1242	1265	16	3	996	983	23	6	559	535	7	1	660	649	14	4	752	703
12	0	2006	2066	17	3	804	757	1	7	617	640	8	1	926	907	15	4	285	302
14	0	654	654	18	3	505	514	2	7	727	748	9	1	441	449	16	4	1299	1275
16	0	960	935	19	3	719	736	3	7	465	423	10	1	649	632	18	4	241	213
18	0	1646	1632	20	3	777	727	5	7	792	753	11	1	1651	1592	19	4	488	484
20	0	478	488	21	3	447	512	6	7	841	838	12	1	845	831	20	4	766	743
22	0	1175	1254	22	3	435	427	7	7	392	430	15	1	1395	1419	24	4	418	395
26	0	663	627	23	3	421	468	8	7	405	416	17	1	431	442	0	5	1022	1088
28	0	372	286	26	3	280	291	9	7	411	383	18	1	478	457	1	5	989	950
1	1	1993	1941	27	3	431	425	10	7	771	757	19	1	820	817	3	5	917	896
2	1	1615	1550	28	3	309	289	11	7	413	413	22	1	642	662	4	5	672	648
3	1	629	651	0	4	787	782	12	7	587	598	23	1	346	356	5	5	425	421
4	1	1408	1320	1	4	199	195	14	7	597	576	24	1	288	260	6	5	296	352
5	1	1999	1932	2	4	575	545	16	7	637	635	25	1	374	375	7	5	936	933
6	1	743	699	3	4	747	715	20	7	591	592	26	1	471	430	8	5	988	1001
7	1	702	715	4	4	1210	1150	21	7	401	325	27	1	257	296	10	5	555	541
8	1	1083	1078	5	4	422	427	0	8	748	740	28	1	360	341	11	5	854	877
9	1	962	949	6	4	769	797	1	8	261	302	1	2	556	567	12	5	989	978
10	1	595	596	7	4	370	329	2	8	291	295	2	2	476	484	14	5	644	620
11	1	196	233	8	4	983	973	3	8	471	472	3	2	665	660	15	5	731	750

Table 38 continued

H	K	FOBS	FCAL
L = 3**			
16	5	702	655
17	5	310	320
18	5	458	416
19	5	837	851
21	5	327	395
23	5	650	630
25	5	315	246
1	6	1355	1393
2	6	568	554
3	6	877	883
4	6	474	494
5	6	1297	1312
6	6	329	371
7	6	450	478
8	6	240	269
9	6	919	907
10	6	415	354
12	6	264	280
13	6	748	742
14	6	310	311
16	6	340	317
17	6	989	1004
18	6	384	332
19	6	326	356
21	6	396	449
23	6	608	606
0	7	861	847
3	7	696	678
4	7	792	740
5	7	439	435
6	7	375	398
7	7	656	641
8	7	942	970
9	7	586	587
10	7	238	222
12	7	503	457
13	7	274	284
14	7	470	450
18	7	680	647
19	7	528	517
1	8	375	422
2	8	630	636
4	8	482	463
5	8	387	381
6	8	330	319
7	8	572	560
8	8	543	519
9	8	358	314
12	8	599	623
13	8	516	541
15	8	604	545
16	8	681	656
19	8	354	376
0	9	537	558
1	9	586	600
4	9	654	713
5	9	485	467
7	9	374	365
8	9	609	641
11	9	611	564
12	9	345	292
13	9	364	330
14	9	357	285
15	9	618	610
1	10	726	724
2	10	344	302
3	10	634	624
5	10	676	711
7	10	346	354
9	10	863	866
L = 4**			
0	0	1456	1436
2	0	776	811
4	0	1803	1793
6	0	1525	1515
8	0	1477	1445
10	0	1294	1198
12	0	1721	1694
14	0	600	589
16	0	415	437
18	0	948	978
20	0	734	693
22	0	1111	1150
26	0	529	545
1	1	1178	1137
2	1	1152	1100
3	1	768	768
4	1	410	431
5	1	1739	1718
6	1	767	772
7	1	404	378
8	1	524	572
9	1	1055	1016
10	1	508	548
11	1	244	248
12	1	516	494
13	1	1092	1086
14	1	329	371
15	1	235	227
16	1	311	231
17	1	784	784
20	1	387	363
21	1	657	657
22	1	410	425
24	1	626	655
25	1	360	375
26	1	474	438
27	1	458	407
0	2	349	355
1	2	916	865
2	2	518	552
3	2	1154	1098
4	2	627	644
5	2	515	471
6	2	932	911
7	2	618	624
8	2	644	624
11	2	1033	1072
12	2	545	548
13	2	559	573
14	2	265	250
15	2	781	786
16	2	237	232
17	2	454	485
18	2	440	398
19	2	294	338
21	2	518	529
24	2	321	256
25	2	780	815
27	2	242	161
1	3	184	166
3	3	297	231
4	3	354	303
5	3	1012	1006
6	3	764	786
7	3	206	208
8	3	280	320
9	3	1044	1006
10	3	932	915
11	3	273	313
12	3	934	937
13	3	965	962
14	3	223	223
16	3	957	970
17	3	590	587
18	3	391	422
19	3	378	381
20	3	577	606
21	3	393	380
22	3	468	456
23	3	389	377
24	3	248	152
26	3	254	251
0	4	715	754
2	4	271	273
3	4	405	347
4	4	1173	1170
5	4	486	443
6	4	631	644
7	4	334	380
8	4	1233	1242
9	4	813	764
10	4	835	870
11	4	275	289
12	4	.31	757
14	4	1061	1051
15	4	424	360
16	4	385	409
17	4	388	382
18	4	776	790
20	4	296	222
22	4	490	490
25	4	290	307
1	5	1341	1330
2	5	871	770
3	5	563	530
4	5	504	508
5	5	962	992
6	5	746	760
7	5	570	553
8	5	297	311
9	5	562	571
10	5	1030	1066
12	5	577	616
13	5	538	564
14	5	599	564
15	5	394	316
16	5	598	600
17	5	561	545
18	5	345	292
19	5	368	314
20	5	275	291
21	5	803	805
23	5	300	331
24	5	387	425
0	6	624	655
1	6	1092	1144
2	6	482	458
3	6	1084	1107
4	6	485	476
5	6	401	377
6	6	364	404
7	6	1215	1178
11	6	700	651
14	6	290	301
15	6	589	629
18	6	313	335
19	6	723	768
20	6	310	287
21	6	507	516
22	6	274	293
1	7	517	503
2	7	954	932
5	7	600	604
6	7	822	821
7	7	420	394
8	7	451	409
9	7	385	385
10	7	463	455
11	7	374	374
12	7	425	480
16	7	703	679
17	7	449	467
20	7	625	629
0	8	517	532
2	8	312	301
3	8	246	140
4	8	335	355
5	8	268	317
6	8	353	417
8	8	423	449
10	8	474	461
11	8	324	227
12	8	422	391
13	8	437	392
14	8	775	778
17	8	264	326
1	9	393	381
2	9	726	732
3	9	426	464
4	9	270	242
5	9	354	329
6	9	628	572
8	9	265	244
9	9	408	345
10	9	380	353
12	9	291	268
13	9	397	390
1	10	737	689
3	10	595	635
5	10	651	701
7	10	612	569
L = 5**			
2	0	1150	1201
4	0	1786	1687
6	0	1161	1146
8	0	1560	1529
10	0	1335	1293
12	0	631	626
14	0	693	714
16	0	444	416
18	0	764	702
20	0	878	881
22	0	473	500
24	0	847	788
26	0	292	357
0	1	522	525
1	1	354	333
2	1	540	543
3	1	1599	1574
4	1	725	732
5	1	205	174
6	1	840	815
7	1	1330	1334
8	1	677	677
9	1	370	334
10	1	651	650
11	1	813	793
12	1	283	265
13	1	202	197
14	1	286	276
15	1	680	666
18	1	263	240
19	1	693	689
21	1	280	263
22	1	521	494
23	1	506	503
24	1	529	525
25	1	501	536
26	1	700	721
1	2	906	911
2	2	409	372
4	2	882	865
5	2	984	957
6	2	497	500
7	2	407	387
8	2	263	238
9	2	904	901
11	2	394	397
12	2	209	193
13	2	767	749
14	2	229	245
15	2	311	227
16	2	361	346
17	2	411	447
23	2	723	699
0	3	419	471
1	3	246	173
2	3	282	270
3	3	470	489
4	3	348	349
5	3	519	509
6	3	410	425
7	3	1101	1082
8	3	466	448
9	3	289	286
10	3	648	617
11	3	918	933
14	3	646	663
15	3	609	608
17	3	275	175
18	3	655	622
19	3	262	223
20	3	421	431
21	3	247	252
22	3	291	274
1	4	699	686
2	4	957	974
3	4	218	213
4	4	477	468
6	4	1069	1103
7	4	473	503
8	4	964	968
9	4	369	341
10	4	547	558
11	4	449	452
12	4	689	898
13	4	646	660
14	4	601	600
15	4	293	271
16	4	782	786
19	4	258	271
20	4	470	464
21	4	265	325
0	5	638	648
1	5	870	890
3	5	947	969
4	5	551	580
5	5	240	253
6	5	452	391
7	5	703	691
8	5	1156	1143
9	5	414	441
10	5	765	722
11	5	366	392
12	5	990	991
14	5	608	572
15	5	520	507
16	5	290	270
17	5	261	207
18	5	450	416
19	5	659	655
22	5	334	315
1	6	916	907
2	6	882	908
3	6	538	524
4	6	358	258
5	6	1064	1057
9	6	827	818
10	6	550	556
13	6	514	506
14	6	241	183
17	6	723	689
18	6	410	426

