CRYSTAL STRUCTURE OF

$ReCl_2(acac)_2$, $ReCl_2(acac)[P(C_6H_5)_3]_2$

AND $ReOCl_2(acac)P(C_6H_5)_3$

X-RAY CRYTAL STRUCTURE INVESTIGATION OF $\mathrm{ReC\ell_2(acac)_2}$, $\mathrm{ReC\ell_2(acac)[P(C_6H_5)_3]_2}$ AND $\mathrm{ReOC\ell_2(acac)P(C_6H_5)_3}$

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SCOPE AND CONTENTS:

The crystal structure of $ReC\ell_2(acac)_2$, $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ and $ReOC\ell_2(acac)P(C_6H_5)_3$ have been determined by single crystal x-ray diffraction methods. The structure of $ReC\ell_2(acac)_2$ has been found to belong to the trans - dicholoro - group of the $M(acac)_2L_2$ type compounds. In $ReC\ell_2(acac)[P(C_6H_5)_3]_2$, the two phosphorus atoms are trans, and the two chlorine atoms are cis to each other. In $ReOC\ell_2(acac)P(C_6H_5)_3$, it has been found that two chlorines are at trans positions and the oxo group and the triphenylphosphine group are cis to each one of the carbonyl oxygen atoms of the acetylacetone group. The bonding of Re-Cℓ, Re-P, and Re-O are individually discussed and compared. The nature of bonding in the acetylacetone groups is also discussed. The intramolecular non-bonded distances between ligand atoms bonded directly to rhenium are compared with other related compounds. The reaction mechanisms for the formation of these three rhenium acetylacetonates have been proposed.

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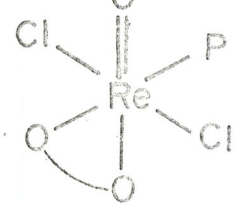
CHAPTER 1

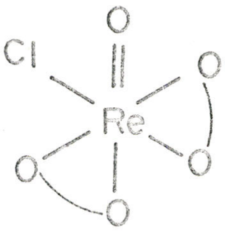
INTRODUCTION

Some β-diketone complexes of rhenium have been synthesized recently by D. E. Grove et al. (1). The structure of none of the complexes obtained has been reported so far. Because each complex as well as the rhenium starting compounds can exist in more than one isomeric form, the investigation of the structures of the products as well as the reactants is necessary before one can attempt to understand the reaction mechanism involved. $ReOC\ell_2(acac)P(C_6H_5)_3$ and $ReC\ell_2(acac)\cdot[P(C_6H_5)_3]_2$ were prepared from the starting material $ReOC\ell_3[(P(C_6H_5)_3)]_2$ which has three geometrical isomers: (A, I-III) shown in Figure 1.1. The yellow isomer which was used for preparing compounds $ReOC\ell_2(acac)\cdot P(C_6H_5)_3$ and $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ was postulated to be isomer A-I (2) since it has been shown (3,4) that the chlorine atom trans to the oxygen atom is more weakly bonded to the rhenium atom and acts as an attack center. The reaction of $ReOC\ell_3[P(C_6H_5)_3]_2$ and acetylacetone in benzene would be expected to give B[†] and C:

B.



C.



[†] For brievity, $P(C_6H_5)_3$ group is replaced by "p" in all the diagrams of this work.

Figure 1.1

Some Geometrical Isomers of
Rhenium Compounds

A. $ReOCl_3[P(C_6H_5)_3]_2$

B. $ReOCl_2(acac)P(C_6H_5)_3$

D. $ReCl_2(acac)[P(C_6H_5)_3]_2$

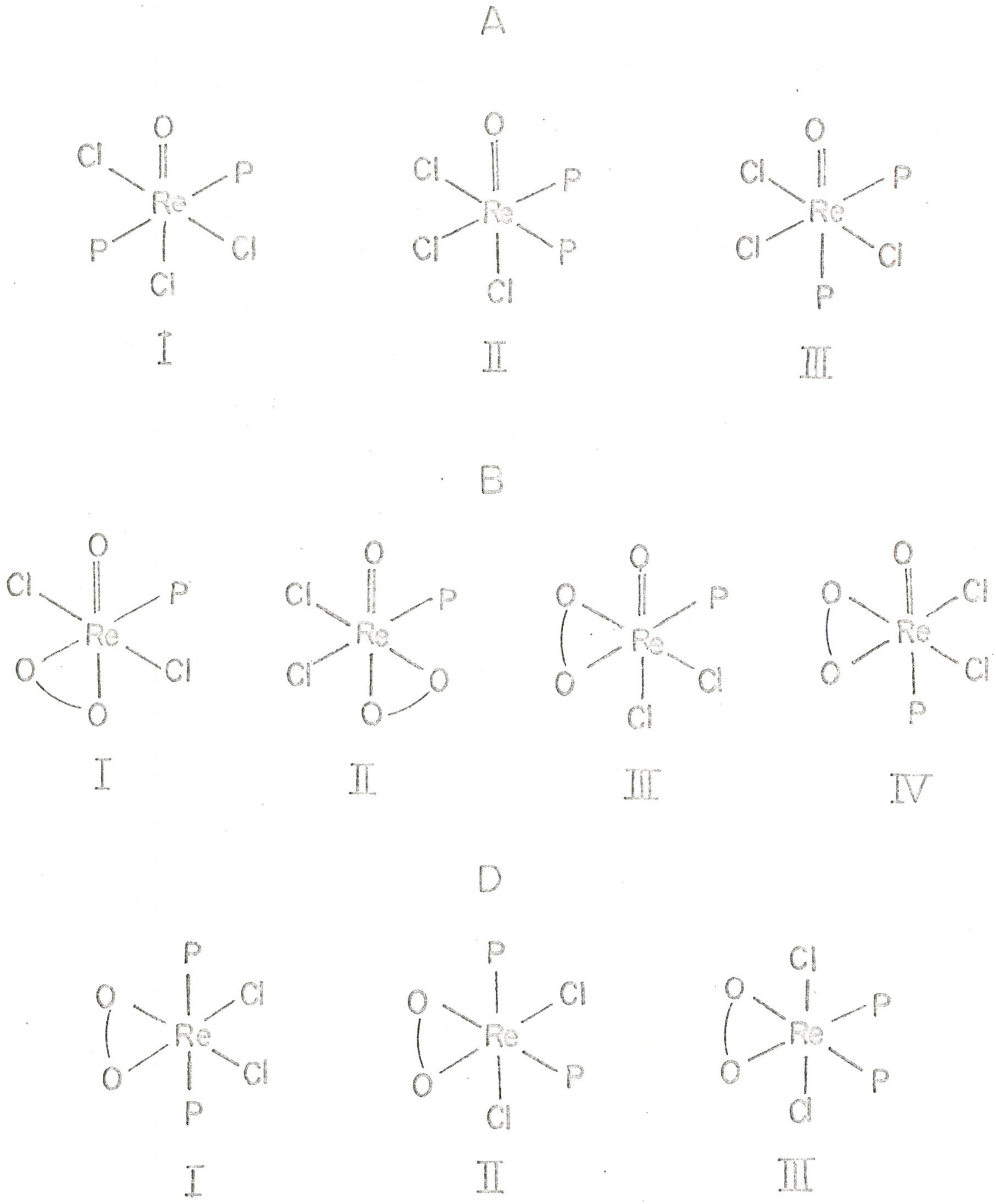


Figure 1.1

A product corresponding to the composition of B(1) was isolated from the reaction mixture, but it was not the main product and decomposed as the reaction proceeded further. No product corresponding to C was isolated. In addition to B, products with formulae $ReC\ell_2(acac)_2$, and $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ have been isolated.

$ReOC\ell_2(acac)P(C_6H_5)_3$ has four possible geometrical isomers (B, I-IV in Figure 1.1) and $ReCl_2(acac)[P(C_6H_5)_3]_2$ has three, (D, I-III in Figure 1.1). A knowledge of which geometrical configuration of complexes B and D occurred in the synthesis process would help us in understanding the reaction mechanism involved.

$ReC\ell_2(acac)_2$ was reported (1) as a bridged dimer with the proposed structure E, Figure 1.2. If this were true, this would represent a new form for a dimer in a metal-β-diketone complex since one acetylacetone group bridging through two metal-oxygen bonds is different from that found in the Ni, Co and Pt cases (F, G and H of Figure 1.2). There was no evidence offered to show whether the chlorine atoms had a cis or trans configuration.

All the above discussion is based on the assumption that acetylacetone group acts as a bidentate ligand chelated by metal-oxygen linkages. Though this is normal, exceptional cases have been observed in Pt(II) and Pt(IV) (5,6,7,8) complexes where β-diketones act as unidentate as well as tridentate ligands. Since no x-ray structural work on rhenium-β-diketonates has been reported so far, we could not exclude this possibility. If any such exceptions occurred, the coordination number of Re in these complexes would probably deviate from six and the interpretation of the reaction mechanism would even be more