Table 38 continued

H	K	FOBS	FCAL
L = 5**			
19	6	316	308
2C	6	313	246
0	7	1306	1341
3	7	470	491
4	7	909	901
5	7	251	243
7	7	324	354
8	7	345	395
9	7	370	328
10	7	380	392
14	7	619	581
18	7	642	630
2	8	582	586
4	8	356	351
6	8	321	357
7	8	259	315
8	8	344	325
10	8	351	350
11	8	253	231
12	8	650	645
15	8	402	371
0	9	572	541
1	9	394	403
3	9	289	317
4	9	642	606
8	9	433	420
L = 6**			
0	0	2035	2008
2	0	563	596
4	0	1578	1551
6	0	1067	1077
8	0	561	569
10	0	783	788
12	0	662	680
14	0	585	548
16	0	768	830
18	0	482	451
20	0	645	600
22	0	945	985
24	0	352	319
1	1	817	781
2	1	812	794
3	1	462	432
[illegible]	1	764	756
[illegible]	1	1094	1109
[illegible]	1	611	633
[illegible]	1	347	321
8	1	759	762
9	1	823	847
10	1	439	[illegible]
12	1	320	330
13	1	777	[illegible]
14	1	392	[illegible]
17	1	728	72C
2C	1	392	438
21	1	492	482
22	1	289	305
23	1	453	423
24	1	527	535
1	2	440	466
3	2	960	980
4	2	440	469
6	2	287	215
7	2	982	961
8	2	361	312
11	2	920	941
14	2	327	369
15	2	694	689
18	2	316	240
19	2	344	369
2C	2	276	285
21	2	571	570
23	2	345	289
1	3	457	445
2	3	866	868
3	3	488	481
4	3	503	518
5	3	560	555
6	3	462	430
8	3	356	349
9	3	517	523
10	3	222	282
12	3	478	575
13	3	630	618
16	3	676	659
17	3	330	338
18	3	392	415
19	3	247	174
22	3	370	369
0	4	885	836
3	4	294	243
4	4	955	975
5	4	303	327
6	4	508	508
7	4	267	312
8	4	953	955
10	4	446	472
11	4	693	682
12	4	619	625
14	4	821	799
15	4	306	284
18	4	674	709
19	4	298	308
1	5	706	746
2	5	646	646
3	5	263	254
5	5	1C78	1097
6	5	860	800
8	5	502	491
[illegible]	[illegible]	667	670
[illegible]	[illegible]	[illegible]	938
[illegible]	[illegible]	[illegible]	637
[illegible]	[illegible]	[illegible]	293
[illegible]	[illegible]	[illegible]	667
16	[illegible]	[illegible]	445
17	5	605	607
2C	5	414	397
0	6	871	890
1	6	649	622
3	6	980	953
4	6	430	426
5	6	375	357
6	6	361	358
7	6	963	958
8	6	270	223
11	6	653	675
12	6	275	188
15	6	628	608
16	6	426	444
1	7	362	341
2	7	901	923
4	7	351	350
5	7	460	418
6	7	728	710
7	7	262	274
9	7	277	294
12	7	368	353
13	7	251	203
15	7	323	314
0	8	842	878
4	8	634	592
5	8	364	316
9	8	287	359
10	8	474	499
2	9	358	367
L = 7**			
2	0	1356	1417
4	0	709	715
6	0	1034	1C53
8	0	318	3C0
10	C	763	705
12	0	411	373
14	0	476	477
16	0	687	676
18	0	655	717
20	C	934	902
0	1	756	758
1	1	453	516
2	1	376	4C5
3	1	699	699
4	1	546	564
5	1	532	539
6	1	435	422
7	1	891	895
8	1	30C	305
9	1	346	412
10	1	314	335
11	1	681	620
12	1	324	262
14	1	366	361
15	1	725	750
16	1	428	409
18	1	636	640
19	1	598	610
21	1	415	370
1	2	276	309
3	2	290	300
4	2	556	575
5	2	554	528
7	2	460	471
9	2	902	911
1C	2	338	324
12	2	338	285
13	2	892	934
14	2	363	373
15	2	571	593
16	2	550	476
17	2	668	717
19	2	628	579
21	2	450	485
0	3	433	378
1	3	422	426
3	3	448	478
4	3	33C	365
5	3	496	511
6	3	495	459
7	3	389	373
8	3	447	438
10	3	232	188
11	3	626	652
13	3	336	392
14	3	943	926
15	3	519	543
17	3	401	359
18	3	442	466
19	3	425	423
20	3	400	370
2	4	862	888
6	4	725	773
7	4	376	398
8	4	268	298
9	4	295	304
10	4	598	571
12	4	599	527
13	4	258	253
14	4	531	499
15	4	298	225
16	4	711	718
0	5	594	598
1	5	453	496
3	5	655	655
4	5	634	641
7	5	721	750
8	5	609	612
10	5	421	446
11	5	539	570
12	5	587	549
14	5	427	437
15	5	550	486
17	5	327	300
1	6	590	583
2	6	450	411
3	6	433	462
4	6	416	361
5	6	878	923
6	6	381	317
8	6	325	368
9	6	741	723
10	6	352	352
13	6	811	630
14	6	264	261
0	7	437	5C3
1	7	306	387
3	7	406	442
4	7	481	5C0
5	7	365	365
6	7	395	378
7	7	305	233
8	7	403	370
9	7	258	249
10	7	405	388
2	8	659	702
L = 8**			
0	0	1447	1466
2	C	297	330
4	0	1214	1194
8	0	726	759
12	0	552	573
14	0	527	540
16	C	336	325
18	0	591	572
1	1	379	405
2	1	531	520
3	1	706	680
4	1	470	467
5	1	586	583
7	1	719	738
8	1	297	350
9	1	677	669
12	1	418	384
13	1	679	692
14	1	252	171
15	1	252	353
16	1	600	606
17	1	660	661
1	2	280	225
2	2	416	415
3	2	242	319
5	2	440	417
6	2	305	320
7	2	429	419
8	2	363	389
11	2	743	749
12	2	389	320
13	2	572	585
14	2	359	394
15	2	895	914
17	2	776	809
1	3	440	370
3	3	657	662
4	3	288	295
5	3	265	250
7	3	404	395
10	3	376	353
12	3	532	603
13	3	512	542
15	3	397	418
16	3	667	720
0	4	725	722
1	4	340	344
4	4	774	780
5	4	275	347
8	4	648	669
10	4	415	408
12	4	394	355
14	4	476	519
1	5	462	494
2	5	644	642
5	5	481	480
6	5	520	482
7	5	354	402
9	5	672	688
10	5	404	378
12	5	260	290
0	6	287	251
1	6	301	360
2	6	249	303
3	6	638	669
7	6	740	731
8	6	372	384
L = 9**			
2	0	1621	1564
4	0	453	393
6	C	722	809
8	0	496	521
10	C	571	534
12	0	411	448
C	1	479	490
1	1	663	682
2	1	326	332
3	1	491	474
4	1	403	447
5	1	604	610
6	1	467	420
7	1	507	522
8	1	317	321
9	1	406	388
11	1	583	565
12	1	326	291
3	2	339	339
4	2	328	316
5	2	626	587
6	2	354	376
7	2	291	291
9	2	544	526
1C	2	293	250
1	3	6C0	550
3	3	456	498
4	3	316	283
5	3	335	403
8	3	354	388
1C	3	303	286
11	3	301	295
2	4	659	672
5	4	286	290
6	4	743	745
1	5	318	281
L = 10**			
0	C	813	853
4	0	862	830
1	1	521	514
2	1	519	494
3	1	348	328

Table 39

Atomic Coordinates and Isotropic Temperature Factors

Name	x	y	z	B*
Rh	0.11298(3)	0.12204(7)	-0.25000	2.25
Cl	0.0770(1)	0.0895(3)	-0.4336(4)	5.07
P1	0.12326(9)	-0.0662(2)	-0.2471(6)	2.28
P2	0.1655(1)	0.1689(3)	-0.1363(4)	2.39
P3	0.0729(1)	0.2767(3)	-0.2305(5)	2.61

* These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors given in Table 40

(Table continued)

Table 39 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0719(2)	-0.1234(8)	-0.2267(7)	2.4(3)
C112	0.0441(3)	-0.0622(6)	-0.1603(9)	4.3(4)
C113	0.0055(3)	-0.1035(7)	-0.1377(8)	4.5(4)
C114	-0.0053(2)	-0.2059(8)	-0.1815(7)	4.6(4)
C115	0.0225(3)	-0.2671(6)	-0.2478(9)	4.7(3)
C116	0.0611(3)	-0.2258(7)	-0.2704(8)	3.1(3)
D	0.431(6)	$x^{1\ddagger}$	0.0333(2)	
E	0.374(7)	$y^{1\ddagger}$	-0.1646(5)	
F	0.412(6)	$z^{1\ddagger}$	-0.2041(6)	
C121	0.1444(3)	-0.1377(9)	-0.3768(7)	2.0(4)
C122	0.1535(3)	-0.2484(8)	-0.3710(8)	3.2(4)
C123	0.1722(3)	-0.2995(6)	-0.469(1)	5.6(5)
C124	0.1819(3)	-0.2400(9)	-0.5726(7)	4.6(5)
C125	0.1728(3)	-0.1293(8)	-0.5784(8)	4.4(4)
C126	0.1540(3)	-0.0782(6)	-0.481(1)	3.7(4)
D	6.065(6)	x^1	0.1631(2)	
E	1.162(6)	y^1	-0.1888(6)	
F	2.662(7)	z^1	-0.4747(6)	
C131	0.1510(5)	-0.1328(7)	-0.121(2)	2.1(4)
C132	0.1303(6)	-0.1529(7)	-0.0126(9)	3.0(4)
C133	0.1503(8)	-0.2012(7)	0.085(2)	4.0(4)
C134	0.1911(5)	-0.2294(7)	0.074(2)	4.0(4)

(Table continued)

Name	x	y	z	B
C135	0.2118(6)	-0.2093(7)	-0.0335(9)	3.0(3)
C136	0.1918(8)	-0.1611(7)	-0.131(2)	2.9(3)
D	5.154(5)	x^1	0.1710(2)	
E	0.66(1)	y^1	0.1811(4)	
F	1.47(1)	z^1	-0.0231(6)	
C211	0.2107(3)	0.0905(6)	-0.183(3)	2.7(4)
C212	0.2409(8)	0.0560(9)	-0.104([illegible])	4.3(4)
C213	0.2751(6)	0.0026(8)	-0.149(2)	3.6(4)
C214	0.2790(3)	-0.0163(6)	-0.273(3)	3.5(4)
C215	0.2488(8)	0.0182(9)	-0.352(1)	6.1(5)
C216	0.2146(6)	0.0716(8)	-0.308(2)	4.3(5)
D	5.210(5)	x^1	0.2448(2)	
E	1.79(2)	y^1	0.0371(4)	
F	1.74(2)	z^1	-0.2281(8)	
C221	[illegible]	0.3102(6)	-0.164(1)	1.6(3)
C222	0.1737(3)	0.3948(9)	-0.0855(7)	3.1(3)
C223	0.1869(3)	0.5004(7)	-0.1094(9)	4.1(4)
C224	0.2106(3)	0.5214(6)	-0.212(1)	4.2(4)
C225	0.2211(3)	0.4368(9)	-0.2896(7)	5.5(5)
C226	0.2079(3)	0.3312(7)	-0.2657(9)	4.7(4)
[illegible]	3.311(6)	x^1	0.1974(2)	
E	0.996(5)	y^1	0.4158(5)	
F	1.90[illegible]	z^1	-0.1875(6)	

(Table continued)

Name	x	y	z	B
C231	0.1657(8)	0.1601(9)	0.0305(7)	2.9(3)
C232	0.1326(	0.1091(8)	0.084(2)	3.8(4)
C233	0.1292(4,	0.1059(7)	0.210(2)	5.7(5)
C234	0.1591(8)	0.1536(9)	0.2825(7)	6.9(5)
C235	0.1922(5)	0.2045(8)	0.229(2)	5.6(4)
C236	0.1955(4)	0.2078(7)	0.103(2)	4.2(4)
D	4.186(5)	x^1	0.1624(2)	
E	1.54(1)	y^1	0.1568(5)	
F	6.22(1)	z^1	0.1565(7)	
C311	0.0767(3)	0.3751(9)	-0.105(1)	2.8(4)
C312	0.0794(3)	0.3329(6)	0.012(1)	3.4(4)
C313	0.0834(3)	0.403(1)	0.1107(9)	5.4(4)
C314	0.0846(3)	0.5151(9)	0.092(1)	6.9(6)
C315	0.0819(3)	0.5573(6)	-0.025(1)	7.9(6)
C316	0.0779(3)	0.487(1)	-0.1235(9)	4.8(4)
D	3.183(6)	x^1	0.0806(2)	
E	1.658(7)	y^1	0.4451(6)	
F	0.665(8)	z^1	-0.0064(8)	
C321	0.0700(5)	0.3672(8)	-0.361(1)	3.4(4)
C322	0.0363(3)	0.432(1)	-0.384(1)	5.7(5)
C323	0.0366(3)	0.5048(8)	-0.4815(9)	6.0(5)
C324	0.0707(5)	0.5120(8)	-0.556(1)	5.0(5)
C325	0.1044(3)	0.447(1)	-0.533(1)	7.0(5)