Figure 1.2

Some Polynuclear Species of

Metal Acetylacetonates

E. $[ReCl_2(acac)_2]_2$

F. $[Ni(acac)_2]_3$

G. $[Co(acac)_2]_4$

H. $[(CH_3)_3Pt(acac)]_2$

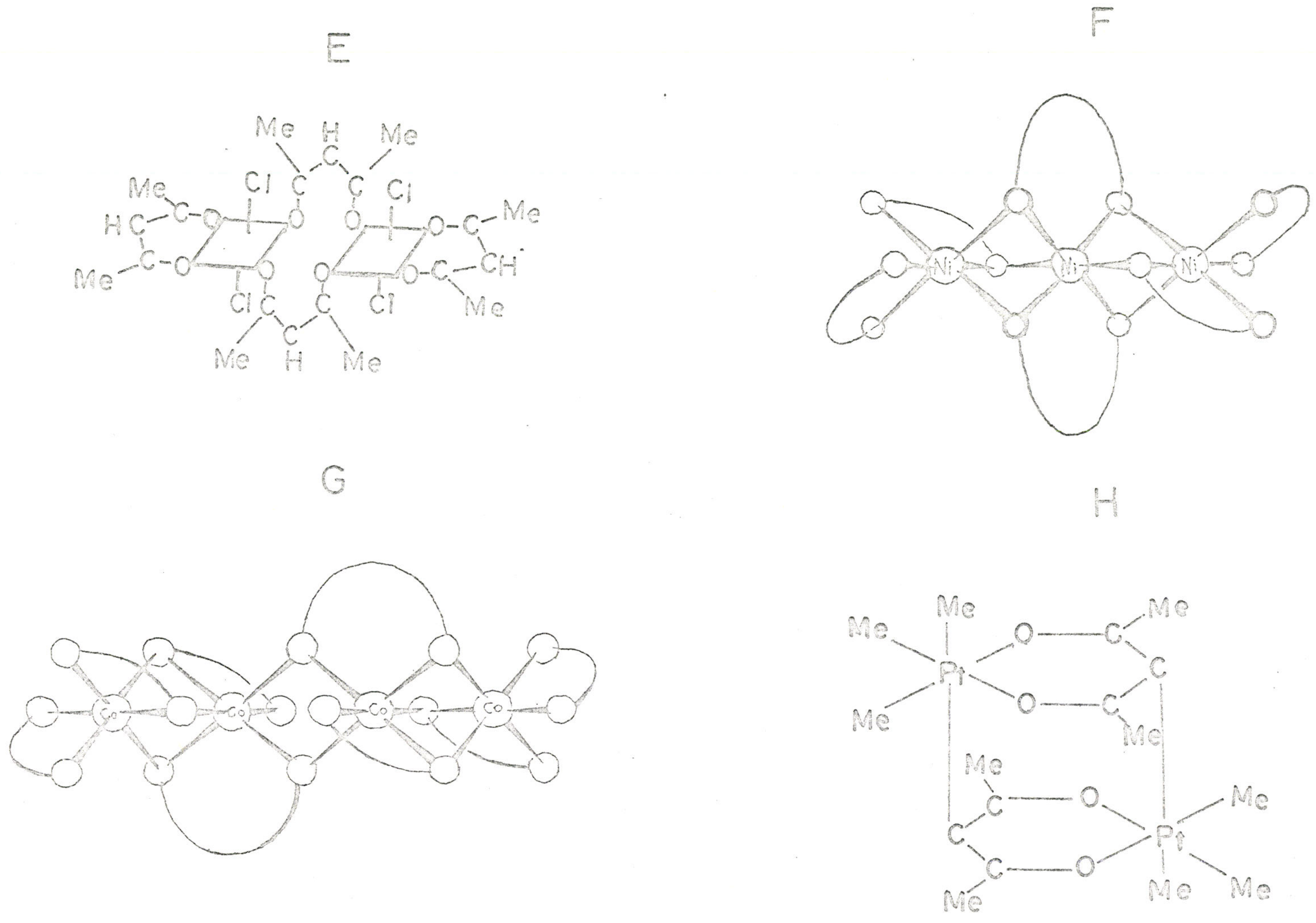

E
Me
H
Me
Cl
Cl
Me
HC
CH
Me
Cl
Cl
Me
H
Me
F
Ni
Ni
Ni
G
Co
Co
Co
Co
H
Me
Me
Pt
O
C
Me
C
O
C
Me
Me
Me
C
O
C
Pt
C
O
Me
Me
Me
Me

Figure 1.2

complicated. Since no unambiguous evidence of the type of bonding between rhenium and the β-diketone group has been presented, x-ray investigation of the structure of these three rhenium-β-diketonates should provide useful information about bonding as well as the geometric details of the structures. It might then be possible to understand the reaction mechanism involved.

Recently, several papers on the crystal structures of compounds which involved multiple bonding between rhenium and oxygen (9, 10, 11) and between rhenium and nitrogen (12, 13, 14, 15) have been published. The common feature of these pseudo-octahedral structures, in addition to the very short Re-O or Re-N distance, is that the central metal is displaced out of the equatorial plane towards the oxygen or nitrogen atom. Bright and Ibers suggest $\overset{e}{\text{tht}}$ non-bonded intramolecular interactions are responsible for this kind of distortion (16). The present work should provide a good test of this suggestion since $\mathrm{ReOC\ell_2(acac)P\cdot(C_6H_5)_3}$ would be expected to show a similar distortion, but the other two complexes: $\mathrm{ReC\ell_2(acac)_2}$ and $\mathrm{ReC\ell_2(acac)\ [P(C_6H_5)_3]_2}$ should not show such distortion. A comparison of the inter-relationship of these three structures should give us a clue as to what feature dominates the structures of these types of complexes.

CHAPTER 2

THE STRUCTURES OF METAL β-DIKETONE COMPLEXES

β-Diketones can bond to metals either as neutral ligands or as β-ketoenolate anions. In addition the anions may bond to the metal ion in a number of ways. As a result, metal complexes containing β-diketones or β-ketoenolate anions exist in a wide range of stoichiometries; some complexes contain only β-ketoenolate anions as ligands, others contain other ligands as well. A summary of the well characterized stoichiometries is given in Table 2.1. The existence of compounds of two different metals with the same stoichiometry does not mean that the compounds will have the same structure; in many cases it is known that different structures exist. It will be noticed that rhenium is one of the elements which forms the most varied selection of β-diketone complexes. Those which have been characterized are summarized in Table 2.2. A very comprehensive review of the chemistry of the metal β-ketoenolates has been published recently by Fackler (115). However, relatively little discussion was devoted to the structures of metal β-diketones. A great many crystal structures of β-diketonate complexes have been published in the past decade and here we attempt to summarize and comment on this work.

2.1 Molecular Structures

Molecular structures of metal β-diketone complexes are mainly dominated by the following factors: (1) The oxidation state of the central metal atom which is closely related to the stoichiometry of the compounds.

TABLE 2.1

WELL CHARACTERIZED STOICHIOMETRIES FOR β-DIKETONE-MATEL COMPLEXES

Stoichiometry	Metals (References)
$M(DK)$ *	Li, Na, K, Cs(17,18); Cu(19); Ag(17); Tl(17,20)
$M(DK)X_2$	B(21,22)
$M(DK)R_2$	B(23,24), Ga, Tℓ(25,26); Au(27,28)
$M(DK)X_4$	Sb(29)
$M(DK)X_2L_2$	Nb, Ta(30,31)
$M)(DK)X_2$	V(32)
$M(DK)(LL)_2$	Cr(33)
$M(DK)(CO)_4$	Mn(34)
$M(DK)OX_2L$	Re(1)
$M(DK)X_2L_2$	Re(1)
$[M(DK)RL]_x$	Mg, Co, Ni(35)
$[M(DK)R_3]_2$	Pt(36)
$[M(DK)O_2OH]_2$	W(37)
$M(DKH)X_5$	Sb(29)
$M(DK)_2$	Be(38); Ca, Ba, Hg(17); Cr(39); Mn(40); Fe(41); Cu(42); Mg, Sr(43); Pt(45); Pb
or $[M(DK)_2]_x$	Zn(132); Co(116); Ni(131)
$M(DK)_2^+$	B(22)
$M(DK)_2L_2$	Ni(47,48); Co(48,49); Mn(40,50); Fe(50-53); Mg(128)
$M(DK)_2X_2$	Ge(54),Ti(55,56); Re(57)
$M(DK)_2X$	Sb, Bi(58)
$M(DK)_2R$	Ti(59-62)
$M(DK)_2O_2$	Mo(63,64)

TABLE 2.1 (continued)

$[M(DK)_2O_2]_2$	U(65)
$M(DK)_2O_2L$	U(66)
$M(DK)_2(OH)_2^+$	As(58)
$M(DK)_2(OH)_3L_3$	Mo(67)
$M(DK)_2R$	Aℓ(68)
$M(DK)_2O$	V(69); Ti(70)
$M(DK)_2L$	Cu(71-73); Co(74); Zn(75,76)
$[M(DK)_2X]$	Ti(77)
$M(DK)_2OX$	V(32)
$[M(DK)_2OX_2]$	V(32); Nv(78)
$[M(DK)_2(LL)]_2$	Cr(79)
$[M(DK)_2O]_2O$	Mo(64)
$M(DKH)_2MX_4$	Ga(80)
$M(DK)_2X_2 \cdot HX$	Pt(29)
$M(DK)_3$	Mn(81); Aℓ(82); Fe(83); Sc(17); Y, Ce, Ln's (84-86); V(87); Cr(88); Mo(89); Re(90); Ru(91); Co(92); Rh, Ir(93); Ti(94); Ga, In(95); Os(91)
$M(DK)_3^+$	Si(96); Ge(95,97); Ti(97,98)
$M(DK)_3^-$	Mg, Zn, Cd, Co, Ni, Mn (99); V(100)
$M(DK)_3^{++}$	P(101)
$M(DK)_3RCO_2$	Zn(102)
$M(DK)_3L$	Lanthanous (103)
$M(DK)_3X$	Zr, Hf(97)
$[M(DK)_3O]^-$	Nb(104)
$M(DK)_4$	Zr, Hf(105); Th, U(106,107); Pu(108); Ce(109); Sn, Pb(110)
$M(DK)_4^-$	En, Tb, Gd(111)

TABLE 2.1 (continued)

* Abbreviations used in Tables 2.1 and 2.2 are:

DKH - β-diketone

DK - β-diketone anion

X - halogen or pseudohalogen

R - alkyl, aryl, or alkoxy

L - donor ligand (e.g. phosphines)

LL - bidentate ligaud (α - dipyidyl)

RCO_2^- - Carboxylate group

TABLE 2.2

β-DIKETONE COMPOUNDS OF RHENIUM

Compounds	References
$Re(DK)_3$	90, 112
$Re(DK)X_2(PR_3)_2$	1
$Re(DK)OX_2PR_3$	1
$Re(DK)_2X_2$	1
$Re(DK)_2XPR_3$	1
$Re(DK)_2OX$	112
$Re(DK)X_3PR_3$	112
$Re_2(CO)_6(DK)_2$	113
$Re_3X_6(DK)_3$	114
$Re(CO)_3(DKH)X$	113

In only a few exceptional cases does the β-diketone act as a neutral ligand, usually the oxidation state of the whole β-diketone group is -1 as can be seen from Tables 2.1 and 2.2, (2) The coordination number of the metal atom has a dominant effect on the structure of metal β-diketone compounds. The commonest linkage between the β-diketone anion and the metal is through the two carbonyl oxygen atoms. This implies that the β-diketone group occupies two sites of the coordination sphere of the metal. When the coordination number of the metal that is obtained by counting the sites occupied from chelated β-diketone groups is different from the normal coordination number, (that which occurs most often for that metal in other compounds) three alternatives have been observed: (A) The metal coordinates to some neutral ligand such as H_2O to complete its normal coordination number. (B) The coordination sphere is completed by polymerization. Examples of the above can be illustrated by a series of Co(II) acetylacetonates. $Co(acac)_2(H_2O)_2$ (49) is a monomer, $Co(acac)_2 \cdot H_2O$ is a dimer and $Co(acac)_2$ (116) is a tetramer. One thing common in this series is that Co(II) has achieved six coordination by method (A) or (B) or a combination of (A) and (B). (C) In case the coordination number by counting sites occupied from chelated β-diketone groups is more than the normal one, the β-diketone group may link to the metal atom through the γ-carbon atom, this effect would reduce the coordination number of the metal by one which is observed in $K[Pt(acac)_2C\ell]$ (7).

the where
In case more than one configuration is possible for a given coordination number, (such as coordination number four which is found in both square planar or tetrahedral complexes), the metal atom seems to have a preferred configuration. For example, compound with the formula

M(DpM)$_2$ (DPM = dipivaloymethane anion), is tetrahedrally coordinated where M = Co, Zn (118) and is square planar where M = Cu, Ni.

For the chelated β-diketone group the variation within the metal β-diketone unit is very small. There are a few factors that can vary from compound to compound, these are: (1) M-O bond length which depends mainly on the size of metal ion and the difference in electronegativity between the metal and oxygen. (2) OMO angle which depends on the M-O bond length since the O ... O non-bonded distance is usually close to 2.8Å, the value observed in a good number of metal β-diketonates (115). (3) The dihedral angle, the angle between OMO and the best least squares plane of the chelate ring OCCCO, is found to vary from 0° (in Zn (DPM)$_2$ (118) to 22° (in Zr(acac$_4$ (120)). This angle is probably influenced by the intramolecular non-bonded distance between atoms directly bonded to the metal. The variation of the geometry of the β-diketone group is even smaller. The geometry of this group will be described in Section 2.2 and the averaged dimensions of metal β-diketone compounds will be shown in Table 2.5. Examples of the β-diketone group bonded to a metal through the γ-carbon atom are rare. However, the variation of its geometry would be expected to be very small.

The following are selected brief descriptions of some types of molecular structures:

(1) M(acac)$_4$ (M = Zr (120), Ce (121), Th, U (122) and M(DBM)$_4$ (M = Ce,Th,U (109)). All of these are eight coordinated compounds with the β-diketone group bonded to the metal through two carbonyl oxygen atoms. They all have the square antiprismatic configuration

with the chelate rings arranged as in Figure 2.3 (B).

(2) $M(acac)_3$ (M = Cr (124), Mn (124), Fe (83, 126) Pd (127))
The metal is octahedrally coordinated by three chelated acetylacetone groups. The inner coordination around the metal ion is very close to a regular octahedron.

(3) $M(acac)_2L_2$ (L = H_2O for M = Mg (128), Co (49), Ni (47) and L = Cℓ for M = Re) The inner coordination around the metal ion is an axially distorted octahedron because of the bond length difference between M-L and M-O of the acetylacetone group.

(4) $M(acac)_2 \cdot H_2O$ M = Co (74) is an octahedrally coordinated dimer and M = Zn (75,76) is a five coordinated monomer.

(5) $M(acac)_2$ There is quite a variation of the molecular structure from metal to metal. M = Cu (136) is a square planarly coordinated monomer and M = Ni (131), Co (116), Zn (132) are all octahedrally coordinated polymers. The Ni and Zn complexes are trimers and the Co complex is a tetramer.

(6) $M(DPM)_2$ As has been mentioned, M = Co, Zn is tetrahedrally coordinated and M = Cu, Ni are square planar coordination.

(7) Pt (II) and Pt (IV) β-diketone complexes The structures vary from compound to compound. Some are monomeric and some are dimeric; some are bonded through two carbonyl oxygen atoms of the β-diketone group and some are bonded through the γ-carbon atom and some may have both types of bonding. However, all Pt (II) β-diketone complexes have a square planar configuration and all Pt(IV)-β-diketone complexes have an octahedral configuration.

2.2 Chemical Bonding

2.2.1 Metal - Ligand Bonding

At least five types of bonding between a β-diketone group and a metal have been postulated. They are:

(a) bonding of the oxygen atoms of the ion to the metal - this usally involves chelation of both carbonyl oxygens to the metal.

(b) the oxygen atom of the β-diketone anion bridging two metal atoms.

(c) σ-bonding of the γ-carbon of the ion to the metal.

(d) bonding of the oxygen atoms of the neutral ligand to the metal usually involving chelation.

(e) π-bonding of the neutral ligand to the metal

(a) Metal-oxygen bonds

Metal ligand linkage via two carbonyl oxygens is the commonest type of β-diketone bonding found in solids. The oxygen atom of the carbonyl group may bond to one or two metal atoms, the first being by far the most common.

Two models have been proposed for β-diketone anions chelated to metal; the two models depend on the amount of π-bonding between the ligand and the metal. The first model is based on the benzenoid structure. This may be pictured in Figure 2.1 (A). The principal evidence for this model is based on stability constants of the complexes. Calvin and Wilson(133) concluded that the complexes possess benzenoid resonance stabilization because substitution of the methyl groups of acetylacetone with groups capable of resonance interaction with the ring (e.g. C_2H_5O-, β-naphthyl-)

Figure 2.1

Three Possible Types of Metal-ligand Bonding in Metal β-diketone Complexes

(A) Benzenoid Structure

(B) Enolate Structure

(C) π-Bonding of the Neutral Ligand to the Metal

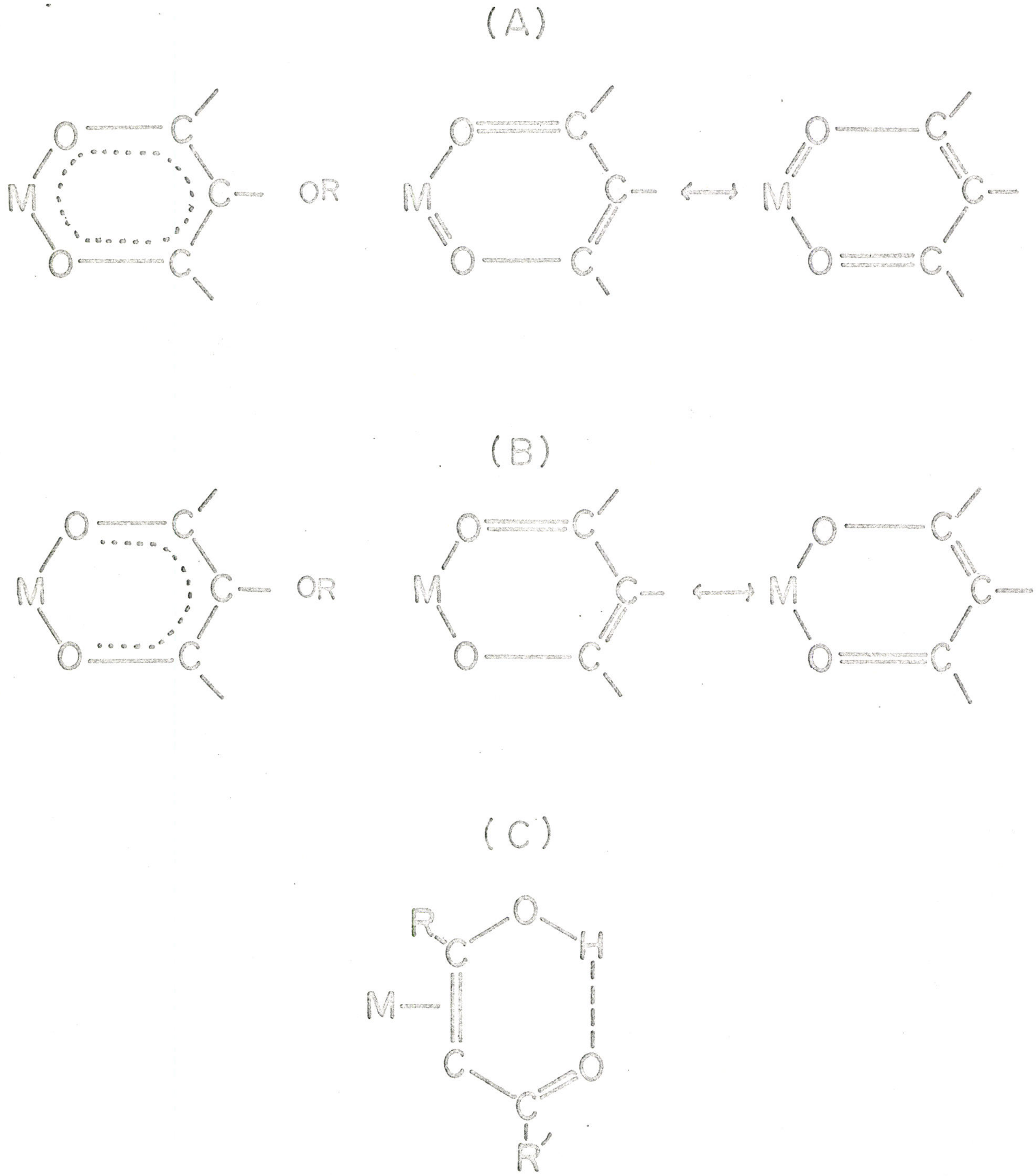


Figure 2.1

resulted in a decrease in the stability of the complex, which was attributed to increased enolate resonance in the substituted complexes and thus a decrease in "benzenoid" character. The metal β-diketone complexes are very thermodynamically stable; thus aluminum acetylacetonate (232) can be vaporized at 314° without decomposition, and the carbon atoms in the ring undoubtedly show considerable aromatic character so there may be some parallelism in structures between benzene and the metal β-diketonates. The alternative model is based on the enolate structure pictured in Figure 2.1 (B). Barnum (233) has shown that the comparison of the ring structure with benzene is superficial since any metal-oxygen π-bonding is through overlap of the metal d_ε orbitals with the π system of the acetylacetonate ion rather than through a p_z orbital as it does in benzene or pyridine. Since the d_ε orbitals are mutually orthogonal π electrons cannot move freely around the ring, and there is a barrier at the metal ion. The barrier is not infinitely high, however, since the orthogonality of the d_ε orbitals is partially removed by strain in the chelate ring, and the metal 4p-oribtals which offer no such barrier also take part in metal-ligand π-bonding. The resulting picture is a delocalized π electron system in the organic part of the ring, with relatively weak π-bonding to the metal, and a barrier at the metal to free π-electron movement in the ring.