(Table continued)

Name	x	y	z	B
C326	0.1040(3)	0.3743(8)	-0.4358(9)	4.6(4)
D	2.351(6)	x^1	0.0703(2)	
E	0.567(9)	y^1	0.4396(6)	
F	2.00(1)	z^1	-0.4586(7)	
C331	0.0202(3)	0.2307(7)	-0.212(4)	3.3(4)
C332	0.003(1)	0.2158(9)	-0.098(3)	4.4(4)
C333	-0.037(1)	0.175(1)	-0.089(1)	6.4(5)
C334	-0.0585(3)	0.1501(7)	-0.193(4)	5.9(5)
C335	-0.041(1)	0.1650(9)	-0.307(3)	11.3(8)
C336	-0.002(1)	0.205(1)	-0.316(1)	7.3(6)
D	1.203(5)	x^1	-0.0191(2)	
E	1.49(2)	y^1	0.1904(4)	
F	1.42(2)	z^1	-0.2027(7)	

‡ These values represent the ring centre of gravity coordinates

(Table continued)

(b) Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	0.051	0.011	-0.129	4.7
H113	-0.014	-0.060	-0.090	5.0
H114	-0.033	-0.236	-0.165	5.1
H115	0.015	-0.341	-0.279	5.2
H116	0.081	-0.270	-0.318	3.4
D	0.431			
E	0.374			
F	1.459			
H122	0.147	-0.291	-0.296	3.5
H123	0.179	-0.379	-0.464	6.1
H124	0.196	-0.277	-0.643	5.1
H125	0.180	-0.087	-0.653	5.9
H126	0.147	0.001	-0.485	4.1
D	6.065			
E	1.162			
F	3.709			
H132	0.101	-0.132	-0.005	3.3
H133	0.135	-0.215	0.162	4.4
H134	0.205	-0.264	0.144	4.4
H135	0.241	-0.230	-0.041	3.3
H136	0.207	-0.147	-0.208	3.2

(Table continued)

Name	x	Y	z	B
D	5.154			
E	0.66			
F	2.51			
H212	0.238	0.070	-0.014	4.7
H213	0.297	-0.022	-0.091	4.0
H214	0.303	-0.055	-0.305	3.8
H215	0.252	0.005	-0.441	6.7
H216	0.193	0.097	-0.365	4.7
D	5.210			
E	1.79			
F	2.78			
H222	0.157	0.380	-0.012	3.4
H223	0.179	0.561	-0.053	4.5
H224	0.220	0.597	-0.229	4.6
H225	0.238	0.452	-0.363	6.1
H226	0.216	0.270	-0.322	5.2
D	3.311			
E	0.996			
F	2.953			
H232	0.111	0.075	0.033	4.2
H233	0.106	0.069	0.249	6.3
H234	0.157	0.151	0.373	7.6
H235	0.214	0.239	0.280	6.2

(Table continued)

Name	x	y	z	B
H236	0.219	0.245	0.064	4.6
D	4.186			
E	1.54			
F	0.99			
H312	0.079	0.252	0.025	3.7
H313	0.085	0.372	0.195	5.9
H314	0.087	0.565	0.164	7.6
H315	0.082	0.638	-0.037	8.7
H316	0.076	0.518	-0.207	5.3
D	3.183			
E	1.658			
F	1.712			
H322	0.012	0.427	-0.330	6.3
H323	0.012	0.552	-0.498	6.6
H324	0.071	0.564	-0.626	5.5
H325	0.129	0.452	-0.587	7.7
H326	0.128	0.327	-0.420	5.1
D	2.351			
E	0.567			
F	3.047			
H332	0.018	0.234	-0.023	4.9
H333	-0.049	0.165	-0.007	7.1
H334	-0.087	0.121	-0.186	6.5

(Table continued)

Name	x	y	z	B
H335	-0.057	0.147	-0.382	12.4
H336	0.011	0.216	-0.398	8.1
D	1.203			
E	1.49			
F	2.46			

Table 40

Anisotropic Temperature Factors ($\mathring{A}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	29.6(5)	25.0(5)	31.0(6)	1.1(6)	- 5(1)	- 3(1)
Cℓ	75(3)	53(3)	64(3)	13(2)	-43(3)	-13(3)
P1	28(2)	28(2)	30(2)	0(1)	- 1(3)	- 5(5)
P2	32(2)	27(2)	32(3)	2(2)	0(2)	- 2(2)
P3	35(2)	32(2)	32(3)	2(2)	3(3)	1(3)

Table 41

Selected Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	Cℓ	2.376(4)	2.398(4)*
Rh	P1	2.334(3)	2.334(3)*
Rh	P2	2.214(4)	2.214(4)*
Rh	P3	2.322(4)	2.324(4)*
P1	C111	1.842(6)	
P1	C121	1.815(9)	
P1	C131	1.859(8)	
P2	C211	1.847(7)	
P2	C221	1.864(7)	
P2	C231	1.839(9)	
P3	C311	1.837(9)	
P3	C321	1.820(9)	
P3	C331	1.838(8)	

* Value corrected for riding

Table 42

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.9(2)
P1	Rh	P3	152.8(1)
P1	Rh	Cℓ	85.2(2)
P1	Rh	H112	67.2
P2	Rh	P3	100.4(1)
P2	Rh	Cℓ	156.2(2)
P2	Rh	H112	115.1
P3	Rh	Cℓ	86.1(2)
P3	Rh	H112	86.7
Cℓ	Rh	H112	88.0
P1	C111	C114	176.6(7)
P1	C121	C124	176.0(6)
P1	C131	C134	178.2(6)
P2	C211	C214	174.9(7)
P2	C221	C224	178.1(6)
P2	C231	C234	175.0(7)
P3	C311	C314	176.7(8)
P3	C321	C324	176.0(7)
P3	C331	C334	176.4(7)
Rh	P1	C111	104.3(3)
Rh	P1	C121	121.5(4)
Rh	P1	C131	121.1(4)

(Table continued)

Atom 1	Atom 2	Atom 3	Angle (°)
Rh	P2	C211	109.7(4)
Rh	P2	C221	114.1(3)
Rh	P2	C231	123.5(4)
Rh	P3	C311	124.7(4)
Rh	P3	C321	117.1(4)
Rh	P3	C331	107.2(3)
C111	P1	C121	105.3(5)
C111	P1	C131	101.2(5)
C121	P1	C131	100.8(4)
C211	P2	C221	100.0(4)
C211	P2	C231	104.3(6)
C221	P2	C231	102.4(5)
C311	P3	C321	101.3(5)
C311	P3	C331	100.4(5)
C321	P3	C331	103.0(5)

Table 43

Selected Intramolecular Non-bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	H112	2.77
Rh	H216	2.94
Cℓ	H126	2.62
Cℓ	H336	2.70
H116	H122	2.18
H126	H216	2.31
H212	H236	2.39
H216	H226	2.31
H312	H332	2.07
C111	H132	2.62
C112	H132	2.68
C122	H116	2.47
C211	H226	2.69
C216	H226	2.44
C231	H212	2.68
C232	H312	2.59
C236	H212	2.55
C312	H332	2.38
C312	H222	2.62
C321	H316	2.51
C322	H316	2.56
C111	C121	2.91(1)

(Table continued).

Atom 1	Atom 2	Distance (Å)
C111	C131	2.86(1)
C121	C131	2.83(1)
C211	C221	2.84(1)
C211	C231	2.91(1)
C221	C231	2.83(1)
C311	C321	2.82(1)
C311	C331	2.82(1)
C321	C331	2.86(1)
C126	C216	3.32(1)
C131	C211	3.44(1)
C132	C232	3.38(1)
C135	C212	3.48(1)
C136	C211	3.20(1)
C136	C212	3.13(1)
C136	C213	3.40(1)
C222	C312	3.37(1)
C222	C316	3.36(1)
P1	P2	3.430(5)
P2	P3	3.485(5)
P1	Cℓ	3.208(6)
P3	Cℓ	3.190(6)

Table 44

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance (Å)
Cℓ	H113	$\bar{x}$, $\bar{y}$, 1/2+z-1	2.71
H123	H213	1/2-x, 1/2+y-1, 1/2+z-1	2.38
H124	H134	x, y, z-1	2.37
H126	H234	x, y, z-1	2.43
H132	H335	$\bar{x}$, $\bar{y}$, 1/2+z	2.00
H212	H225	1/2-x, 1/2+y-1, 1/2+z	2.34
H213	H325	1/2-x, 1/2+y-1, 1/2+z	2.47