Crystal structure analysis of this kind of complex reveals that the chelate ring is nearly planar, though metals sometimes are out of the plane consisting of the OCCCO chelate members. The C-O and C-C bonds in the ring are intermediate between single and double bonds, and within the experimental error, equivalent sets of bonds are equal in length. This evidence, however, could be proof of the delocalization of the electrons in the chelate system, but could not distinguish between the "benzenoid" or "enolate" structure since these phenomena would be expected for both models.

The way to determine the character of the M-O bond by x-ray studies is by means of the bond length. Variation of bond length with theoretical bond order is well known for carbon compounds, where the bond length changes from 1.54 Å for the C-C single bond (diamond) to 1.39 Å for the C-C partial double bond that is observed in benzene. The difference of about 0.15 Å is an easily measurable change. Based on the assumption that the bond length vs. bond order is close to being linear, according to Cruickshank's (188) data, the difference of bond length between S-O single bond and S-O partial double bond (of the order 1.5) is 0.20 Å and the difference for P-O is 0.17 Å. There is no similar data for metal oxygen bonds, however. Applying Pauling's empirical rule: $D(n) = D(1) - 0.6 \log n$ (where $D(n)$ is the length of the bond order n Cotton and Lippard (11) estimated the bond length of the Re-O double bond and triple bond. If Pauling's formula is applied here for our present purpose, we could estimate that the difference of bond length between an M-O single bond and an M-O partial double bond (of the order 1.5) would be about 0.11 Å. In order to study the character of M-O bond in the metal β-diketonate complexes carefully, a detailed comparision between the M-O bonds in β-diketone complexes and other compounds containing M-O single bonds such as those with hydrate, acetate, hydroxide and some aminoate ligands have been made. These comparisions are restricted to complexes which have the same central metal atom with the same oxidation state and environment (octahedral etc.). The reason for doing this is to prevent the inclusion of any other factors that might have different influences on the lengths of the bonds. Transition metals and non-transition metals are both included for comparison. It would be desirable to include as many examples as possible; the limited number of examples are listed in Table 2.3. There is a brief description for each case and the values of M-O bond mentioned are averaged ones.

The Be-O bond length in the bisacetylacetonate is 0.05 Å longer than in other Be compounds which is an abnormal case in this comparison. The reason for this is presumably the lack of low lying orbitals to accommodate the π-electrons of the chelate system. The estimated standard deviation in bond length in this work was not stated, so there is some doubt about this result. Of the other cases, Ni(II) and Pd(II), square planar, and Cr(III) octahedral, and Zn(II) tetrahedral, are nearly equal in M-O bond length both for β-diketone and other complexes included in comparison. For the remaining cases, the M-O bond length in β-diketone complexes is about 0.04 Å shorter than in the other complexes except the Co(II) octahedron in which case it is even shorter, of the order 0.07 Å. since examples available for comparison are few, and the errors in bond lengths are large the short M-O bond in Co(II) octahedral and the large M-O bond in Be(II) tetradral β-diketonate may not be meaningful. The Cu(II)-O bond lengths in the square planar or distorted octahedral case may be valid because seven β-diketone and fifteen non-β-diketone complexes have been included. For this particular case, the M-O bond is 0.04 Å shorter in β-diketone

TABLE 2.3

COMPARISON OF THE M-O BONDED DISTANCES BETWEEN β-DIKETONE COMPOUNDS AND NON-β-DIKETONE COMPOUNDS

2.3.1 Be(II) Tetrahedral

Compound	Be-O Bond Length (Å)			Ref.
	Range	Wt	Average	
A. β-diketone compound				
$Be(acac)_2$	1.68-1.73	4	1.70	135
B. Non-β-diketone compound				
β-Be(OH)	1.57-1.69	4	1.64	136
$Be_4O(OAc)_6$	1.666	12	1.666	137
$Be_4O(OAc)_6$		4	1.624	
		Av.	1.652	

2.3.2 Mg(II) Octahedral

Compound	Mg-O Length (Å)			Ref.
	Range	Wt	Average	
A. β-diketone compound				
$Mg(acac)_2(H_2O)_2$*	2.027-2.04	4	2.039	128
B. Non-β-diketone compound				
$MgCl_2.12H_2O$		6	2.06 (.007)	138
$MgSO_4.4H_2O$	2.03-2.09	6	2.07	139
$MgSO_4.6H_2O$	2.044-2.083	6	2.06	140
$(NH_4)_2MgSO_4.6H_2O$		6	2.07	141
$Ce_2Mg_3(NO_3)_{12}.2H_2O$		18	2.06	142
$MgSO_4.7H_2O$		6	2.065	143
		Av.	2.06	

* $Mg-OH_2$ was not included

TABLE 2.3 (continued)

2.3.3 Zn (II) Tetrahedral

Compound	Zn-O Bond Length (Å) Range	Wt	Average	Ref.
	A. β-diketone compound			
$Zn(DPM)_2$		4	1.962	118
	B Non-β-diketone compound			
$Zn_4O(OAc)_6$		4	1.96	144
		12	1.98	
		Av.	1.975	

2.3.4 Zn (II) Pyramidal

Compound	Zn-O Bond Length (Å) Range	Wt	Average	Ref.
	A. β-diketone compound			
$Zn(acac)_2 \cdot H_2O^*$	2.01-2.04	4	2.025	75.76
	B. Non-β-diketone compound			
Zinc Glutamate dihydrate*	2.03-2.10	4	2.065	145

* $Zn-OH_2$ length was not included

TABLE 2.3 (continued)

2.3.5 Pd(II) Square Planar

Compound	Pd-O Bond Length (Å) Range	Wt	Average	Ref.
	A. β-diketone compound			
Pd(Phacac)$_2$	1.965-1.976	4	1.971	146
Pd(DBM)$_2$	1.957-1.962	4	1.960	147
		Av.	1.966	
	B. Non-β-diketone compounds			
Bis-N-ethyl-salicyaldimine Pd(II)		2	1.94	148
Bix-N-butyl-salicyaldimine Pd(II)		2	2.00	149
		Av.	1.97	

2.3.6 Cr(III) Octahedral

Compound	Cr-O Bond Length (Å) Range	Wt	Average	Ref.
	A. β-diketone compounds			
Cr(acac)$_3$	1.95-1.97	6	1.951	124
$[Cr(acac)_2.Ph_2PO_2]_2$	1.939-1.967	8	1.954	150
		Av.	1.953	
	B. Non-β-diketone compounds			
$[Cr(acac)_2P_2PO_2]_2$	1.946-1.968	4	1.959	150
$K[Cr(C_2O_4)_2(H_2O)_2]3H_2O$	1.92-2.02	6	1.957	151
$K_3[Cr(C_2O_4)_3].3H_2O$	1.88-1.93	6	1.90	152
$(NH_4)_3[Cr(C_2O_4)_3].2H_2O$	1.89-2.06	6	1.96	153
$KCr(SO_4)_2.12H_2O$		6	1.94	154
		Av.	1.948	

TABLE 2.3 (continued)

2.3.7 Co(III) Octahedral

Compound	Co-O Bond Length (Å)			Ref.
	Range	Wt	Average	
A. β-diketone compounds				
$Co(acac)_2.(H_2O)_2$*	2.05-2.06(.01)	4	2.06	49
$[Co(acac)_2.H_2O]_2$+*	1.89-2.04	6	2.02	74
$[Co(acac)_2]_4$+	1.93-2.14	6	2.055	116
		Av.	2.043	
B. Non-β-diketone compounds				
$CoSO_4.6H_2O$	2.05-2.14	12	2.11	155
$(NH_4)_2Co(SO_4).6H_2O$	2.07-2.107	6	2.11	156
		Av.	2.11	

* $Co-OH_2$ was not included.

\+ Co-O bonded lengths from oxygen atom bridging two metal atoms were not included.

2.3.8 Ni(II) Octahedral

Compound	Ni-O Bond Length (Å)			Ref.
	Range	Wt	Average	
A. β-diketone compounds				
$Ni(acac)_2(H_2O)_2$*	2.01-2.02	4	2.015	47
$AgNi(acac)_3.2AgNO_3.H_2O$		6	2.04	157
$[Ni(acac)_2]_3$		12	2.01	131
		Av.	2.02	
B. Non-β-diketone compounds				
$Ni(OAc)_2.4H_2O$	2.06-2.12	6	2.10	158
$Ni(C_7H_6O_3).2H_2O$	2.02-2.04	6	2.03	159
$(NH_4)_2NiSO_4.6H_2O$	2.04-2.09	6	2.07	160
$NiSO_4 6H_2O$	2.03-2.05	6	2.04	161
		Av.	2.06	

* $Ni-OH_2$ was not included

TABLE 2.3 (continued)

2.3.9 Ni(II) Square Planar

Compound	Ni-O Bond Length (Å) Range	Wt	Average	Ref.
	A. β-diketone compound			
$Ni(DPM)_2$		4	1.836	119
	B. Non-β-diketone compound			
Bis-salicylaldoximato Ni(II)		2	1.836	162
Bis-salicylaldiminato Ni(II)		2	1.84±.03	163
Bix-N-Methyl-salicylaldimine-Ni(II)		2	1.80	164
N-Phenyl-salicylaldiminato-Ni(II)		2	1.825	165
Bis (N-isopropyl-3-ethyl-salicylaldiminato)-Ni(II)	1.875-1.892	2.	1.884	166
		Av.	1.837	

TABLE 2.3 (continued)

2.3.10 Cu(II) Square Planar or Distorted Octahedral

Compound	Cu-O Bond Length (Å) Range	Wt	Average	Ref.
	A. β-diketone compounds			
$Cu(acac)_2$		4	1.92	130
$Cu(Etacac)_2$	1.89-1.92	4	1.91	167
$Cu(Phacac)_2$	1.914-1.931	4	1.922	168
$Cu(3Phacac)_2$	1.902-1.911	4	1.906	169
$Cu(3Meacac)_2$	1.907-1.908	4	1.908	170
Bis-salicylaldehydato Cu(II)	1.90-1.94	4	1.92	171
Bis-salicylaldehydato Cu(II)	1.86-1.98	4	1.92	172
		Av.	1.915	
	B. Non-β-diketone compounds			
$CuSo_4.3H_2O$		4	1.96	173
$CuCl_2.2H_2O$		2	2.01	174
$K_2CuCl_4.2H_2O$		2	1.97	175
$Cu_2Br(OH)_3$		4	1.92	176
$Cu_2Cl(OH)_3$		4	2.02	177
$C_{22}Cl(OH)_3$	1.915-2.052	4	1.98	176
$CuSO_4$	1.89-2.00	4	1.95	178
$Cu(OH)_2$	1.93-1.94	4	1.94	179
Copper proline dihydrate		2	2.03	180

TABLE 2.3 (continued)

2.3.10 (cont'd)				
$Cu(C_6H_4.OHCO_2)_2.4H_2O$	1.84	2	1.84	181
	1.92	2	1.92	
NN'-Disalicylidene-ethylene dimine Cu(II)	1.94-2.03	2	1.98	182
Bis-N-methylsalicylaldimine Cu(II)		2	1.90	183
Bix(Venzene-azo-β-Naphthol)-Cu(II)		2	1.93	184
NN'-Ethylene-bis-(acetylacetoneiminato) Cu(II)	1.92-1.96	2	1.94	185
NN'-disalicyldene-propane-1,2 diamine $Cu(II).H_2O$	1.88-1.94	2	1.91	186
		Av.	1.953	

complexes than that in non-β-diketone complexes, this trend is also found with some other metals, -- Mg(II) and Ni(II) octahedral and Zn(II) pyramidal. It should be noted that this shortness of the M-O bond length in metal β-diketonate complexes is not directly associated with the electronic configuration of the non-bonding dε orbitals; the fully vacant dε in Mg(II) and fully occupied dε in Ni(II) octahedral make no distinct difference. If the M-O bonds in β-diketone compounds are on the average 0.04 Å shorter than those in non-β-diketone compounds and if this is statiscally meaningful, then the conclusion is that the "benzenoid" structure does exist in β-diketone compounds. Using Pauling's empirical formula, we can find that the difference of 0.04Å corresponds to the bond order of 1.16 for the M-O bond in metal-β-diketone compounds.