Fig. 14

A General View of the Red Form of $RhC\ell(P(C_6H_5)_3)_3$

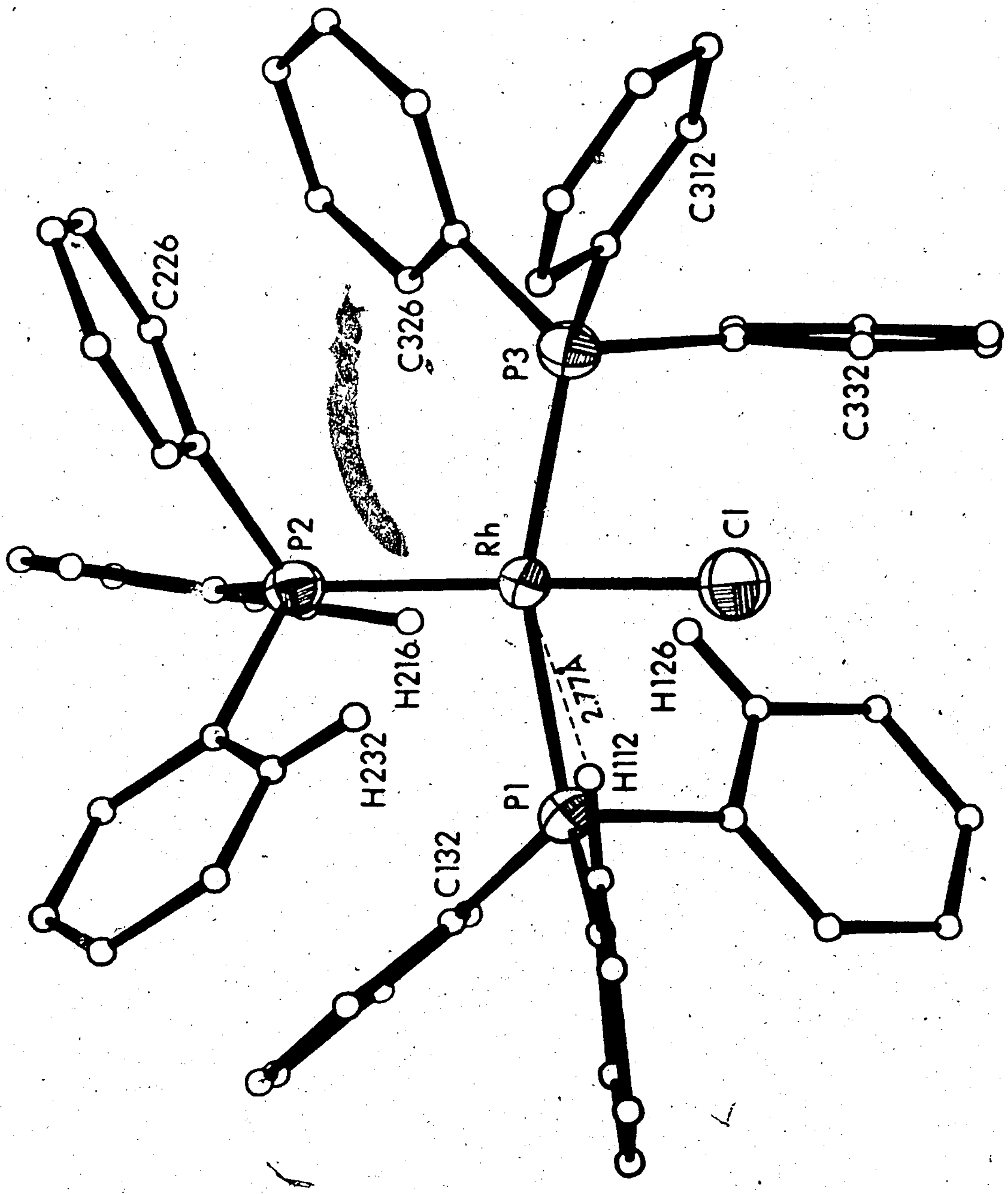


Fig. 15

Central Geometry Viewed down the P1-P3 Direction

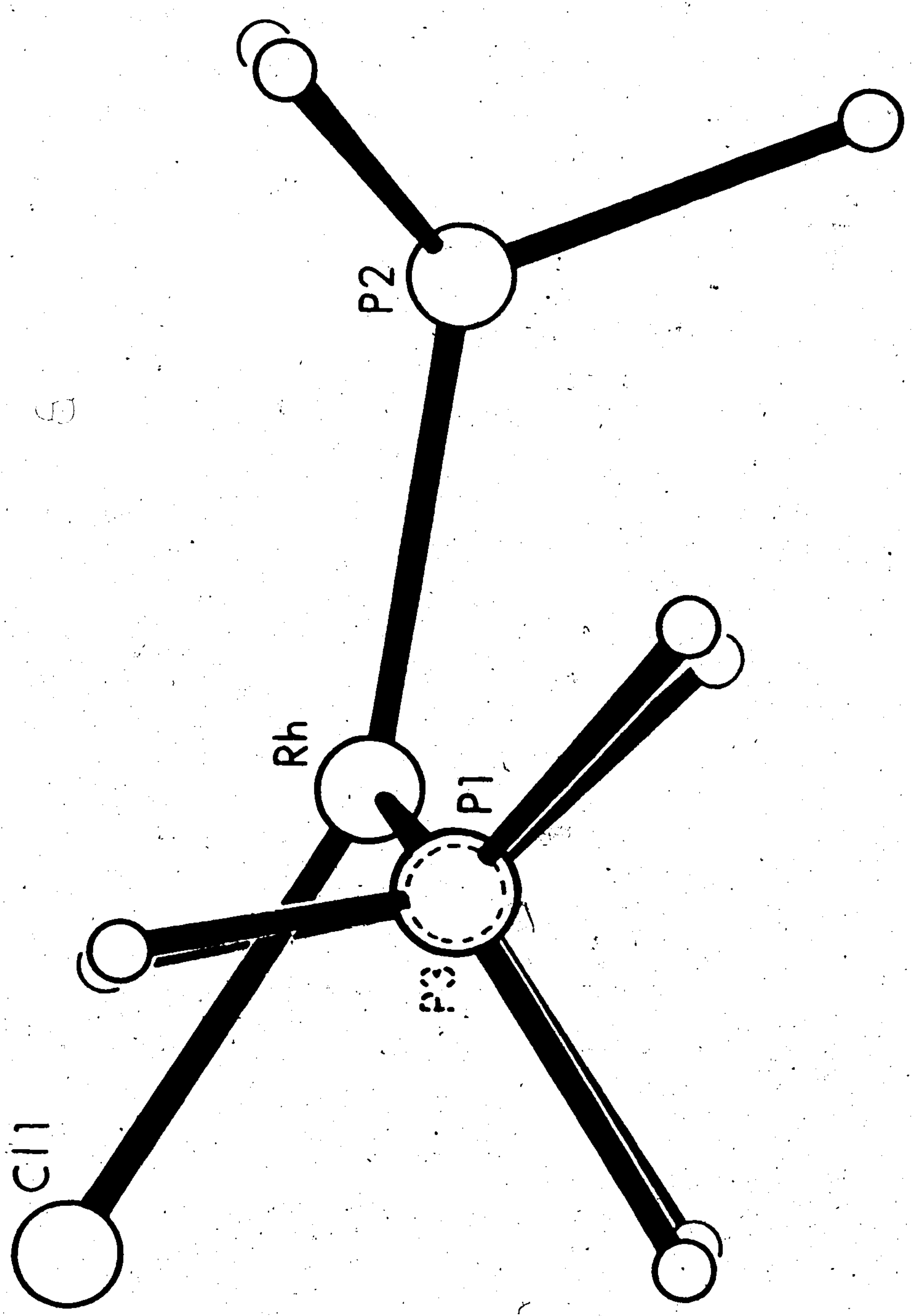
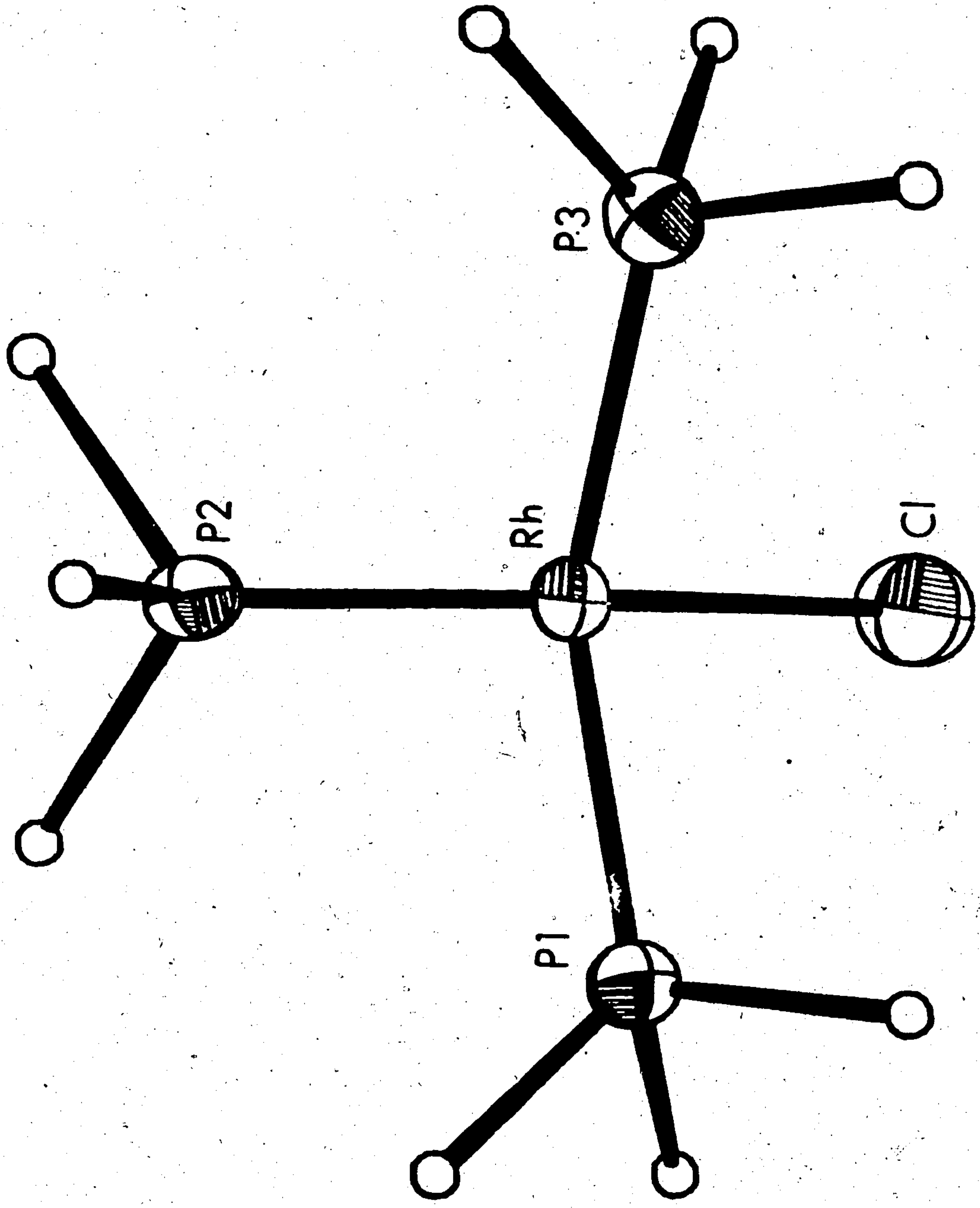


Fig. 16

View Perpendicular to the P1-P2-P3 Plane



Discussion

The molecular structure of $RhC\ell(P(C_6H_5)_3)_3$ in the red crystalline modification is shown in Fig. 14. Simplified views of the central portion of the molecule are given in Figs. 15 and 16. These diagrams should be compared with Figs. 11, 12 and 13 to observe the major differences and similarities between the molecular structure in the red and orange allotropes. To a first approximation the rhodium coordination is square [illegible] but a pronounced distortion towards a tetrahed[illegible]etry is evident in Fig. 15. This distortion is greater than that observed for the orange modification as is clearly indicated by a comparison of Cℓ-Rh-P2 angles - 156.2(2)° (red) and 166.7(2)° (orange) - and P1-Rh-P3 angles - 152.8(1)° (red) and 159.1(2)° (orange). The actual deviations from planarity for the $RhC\ell P_3$ fragment are given in Table 45. The magnitude of the distortion in the red form is sufficiently great that the only significant interligand repulsions occur between ligands directly bonded to rhodium. Both forms distort from the planar geometry in the same way i.e. towards a tetrahedral geometry. This should be compared with a pyramidal distortion observed in $RhLC\ell$ (where L is the tridentate phosphine ligand $(C_6H_5)P((C_3H_6)P(C_6H_5)_2)_2$ [140].

Table 45

Weighted Mean Molecular Planes for $RhC\ell(P(C_6H_5)_3)_3$ [a]

Atoms Contained in the Planes	Modification	Equation
Rh, Cℓ, P1, P2, P3	red	$-0.6629X - 0.2857Y + 0.2690Z = -4.8112$
.. ..	orange	$-0.1624X + 0.1708Y + 0.9718Z = 4.298$

Distances of Atoms from Planes

Atom	Distance (Å) red	Distance (Å) orange
Rh	0.010	-0.014
Cℓ	-0.489	-0.290
P1	0.469	0.419
P2	-0.436	-0.276
P3	0.492	0.234

[a] The orthogonal coordinate system (X,Y,Z) corresponds to the crystal abc axes.