This is an indication that the probability of the "benzenoid" structure is rather small, and much less than the enolate structure.

(b) M-O bonds from oxygen atom bridging two metal atoms

Other types of M-O bonds have been found in the Ni(II) and Co(II) polynuclear species of β-diketone complexes. The lengths of these three types of M-O bonds are collected in Table 2.4 where M-O (1) is for oxygen bonded and coordinated to only one metal, M-O (2) is for oxygen bonded to one metal but bridging two metals and $M\text{-}O(2)_p$ is for oxygen bonded and bridging two metals. Both M-O(2) and $M\text{-}O(2)_p$ are about 0.1-0.2 Å longer than M-O(1). They are probably loosely coordinated covalent bonds.

(c) $M\text{-}C(\gamma)\ \sigma$-bond

M-C bond linking the metal and β-diketone ligand through the γ-carbon has been found both in Pt(II) and Pt(IV) complexes. In the

TABLE 2.4

M-O DISTANCE FROM OXYGEN ATOM BRIDGING TWO METAL ATOMS

Compound	Type	Bond Length (Å)	Std. Div. (Å)	Ref.
$[Co(acac)_2 \cdot H_2O]_2$	Co-O(1)	2.021	.017	74
$[Co(acac)_2]_4$	Co-O(1)	2.055	.026	116
$[Ni(acac)_2]_3$	Ni-O(1)	2.056	.01	49
$[Co(acac)_2]_4$	Co-O(2)	2.237	.026	?
$[Ni(acac)_2]_3$	Ni-O(2)	2.123	.05	
$[Co(acac)_2]_4$	$Co-O(2)_p$	2.13	.03	
$[Co(acac)_2 \cdot H_2O]_2$	$Co-O(2)_p$	2.162	.016	

Pt(IV) complexes, the M-C (γ) bond is a weakly covalent bond both for the β-diketone as a unidentate ligand and tridentate ligand. For the unidentate case, the M-C(γ) bond length in trimethyle-(acetylacetonyl) -2,2- bipyridyl platinum (6) is 2.36 Å compared with the average 2.05 Å for Pt-C (methyl carbon) in the same complex. For the tridentate ligand case, the M-C (γ) bond is still longer with the value of 2.56 Å as observed in ethyl (trimethyl platinum) acetoacetate (189) compared with the average 2.17Å for the M-C (methyl carbon) bond in the same complex. The role of the γ -carbon here is to complete the six coordination for Pt(IV). This case is similar to Cu(II), though the Cu(II)-C(γ) distances which are listed in Table 2.6, are much longer. The Pt-C(γ) bond length in Pt(II) complexes is much shorter, the value of 2.13 Å is observed in $KPt(acac)_2Cl$(7). More examples are not available.

(d) Bonding between metal and neutral β-diketone group

All the above descriptions have one thing in common that the β-diketonate anion $(RCOCHCOR')^{-1}$ has the overall charge of -1. It is also reported that the neutral ligand group ($RCOCH_2COR'$) can coordinate to certain metals like Sb (29) and Ga (80). It was believed (80) that the metal ligand linkage would probably be through two metal-oxygen bonds like the β-diketonate anion chelates. The difference between these two types of M-O bonding and the geometry of the chelate ring of the neutral β-diketone group is unknown, mainly because no crystal structure has been reported.

(e) π-bonding of the neutral ligand to the metal

Another way of bonding the neutral β-diketone group to the metal is through metal-olefinic π-bonds like that shown in Figure 2.1 (C). This was found in the compound of PtCℓ(acac).(Hacac) (190) based on assignments of IR and NMR spectra. However, detailed structural information concerning this type of bonding is lacking.

2.2.2 The Chelated β-Diketone Group

The five members OCCCO, of the chelated β-diketone group in metal complexes are usually planar, though the plane containing OMO is not coplanar with the organic group. In the acetylacetone system, one methyl group is usually displaced more than the other one, from the chelate plane (average of 40 rings : 0.13 and 0.04 Å, respectively)this is probably a crystal packing effect (128).

In many β-diketone complexes, the C-O distance lies between a C-O single and double bond distance. The C-C separation in the ring is also between a C-C single bond and double bond distance and close to the bond length of 1.392 Å in benzene. The separation between C(ring) and C(aliphatic) is close to 1.52 Å which is close to the value found for a C-C bond consisting of an sp^2 and an sp^3 hybrid (191). The sum of the angles around the β-carbon atom in the ring is close to 360° which is necessary for the chelate group to be planar. The individual angle of 120° subtended at this carbon is also in agreement with the angle of sp^2 hybridization. A comparison of molecular dimensions of the chelate ring in some selected β-diketone complexes is listed in Table 2.5.

2.3 Inner Coordination

In simple β-diketone metal complexes coordination numbers of eight, six, five and four occur commonly. The β-diketone group imposes some

TABLE 2.5

DIMENSIONS IN METAL-β-DIKETONE COMPOUNDS

Compound	M-O	C-O	C-C (ring)	C-C (aliphatic)	OMO	Dihedral angle (O)	Ref.
	Four Coordinate Planar						
Ni(DPM)$_2$	1.836	1.314	1.390	1.514	94.6	.5	119
Cu(acac)$_2$	1.92	------	------	------	93.5	2	130
	Four Coordinate Tetrahedral						
Zn(DPM)$_2$	1.962	1.274	1.405	1.517	94.7	0	118
	Five Coordinate						
Zn(acac)$_2$.H$_2$O	2.02	1.291	1.395	1.510	88.5	12	75,76
VO(acac)$_2$	1.97	1.285	1.397	1.52	87.5	12	192
	Six Coordinate Monomeric						
Ni(acac)$_2$.2H$_2$O	2.055	1.275	1.420	1.48	92.0	16	47
Re(acac)$_2$Cl$_2$	1.991	1.276	1.393	1.531	89.2	2.2	
Cr(acac)$_3$	1.951	1.263	1.388	1.517	91.1	---	124
	Six Coordinate Polymeric						
[Co(acac)$_2$]$_4$	2.055	1.277	1.469	1.565	---	12	116
[Co(acac)$_2$H$_2$O]$_2$	2.021	1.245	1.421	------	---	8	74
[Ni(acac)$_2$]$_3$	2.01	1.33	1.55	------	---		131
	Eight-Coordinate						
Zr(acac)$_4$	2.198	1.270	1.399	1.517	75.0	22	120

restriction on the structure since if the group is bonded through the oxygen atoms (as is most common) the atoms must be cis and subtend an angle of 80-90° at the metal and the oxygen-oxygen distance is typically 2.6-2.8 Å. We will survey briefly the geometries observed for the individual coordination numbers.

2.3.1 Eight Coordination

Two configurations dominate the classic chemical examples of eight coordination. The stable $Mo(CN)_8^{4-}$ ion has eight bonds from the central atom directed toward the vertices of a dodecahedron with triangular faces (Figure 2.2 A). The TaF_8^{-3} ion (in the sodium salt) assumes the more obvious square antiprismatic configuration, a decahedron having eight triangular and two square faces (Figure 2.2 B).

$M(acac)_4$ complexes exist in two crystal modifications, α and ß, but the molecular stuctures in the two forms are identical. The metal ion is surrounded by eight oxygen atoms with a square anitprismatic arrangement and this is found in $Ce(acac)_4$, $Th(acac)_4$ and $Zr(acac)_4$. Because of various possible arrangements of the rings it is possible for three isomers to exist even for the square antiprismatic arrangement of the oxygen atoms (Figure 2.3 A,B,C). It has been found that all the compounds listed above in both crystal modifications have the structure shown in Figure 2.3B.

$Ce(DMB)_4$ (105) also has the structure shown in Figure 2.3 B but some distortion has been observed in this structure, presumably because of the presence of the bulky phenyl groups.

Compounds of the type $M(acac)_3 . xH_2O$ * where M is Y (193) or La(194)

---

* x=3 for M=Y and x=2 for M=La

Figure 2.2

Two Configurations of Eight Coordination

(A) Dodecahedral with Triangular Faces

(B) Square Antiprism

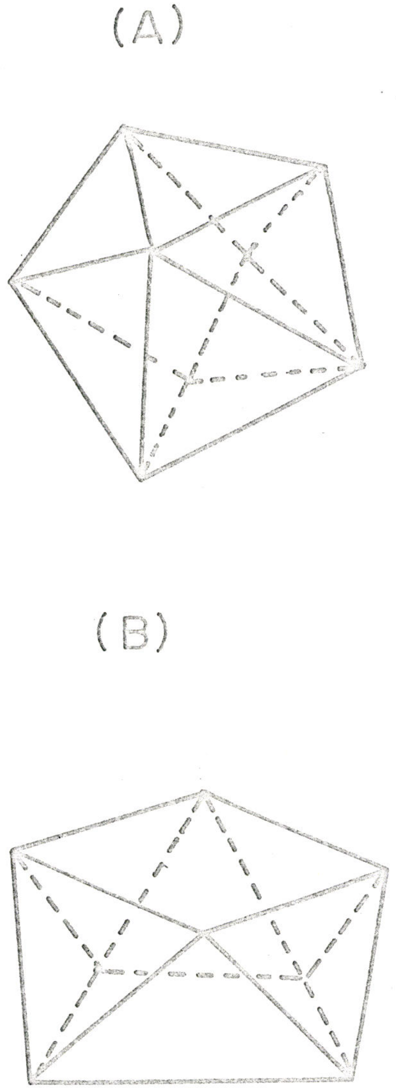


Figure 2.2

Figure 2.3

Three Possible Isomers of $M(acac)_4$ and $M(DBM)_4$ (A, B and C) and the Configurations of $M(acac)_3 \cdot xH_2O$ for M=Y, La (D)

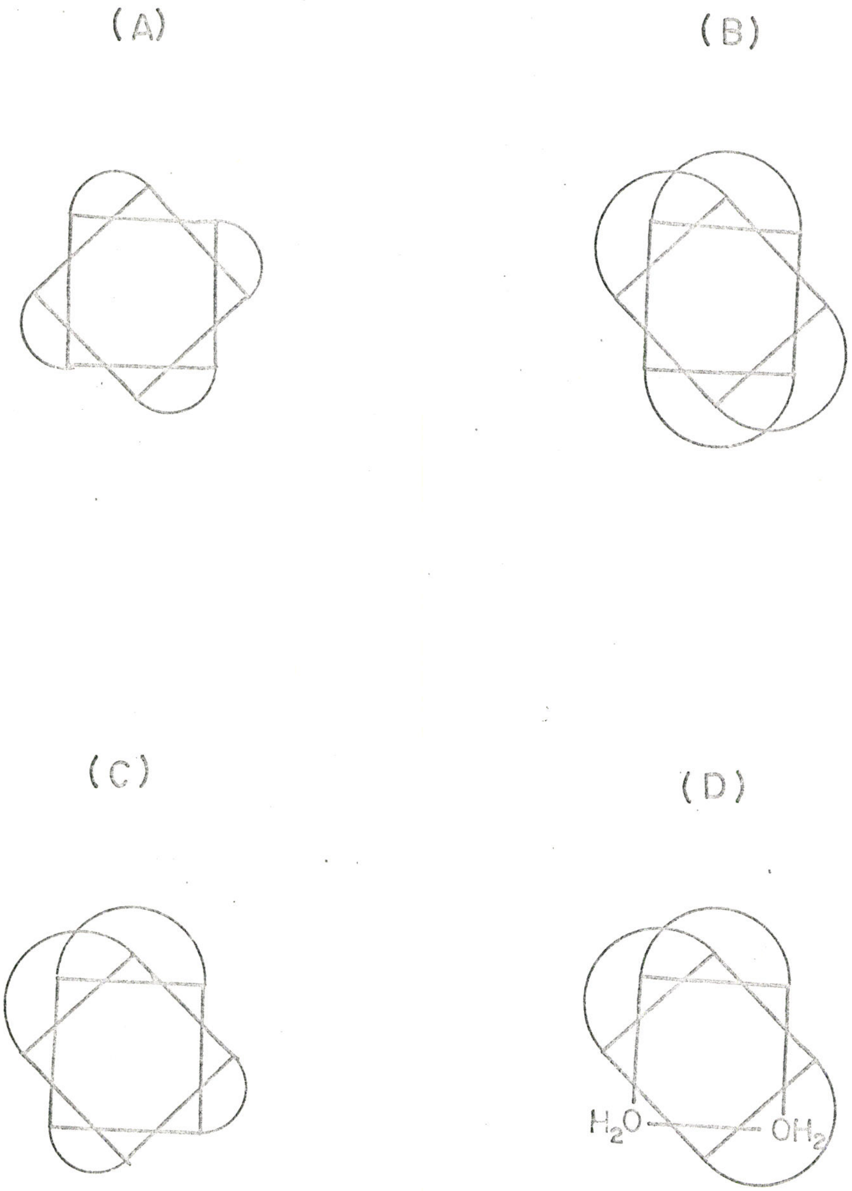


Figure 2.3

also show eight coordination about the central metal. The configuration is similar to Figure 2.3 B with one chelate ring being substituted by two hydrated oxygen atoms as shown in Figure 2.3 D.

2.3.2 Six Coordination

There are several types of the β-diketone complexes which show six coordination : $M(acac)_3$, $M(acac)_2.2H_2O$, $M(acac)_2.L_2$ and $[M(acac)_2]_n$ (polymers)

(a) $M(acac)_3$

Crystal structures have shown that metal is surrounded by six oxygen atoms with a regular octahedral arrangement both for the α- and γ-crystal modifications (83,124,126) (Astbury's notation). No information about β-form has been reported. The inner coordination of $Mn(acac)_3$ was reported to be a distorted octahedron by Morosin (125).

(b) $M(acac)_2.\ 2H_2O$

The molecular structure is a tetragonally distorted octahedron around the metal, the two hydrated oxygens are trans to each other, and M-O bond lengths are much longer than the M-O (carbonyl) bond length. The molecular structure of $Re\,C\ell_2(acac)_2$ (57) is closely related to the above structure, if the hydrated oxygens are replaced by chlorines. There is no detailed work on the structure of $Mo\,O_2(acac)_2$ (195) though the cell parameters have been reported. $Ti\,C\ell_2(acac)_2$ (129) has trans and cis isomers in solution but no single crystal work has been done. However, a structure closely related to it with the formula $Ti[C\ell(acac)_2]_2.CHC\ell_3$ (177) shows the cis configuration of the two acetylacetonates around titanium.

(c) Polynuclear species

Some metal β-diketone complexes appear to have less than six coordination, based on the simple formula but six coordination is achieved by polymerization. Several cases have been found so far, and the form of the polymerization, differs from metal to metal. There are two main methods of linking sub-molecular units, through oxygen bridges as are found in Ni(II) (131), Co(II) (116) and Zn(II) (132) acetylacetonates, and through the active methylene bridges such as are found in Pt(IV)--β-diketone complexes (5,6,189).

Bisacetylactonato-nickel (II) is an octahedrally coordinated trimer while its cobalt analog is a tetramer. All the metal atoms are surrounded by six oxygen atoms in nearly octahedral arrangement. In the trimer, the neighbouring metals share a triangular face, that is, three oxygens are common for the two central metals. For the cobalt tetramer, the same pattern has been observed for bridging from the center to the terminal metals. But the bridging of the two central metals is rather different because they share an edge of two octahedra so that only two oxygen atoms are common for the two neighbouring metal atoms.

For the octahedron consisting of two chelated β-diketonate group and two other ligands three possiblities exist: (A) Two non-chelate ligands are trans (t) to each other. If these two ligands are identical, as in $\mathrm{Re\,C\ell_2(acac)_2}$, then the molecule (or subunit) is centro-symmetric and no d or ℓ form exists. If the two non-chelate ligands are in the cis configuration, we have two optically active isomers the (B) d and (C) ℓ forms. The nickel trimer corresponds to the combination of three sub-molecular units dtℓ. The complete molecule is, of course, centro-symmetric. Likewise, the cobalt tetramer consists of four submolecular units ddℓℓ.

The whole molecule is also centro-symmetric. The molecular structures of Ni and Co polymers have been shown in Figure 1.1 F and G, respectively.

$Co(acac)_2 \cdot H_2O$ (74), unlike its Zn (75,76) analog, exists as a dimer in the solid state. The linking of two sub-molecular units to share the edge of two octahedra is similar to the bonding of the two central metals in the cobalt tetramer case. The configuration can be assigned, according to the previous notation, dl. Again, the molecule is centro-symmetric.

Some Pt(IV) complexes are dimeric. The β-diketonate group acts as a tridentate bridge group. Two oxygen atoms coordinate to one of the Pt metals and the γ-carbon is bonded weakly to the other Pt. The Pt coordination sphere is completed by three other ligands, these being methyl groups for $[Me_3Pt(OC\text{-}nC_3H_7)_2CH]_2$ (5) and $[Me_3Pt\text{-ethyl acetoacetate}]_2$ (189).

(d) Other examples

A rather interesting example is the complex trimethyl-(acetylacetonyl)-2,2' - bipyridyl-platinum (6) in which the β-diketone group acts as a unidentate ligand bonded to the metal through the active methylene group. Otherwise, Pt would have more than six coordination if the two oxygen atoms were bonded.

2.3.3 Five Coordination

There are two typical ideal configurations for five coordination the square pyramid and the trigonal bipyramid. Five coordinated metal β-diketonates are not common; only three examples have been found so far: $Zn(acac)_2 \cdot H_2O$ (75,76). $VO(acac)_2$ (192) and $VO(Phacac)_2$ (196). The configurations of all these three are square pyramidal, though the zinc complex is distorted towards a trigonal bipyramid. The metal atoms are displaced towards the center of gravity of the pyramid rather than being at the center of the base. The two β-diketone groups are nearly planar, but not coplanar with each other; the dihedral angle between the two groups varies from 10-15°.

2.3.4 Four Coordination

Two distinct configurations are found for four coordination, tetrahedral and square planar. The β-diketone complexes of four coordinated Ni(II), Cu(II) and Pd(II) are square planar and the Zn(II), Fe(II) and Cr(II) compounds are tetrahedrally coordinated about the metal.

Ni(DPM)$_2$ (119) has a square planar configuration around the metal and its Cu analog is isomorphous. All the other Cu-β-diketone complexes are also square planar but differ from the above compound in that the copper atom is weakly bonded to the γ-carbon atom at about 3.0-3.5 Å, giving a grossly distorted octahedral arrangement. This is listed in Table 2.6.

The intermolecular Cu-C(γ) distance is affected by the substitution of large groups on the γ-carbon as can be seen in the last two examples, in Table 2.6 where the distances are much longer.

The structure of Pd(Phacac)$_2$ (146) is closely related to the Cu analog but the intermolecular Pd-C(γ) distance is much longer (3.75 Å), since Pd(II) favors four coordination, and rarely shows six coordination.

Zn(DPM)$_2$ (118), unlike its nickel analog, is a distorted tetrahedron. It should be noted that the OMO angle is quite large, presumably because ideally it should approach the tetrahedral angle (109°30'). An alternative

TABLE 2.6

Cu-C(γ) DISTANCES

Complex	Distance (Å)	Ref.
Cu(acac)$_2$	3.075(14)	130
Cu(Etacac)$_2$	3.12(2)	167
Cu(Phacac)$_2$	3.02(1)	168
Cu(3-Phacac)$_2$	3.5	169
Cu(3-Meacac)$_2$	3.216(7)	170

explanation is based on the presence of a short M–O bond since the Ni(II) (119) compound shows a similar effect. The Fe and Co analogs are believed to be isomorphous with the Zn $(DPM)_2$.