It should be noted that the orange form is metastable and converts to the red form on prolonged reflux during the preparation. The methods of preparation of the two forms differ only in the nature of the excess reagent (see Chapter II and references therein). The red form is prepared by slow addition of triphenylphosphine to 'rhodium trichloride' i.e. the rhodium trichloride is normally in excess, whereas the orange form is prepared such that triphenylphosphine is the excess reagent. The difference is then kinetic and suggests that the immediate precursors to the forms of $RhC\ell(P(C_6H_5)_3)_3$ are different and dependent on the reaction conditic In the orange form the product is not produced in its ground state. It could thus be temporarily locked[119] in the metastable geometry by the particular arrangement of the triphenylphosphine groups.

The rhodium-ligand distances (uncorrected for thermal motion) of this study, the equivalent values reported by Mason *et al.*,[138,140] and the relevant data on $RhLC\ell$ are compared in Table 46.

The two determinations of the red form are in excellent agreement and no significant deviations can be detected. For the red form the rhodium-phosphorus bond lengths to the chemically equivalent phosphorus atoms

Table 46

Distances (in Å) from Structures Containing the $RhC\ell P'_3$ Fragment

	$RhC\ell P'_3$,[a]	$RhC\ell P'_3$,[a]		RhLCℓ
	(red)	(red)[c]	(orange)	
Rh-Cℓ	2.376(4)	2.386	2.404(4)	2.381(2)
Rh-P (P *trans* to Cℓ)	2.214(4)	2.210	2.225(4)	2.201(2)
Rh-P	2.322(4)	2.320	2.304(4)	2.288(2)
(P *trans* to P)	2.334(4)	2.331	2.338(4)	2.288(2)[b]
ΣRh-ligand	9.246	9.244	271	9.158
ΣRh-P	6.870	6.861	6.867	6.777
	this work	(138,140)	Chap. V	(140)

[a] P' represents triphenylphosphine

[b] related by symmetry to the value above

[c] most recent values for this work are available as a private communication in ref. 140

(P1 and P3) are the same within experimental error in contrast to an apparently significant difference in the orange form. In all four structure determinations the chemically unique rhodium-phosphorus bond is substantially shorter than the other two. As mentioned in

Chapter V this extreme shortening may be attributed to significant π-acidity of triphenylphosphine. The complex RhLCℓ shows considerably shorter rhodium-phosphorus distances than $RhC\ell(P(C_6H_5)_3)_3$.

In $RhC\ell(P(C_6H_5)_3)_3$, (red form), the rhodium atom has one particularly close contact[142] with an *ortho* hydrogen of the 11 phenyl group. This contact (Rh-H112, 2.77 Å) is apparently caused by repulsions involving atoms on the opposite side of the phenyl group (Table 43). No attractive character is attached to this contact. It should be noted that the short contacts in the orange form and RhLCℓ involve phenyls attached to the chemically unique phosphorus and correspond to H216 in Fig. 14.

There appears to be a significant difference ($\Delta/\sigma \sim 4$) between the rhodium-chlorine bond lengths observed in the red (2.376(4) Å) and the orange (2.404(4) Å) forms. This difference persists even when the bond lengths are modified for the effects of thermal motion. This variation could be the result of the greater interligand repulsions which are present in the orange crystals and it is reasonable that the effect should be noticeable in the weaker rhodium-chlorine bond rather than the rhodium-phosphorus bonds. Although the rhodium-phosphorus and rhodium-chlorine bond lengths support this view the difference may simply be an artifact of the data and thus not significant.

The geometry of the triphenylphosphine ligands is normal with respect to the angles C-P-C and Rh-P-C (Table 42): C-P-C, free ligand ~ 103°;[129] complexed ligand ~ 102°; Rh-P-C ~ 115°. However the geometry is abnormal with respect to the phosphorus-carbon distances. The average of the six-phosphorus-carbon distances involving P1 and P3 is 1.835 Å whereas the other three distances involving P2 average 1.850 Å cf. 1.828 Å for the free ligand. No comparable trend is reported in RhLCℓ. In fact in this molecule there is no apparent difference between P-C (sp^2) and P-C (sp^3) which has been observed in other phosphine complexes where the phosphorus is attached to aryl or alkyl substituents[143]. The comparable values for the orange form were 1.838 Å and 1.855 Å respectively. Combining the data from the two modifications gives mean phosphorus-carbon bond lengths of 1.837(4) Å and 1.852(5) Å for the two types of triphenylphosphine ligands. By normal crystallographic standards the phosphorus-carbon bonds of the phosphine *trans* to the chlorine atom are significantly larger than normal (Δ/σ ~ 4) while no convincing difference is observed between the phosphorus-carbon distances of the mutually *trans* phosphines, typical literature values[17,18,129] and the average phosphorus-carbon bond distance (1.827(9) Å) observed in the dioxygen derivatives as mentioned in Chapters III and IV.

It would be pleasing if the extremely short rhodium-phosphorus bond, the lengthening of the associated phosphorus-carbon bonds and π-bonding could be related in a simple manner. Arguments using covalent radii for spherical atoms, to explain metal-phosphorus distances are tenuous since the geometry about the phosphorus atom is far from tetrahedral [143] and an anisotropy of covalent radius is expected as a result of the different mixtures of 's' and 'p' character in the various bonds [144]. Since the 3s and 3p orbitals have distinctly different radii [145] then σ-bonding alone would predict short metal-phosphorus and long phosphorus-carbon bond lengths when compared to values based on a simple covalent radius (r_{sp^3}) for phosphorus. As mentioned the angular properties of the coordinated triphenylphosphine are essentially the same as the free ligand so such a description cannot explain the phosphorus-carbon distance variation. The difference could be explained by greater participation of phosphorus 3d orbitals in the phosphorus-carbon σ-bonding, if the argument concerning the differences in radial properties of the phosphine atomic wave functions is extended to include these orbitals.

The π-acidity of phosphine ligands involves phosphorus 3d orbitals and the σ and π components of the bonding are not separable in this case, thus the 3d orbitals should also participate in σ-bonding. The lengthening of the phosphorus-carbon bonds should then be related to the extremely short rhodium-phosphorus bond and π-bonding.

While this explanation may look plausible certain conflicting evidence does exist particularly in the structure of RhLCℓ which should show very similar features to $RhC\ell(P(C_6H_5)_3)_3$ with differences due tc the constraints of the tridentate phosphine ligand. As indicated previously the long phosphorus-carbon bonds do not exist in this structure. The explanation is then either incomplete or incorrect. The probability of an error of this magnitude and direction (0.02 Å too long) in any of the structures under consideration seems low. There is a difference in the nature of the inductive effects [146] of the substituents of the chemically unique phosphorus atoms in these structures. In $RhC\ell(P(C_6H_5)_3)_3$ the three substituents are electron withdrawing phenyl groups whereas there is only one electron withdrawing phenyl group and two electron donating aliphatic chains in RhLCℓ. Thus the observed phosphorus-carbon bond lengthening might be very specific to triarylphosphines in an extensive π-bonding situation. Considerably more data are required to solve this problem.