The β-diketonate complexes of Pt(II) are all four coordinate and of square planar symmetry (7,190). This forces the β-diketonate group to act as a unidentate ligand in some compounds so that the four coordination is preserved. The structure of KPt $(acac)_2Cl$ (7) is shown in Figure 2.4.

2.4 Crystal Structures

As we have mentioned earlier different β-diketone complexes which have very similar molecular structures often exist in different crystal forms; even many given complexes exist in more than one crystal form. Since the molecular form is essentially unchanged in the different crystal forms, the difference must arise from the packing of the molecular units. At least two systems, $M(acac)_4$, and $M(acac)_3$ show polymorphism, whereas the isomorphous series, $M(DBM)_4$, $M(acac)_2 2H_2O$ exist in only one crystal form. We will discuss these systems here.

$M(acac)_4$

Compounds of the stoichiometry $M(acac)_4$ where M is Zr^{IV}, Th^{IV}, Ce^{IV}, and U^{IV} are dimorphous and both forms have monoclinic symmetry. In both crystalline forms the molecule is bis-dispheriodal with local symmetry ($\bar{4}2$ m). The α form has the space group $P2_1/c$ and is found for the Ce, Th and U complexes. The β-form has the space group C2/c and exists for Zr and Th. The unit cells of the two forms have almost the same volume. Although Hoard (120) has discussed the various molecular

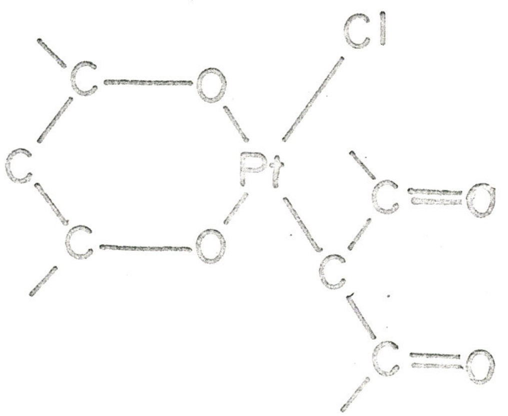


Figure 2.4

Structure of $Pt(acac)_2Cl$ anion in $K[Pt(acac)_2Cl]$ complex forms which M(acac)$_4$ might take, apparently no one has discussed the relationship between the packing of the two forms. Cursory examination of the packing suggest the relationship is not simple. It has been suggested by Comyns (197) that Po(acac)$_4$ should be isomorphous with the β-modification and it has been suggested that Pu(acac)$_4$ also has this crystal form.

M(DBM)$_4$

Only one crystalline form is known for this series. Wolf and Barnighausen (109) have shown that Ce, Th and U form an isomorphous series of compounds with orthorhombic symmetry and the space group Pccn.

M(acac)$_3$

Barker (123) first discovered from the axial ratios of the unit cell that trivalent metallic acetylacetonates exist in three different forms. More accurate work was done by Astbury who confirmed Barker's findings. Astbury also showed that for his nomenclature the α-form (Al,Cr,Mn,Co and Ga) had monoclinic symmetry, space group P2$_1$/c, the β-form (Sc,Ga and In) has orthorhombic symmetry, space group Pmn2, and the γ-modification (Fe,Ga) has orthorhombic symmetry and space group Pbca. Rh(acac)$_3$ is also believed to exist in the α form. Although the crystal structure of the α and γ forms has been studied in detail the papers were concerned with the molecular structure and do not discuss the packing relationships between the α and γ forms. It is obvious that the γ form has a unit cell twice the size of the α form and from the symmetry relationships of the two space groups one would have expected doubling along the b-axis.

A close examination of the lengths of the cell edges and a comparison of the position of the metal atoms suggests that the two cells are related by

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{ortho}} = \begin{pmatrix} 0 & 2 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \text{Sin } \beta_m \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{monoclinic}}$$

with the metal atoms shifted approximately 1/4c along the c axis. However such a transformation destroys the symmetry relationship between the two cells which we noted above. The problem is complicated and merits further study, but this lies outside the scope of this thesis.

$M(acac)_2(H_2O)_2$

An isomorphous series is known for Mg^{II}, Co^{II} and Ni^{II}. Anhydrous nickel and cobalt acetylacetonates are polymerised and Morosin has suggested that a similar effect may be shown by anhydeous $Mg(acac)_2$.

Many crystalline forms are know for the series of compounds of stoichiometry $M(acac)_2$, but in this case the different crystalline forms are caused by different molecular structures. Many of the compounds are polymerised. Obviously the packing of molecular units in the crystal is a subject which deserves further consideration.

CHAPTER 3

METHOD OF CRYSTAL STRUCTURE ANALYSIS

3.1 Introduction

Crystals are composed of groupsof atoms repeated at regular intervals with the same orientation in three dimensions. The basic unit of the crystal, known as the unit cell, is defined by six elementary quantities $\underline{a}, \underline{b}, \underline{c}, \alpha, \beta$, and γ where $\underline{a}$, $\underline{b}$ and $\underline{c}$ are three non-coplanar translation vectors which are sufficient to describe the repetition of the crystal and α, β and γ are interaxial angles between $\underline{b}$ and $\underline{c}$; $\underline{c}$ and $\underline{a}$ and $\underline{a}$ and $\underline{b}$, respectively.

X-ray diffraction by a crystal is governed by certain conditions such as Bragg's Law which indicate that for certain incident angles and wave lengths a crystal will reflect the x-ray beam strongly. The conditions for constructive reflection are that (198) the incident and diffracted beams are coplanar with the normal to a crystal lattice plane and make equi-angles with it and that (Figure 3.1)

$$2d \sin \theta = n\lambda \tag{3.1}$$

where d is the distance between two adjacent lattice planes. θ is the angle between the incident ray and the plane or the diffracted ray and the plane. The integer n is called the order of reflection and λ is the wave length of the x-ray. The lattice planes are designated by the Miller indices h, k, ℓ which are defined so that the $hk\ell$ plane intersects $\underline{a}$ at $\underline{a}/h$, $\underline{b}$ at $\underline{b}/k$ and $\underline{c}$ at $\underline{c}/\ell$ (where h, k, ℓ are integers).

The Bragg equation determines the conditions for reflection from

Figure 3.1

Bragg's Reflection Law

Derivation of the Bragg Equation

$$2d\sin\theta = n\lambda$$

here d is the spacing between parallel planes and $2n\pi$ is the difference in phase between reflections from successive planes.

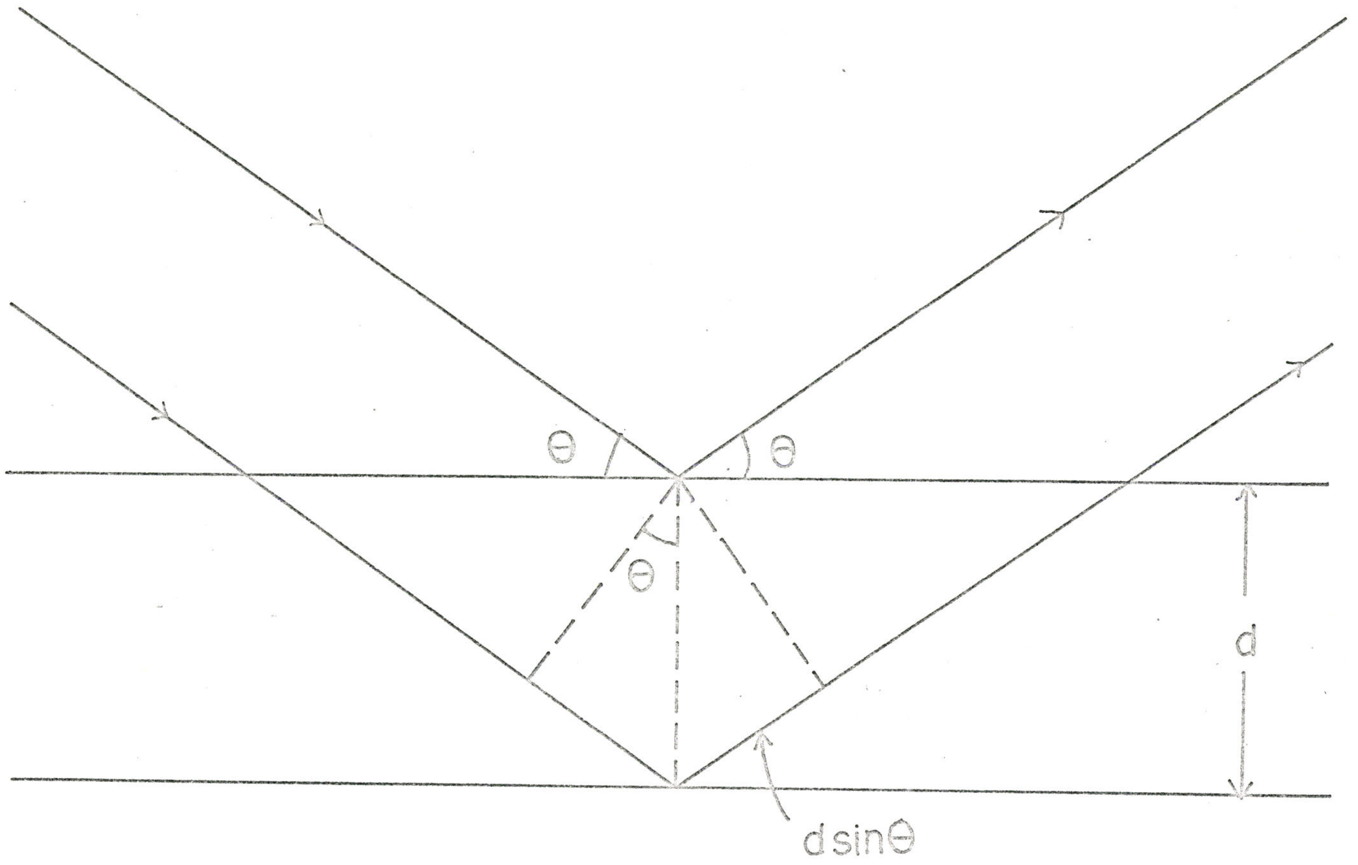


Figure 3·1 Bragg's Reflection Law

a crystal plane (hkℓ), but the relative intensities of the various reflections depend on the contents of the unit cell, that is on the number, type and distribution of atoms in the unit cell. The problem is how to determine the amplitude of the wave scattered in a given direction by all the atoms in the unit cell. The structure factor F(hkℓ) for a given hkℓ reflection is the reflection amplitude divided by the amplitude of the wave scattered by a single point electron for the same wavelength. The value of F(hkℓ) is given by

$$F(hk\ell) = \sum_{i=1}^{N} T_i f_i \exp 2\pi i \,(hx_i + ky_i + \ell z_i) \qquad (3.2)$$

where f_i is the scattering factor of the ith atom in the unit cell and is a Fourier transform of electron density $\rho(x,y,z,)$, x_i, y_i and z_i are fractional coordinates of the ith atom along three crystallographic axes, a, b and c, respectively. The temperature dependent term can be written as

$$T_i = \exp\left(-B_i \frac{\sin^2\theta}{\lambda^2}\right) \qquad (3.3)$$

where B_i, the Debye-Waller temperature factor (199,200), accounts for the thermal motion of the atoms about their mean postions. When the atomic motion is non-isotropic T can be expressed in the form:

$$T = \exp{-2\pi i}\,[b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{13}h\ell] \qquad (3.4)$$