Finally the structural trends of $RhC\ell P_3'$ and its derivatives can be analysed. The molecules fall into two classifications: (a) coordinatively unsaturated - $RhC\ell P_3'$, $RhC\ell(P_2'(CS)$, $RhC\ell P_2'(C_2F_4)$, (b) coordinatively saturated - $(O_2)RhC\ell P_3'$, $[(O_2)RhC\ell P_2']_2$. The trends corresponding to ligand replacement within each group can be analysed and then trends associated with ligand addition can be deduced. The three species present in group (a) contain a common structural fragment $RhC\ell P_2'$ with the only differences being due to the ligand *trans* to the chlorine atom. The data for these complexes are summarised in Table 47. These data show a small range of rhodium-chlorine distances (the value 2.404(4) Å for the orange form of $RhC\ell(P(C_6H_5)_3)_3$ should probably be excluded from the comparison for reasons cited earlier). The significant changes in the rhodium-phosphorus bond lengths *cis* to the chlorine atom must then reflect changes in rhodium-phosphorus π-bonding [141] and the ligands can be arranged in order of π-acidity - C_2F_4 > CS > $P(C_6H_5)_3$.

[illegible] 47

Ligand *trans* to Cℓ	[illegible]ℓ (Å)	R[illegible]	[illegible] (*trans* to P) (Å)	Ref.
$P(C_6H_5)_3$(red)	2.3[illegible](4)	[illegible].3[illegible]8	2.334(3) 2.322(4)	This work
$P(C_6H_5)_3$(red)	2.386	2.326	2.320 2.331	138,140
$P(C_6H_5)_3$(orange)	2.404(4)	2.321	2.304(4) 2.338(4)	Chap. V
CS	2.386(3)	2.336	2.335(2) 2.337(2)	121
C_2F_4	2.375(8)	2.372	2.374(8) 2.370(8)	138

The group (b) compounds are compared in Table 48. The common structural fragment is $O_2RhC\ell P'_3$. The geometry of these complexes can be treated as trigonal bipyramidal and the differences occur in an axial position. Within this series the rhodium-chlorine distances are effectively constant. The greatest changes occur in both the axial and equatorial rhodium-phosphorus distances. In the *tris*-phosphine complex these distances are longer by approximately 0.06 Å and 0.08 Å respectively. This difference must be mainly due to the different axial ligands P' and O2'. The oxygen in the axial position has no

Table 48

	$O_2RhC\ell P'_3$ Distance (Å)		$[O_2RhC\ell P'_2]_2$ Distance (Å)	
equatorial				
Rh-Cℓ	2.391(3)		2.390(3)	
Rh-P	2.357(3)		2.277(3)	
Rh-O_2	2.043[a]	2.081(8) 2.005(8)	2.090[a]	2.198(7) 1.983(7)
axial				
Rh-P	2.375[a]	2.362(4) 2.387(4)	2.314(3)	
5th other ligand	P'		O2'	

a - average of two distances.

vacant orbitals in a suitable geometry to accept π-electrons from the rhodium. Thus in $O_2RhC\ell P'_3$ there are four ligands (3P' and O_2) competing for π-electron density whereas in the half unit of [illegible]$hC\ell P'_2]_2$ there are only three ligands (2P' and O_2) [illegible] would be reasonable to expect the observed trend but not perhaps the magnitude. The average rhodium-oxygen distance is greater in the dimeric species than in the monomeric *tris*-phosphine complex. However while the average is higher one distance is short (1.983(7) Å) and the other very long (2.198(7) Å). While it is difficult to assess how much of this assymmetry is due to the nature of the bridge in the dimer the difference parallels the trend observed in $O_2RhC\ell P'_3$. In this latter case the rhodium-oxygen (O pseudo *trans* to P) distance was significantly longer than the rhodium-oxygen distance involving O pseudo *trans* to $C\ell$. In the dimeric species the magnitude of the difference is much greater. In discussions of the '*trans*' effect it is convenient to view the molecules as having a distorted octahedral geometry (i.e. each oxygen occupies a separate site rather than O_2 occupying a single coordination site). If the '*trans*' effect is modified by the extent of π-bonding [139,141] and the difference in rhodium-phosphorus bond lengths ($O_2RhC\ell P'_3$ to $[O_2RhC\ell P'_2]_2$) reflects an increase in the π-bonding, then a more marked assymmetry for the bound dioxygen in $[O_2RhC\ell P'_2]_2$ would be expected regardless of the constraints due to bridge formation.

The changes in geometry that accompany the chemical reaction:

$$RhC\ell P'_3 + O_2 \rightarrow O_2RhC\ell P'_3$$

can be summarised as follows:

(1) An oxygen molecule can be expected to approach an open site of $RhC\ell P'_3$ to form a square pyramidal intermediate which transforms to a trigonal bipyramidal structure by normal angular deformation. This is supported by the only major angular changes upon oxygenation being within the equatorial plane ligands (see Tables 12, 22, 32, and 42).

(2) The rhodium-phosphorus bond lengths increase.

(3) No change in rhodium-chlorine distances.

The constancy of the rhodium-chlorine distances throughout the series and the variation in rhodium-phosphorus bond lengths supports the concepts of π-bonding for the ligands P' and O_2. Electro neutrality for the rhodium atom is then achieved by variations in the π-bonding components.

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Appendix 1

Programmes Used

Author	Title	Description
D.P. Shoemaker	MIXG2	Calculates Picker diffractometer settings
M.J. Bennett	PMMO	Calculates intensities, makes LP corrections for Picker data
M. Elder	D-refine	Refines axial lengths (modified by K. Simpson)
A. Zalkin	FORDAP	Fourier summation for Patterson or electron density maps
M.J. Bennett	MMMR	Calculates starting parameters for rigid bodies or hindered rotors.
W.C. Hamilton	GONO9	Absorption correction calculator
C.T. Prewitt	BURP	Enlarged version of SFLS5HR structure factor calculation and least squares refinement (modified by B. Foxman and W. Brooks)
G.J. Williams	CROMERS	Calculates form factors curves from Cromer's coefficients
J.S. Wood	MGEOM	Calculates bond lengths, angles and best planes

W. Busing and H.A. Levy	ORFFE II	Calculates bond lengths, angles and associated errors (modified by B. Penfold, W.L. Brooks and M. Elder)
C. Johnson	ORTEP	Writes plot command tape for Calcomp plotter
M. Cowie	PUBE	Sorts reflection data according to any desired hkl sequence
R.C. Elder	PUBTAB	Tabulates reflection data for publication (modified by M. Cowie)

All programmes were run using an IBM 360 model 67 computer.

Appendix 2

Conventional Crystallographic Symbols as Defined in Vol. I, Page xi, of the International Tables for X-ray Crystallography

h,k,ℓ	indices of the reflection from a set of parallel planes
a,b,c	lengths of unit cell edges
α, β, γ	interaxial angles
a^*, b^*, c^*	lengths of reciprocal unit cell edges
$\alpha^*, \beta^*, \gamma^*$	interaxial angles in reciprocal space
$x_i, y_i, z_i,$	fractional coordinates of an atom i in units of a,b,c
$F_{hk\ell}$	structure factor for the unit cell, corresponding to the Bragg reflection $hk\ell$.
$\overline{u}^2$	mean square amplitude of atomic vibration
B	Debye isotropic thermal parameter; $B = 8\pi^2\overline{u}^2$
$U_{11}, U_{22}, U_{33},$	anisotropic thermal parameters used to describe ellipsoidal electron distribution of the anisotropically vibrating atom; the temperature factor expression is then: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}b^2B^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}h\ell a^*c^*\cos\beta^* + 2U_{23}k\ell b^*c^*\cos\alpha^*)]$
F_o	observed structure factors
F_c	calculated structure factors