In general, the structure factor is a complex quantity which is composed of the real part (A') and imaginary part (B') that is F=A'+iB'

$$A' = \sum_{i=1}^{N} T_i\, f_i \cos 2\pi\,(hx_i + ky_i + \ell z_i)$$

and
$$B' = \sum_{i=1}^{N} T_i\, f_i \sin 2\pi\,(hx_i + ky_i + \ell z_i) \qquad (3.5)$$

and
$$F^2 = A'^2 + B'^2$$

$\alpha_{hk\ell} = \tan^{-1} B/A$ is the phase angle of F and is not generally an observable quantity, the only observable quanitity being the intensity which is proportional to FF*. A more fundamental interpretation of the structure-factor equation is possible by considering each element of volume of the unit cell separately. Thus if $\rho(x,y,z)$ is the electron density at the point (x,y,z), and V is the volume of the unit cell, the amount of scattering matter in the volume element $V\,dx\,dy\,dz$ is $\rho V\,dx\,dy\,dz$ and the structure factor equation is

$$F(hkl) = \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z) \exp 2\pi i(hx + ky + \ell z)\, dxdydz \qquad (3.6)$$

Since a crystal is periodic in three dimensions, the distribution of electron density can conveniently be represented by a Fourier series as given in the following proof, let

$$\rho(x,y,z) = \sum_{h'}\sum_{k'}\sum_{\ell' = -\infty}^{\infty} K\,(h',k',\ell') \exp -2\pi i\,(h'x + k'y + \ell' z) \qquad (3.7)$$

substituting into (3.6):

$$F(hkl) = \int_0^1 \int_0^1 \int_0^1 \sum_{h'}\sum_{k'}\sum_{\ell' = -\infty}^{\infty} VK\,(h',k',\ell') \exp -2\pi i(h'x + k'y + \ell' z)$$

$$\exp 2\pi i\,(hx + ky + \ell z)\, dxdydz$$

$$= \int_0^1 \int_0^1 \int_0^1 \sum_{h'}\sum_{K'}\sum_{\ell' = -\infty}^{\infty} VK\,(h' K' \ell') \exp -2\pi i\,[\,(h'-h)\,x +$$

$$(K'-K)\,y + (\ell'-\ell)\,z]\, dxdydz$$

The above integration will have non-zero value only if $h'=h$, $K'=K$ and $\ell' = \ell$. Under these condition:

$$F\ (hk\ell) = \int_0^1\int_0^1\int_0^1 VK\ (hk\ell)\ dxdydz = VK\ (hk\ell) \qquad (3.8)$$

This means that the Fourier coefficients are directly related to the corresponding structure factors, and

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_{\ell=-\infty}^{\infty} F\ (hk\ell)\ \exp - 2\pi i\ (hx + ky + \ell z) \qquad (3.9)$$

In x-ray crystallography, it is found advantageous to use the vectors in reciprocal space, the primitive translation $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ of the reciprocal lattice being defined by :

$$\begin{aligned} &\underline{a}.\underline{a}^* = \underline{b}.\underline{b}^* = \underline{c}.\underline{c}^* = 1 \\ &\underline{a}.\underline{b}^* = \underline{a}.\underline{c}^* = \underline{b}.\underline{a}^* = \underline{b}.\underline{c}^* = \underline{c}.\underline{a}^* = \underline{c}.\underline{b}^* = 0 \end{aligned} \qquad (3.10)$$

Equations (3.10) defines the magnitude and directions such that, for example, $\underline{a}^*$ is perpendicular to the plane $(\underline{b},\underline{c})$ and in fact is given by:

$$a^* = \frac{\underline{b} \times \underline{c}}{\underline{a}.|\underline{b} \times \underline{c}|} \qquad (3.11)$$

Similar expressions obtain for other vectors. α^*, β^* and γ^* are reciprocal interaxial angles. The reciprocal lattice has a definite orientation relative to the crystal lattice. The properties of the reciprocal lattice that make it of value in diffraction are : (1) The vector r^* $(hk\ell)$ from the origin to the point $(hk\ell)$ of the reciprocal lattice is normal to the $(hk\ell)$ plane of the crystal lattice. (2) The length of the vector r^* $(hk\ell)$ is equal to the reciprocal spacing of the plane $(hk\ell)$ of the crystal lattice.

X-ray diffraction provides direct information about the reciprocal lattice's dimension. From either (3.1) or the relations between real and reciprocal lattices, the unit cell constants can be calculated. For ordinary photographic methods, because of the shrinkage of the x-ray film, accurate parameters are obtained by calibrating with some substance whose cell parameters have been accurately measured.

The space group which is a measure of the symmetry of a crystal can sometimes, be determined directly from x-ray photographs by examining planes of symmetry in the diffraction pattern and systematic absences of x-ray reflections. Often the above information alone is insufficient to determine the space group unambiguously, and other methods such as examination of the external appearance of the crystal, the presence of optical activity and peizo- and pyro- electricity may be tried. The statistics of the x-ray intensities (201) can also be used for space group determination.

In order to obtain the structure factor from the intensity I, the relation between these two can be expressed as:

$$I(hk\ell) = L\ P\ A\ F(hk\ell)F^*(hk\ell) \qquad (3.12)$$

where L is the Lorentz correction factor which depends upon the technique used.

$P(hk\ell) = \frac{1+\cos^2 2\theta}{2}$ is the polarization correction factor.

A = absorption correction factor which depends on the shape and the size of the crystal sample and the relation of the direction and diffracted beams to the shape.

The structure factor obtained in this way is known as the observed structure factor $F_o(hk\ell)$ for reflection $hk\ell$. On the other hand it is necessary to propose some model for the structure and to calculate the magnitude and phase of the structure factor for this reflection. This is known as calculated structure factor $F_c(hk\ell)$ and is determined by (3.2). f_2 in (3.2) is known as the atomic scattering factor which is roughly proportional to the number of electrons for that atom and its amplitude falls off as $\sin\theta/\lambda$. The decrease with angle is because electrons at different positions in the atom do not scatter in phase for $\theta \neq 0$ and this interference weakens the net amplitude of scattering from any single atom. When the frequency of the incident x-ray approaches the characteristic frequencies of the electrons and resonance phenomena occur, the scattering power of a bound electron may be greater or less than that of a free electron. These effect may be taken into account by representing the atomic scattering factor f as a complex number:

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

where $\Delta f'$ and $\Delta f''$ are called the real and imaginary dispersion corrections.

3.2 Fourier Method

The three dimensional electron distribution is directly related to the structure factor according to (3.9). In practice if the phase of the observed structure factor is known, then the electron density can be calculated in the form:

$$\rho_o(x,y,z) \doteq \frac{1}{V} \sum_h \sum_k \sum_{\ell=-\infty}^{\infty} F_o \; (hk\ell) \; \exp - .2\pi i \; (hx + ky + \ell z) \qquad (3.13)$$

If the above equation is integrated with respect to some coordinates, say z, then:

$$\rho_o \; (x,y) = \int_0^1 \frac{1}{V} \sum_h \sum_k \sum_{\ell=-\infty}^{\infty} F_o \; (hk\ell) \; \exp -2\pi i \; (hx + ky + \ell z) \; \underline{c}dz$$

$$= \frac{1}{A} \sum_h \sum_k \sum_{\ell=-\infty}^{\infty} \exp -2\pi i \; (hx + ky) \int_0^1 F_o \; (hk\ell) \; \exp -2\pi i\ell dz$$

Where A=V/c̲ is the area of the unit cell projected on (001). The above integrand has a non-zero value only if $\ell=0$, that is

$$\rho_o (x,y) = \frac{1}{A} \sum_h \sum_{k=-\infty}^{\infty} F_o (hk0) \exp -2\pi i (hx + ky) \qquad (3.14)$$

This corresponds to the electron density projected along the c̲ axis. According to (3.15) only zero level reflections (hk0 in this case) need be used. The phase of F_o used in Fourier summation cannot be measured directly and so for estimating this, the phase of F_c may be used. If $F_o \lesssim F_c$ and the model is basically correct, it is probably that they may have the same sign. If $F_o >> F_c$, F_o may reasonably have any sign. Under such circumstance, the reflection is left out in the summation.

If F_c is used in (3.9), then the electron density proposed corresponding to the model is obtained:

$$\rho_c (x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_{\ell=-\infty}^{\infty} F_c (hk\ell) \exp - 2\pi i (hx + ky + \ell z) \qquad (3.15)$$

and substracting from (3.13), then:

$$D(x,y,z) = \rho_o (x,y,z) - \rho_c (x,y,z)$$
$$= \frac{1}{V} \sum_h \sum_k \sum_{\ell=-\infty}^{\infty} [F_o(hk\ell) - F_c(hk\ell)] \exp -2\pi i (hx + ky + \ell z) \quad (3.16)$$

The function D(x,y,z) is called the difference synthesis and represents the difference of the electron distribution between the actual structure and the proposed model. Analogously the projected difference synthesis can be obtained by substituting $F_o(hk\ell) - F_c(hk\ell)$ in (3.15).

The electron density, either three dimensional or in projection, is useful in confirming the known atomic coordinates and from the character of the electron density in the vicinities of the atom positions, we can make corrections to these coordinates. The difference synthesis, has a fundamental property which makes it useful in refinement: When the proposed model exactly matches the actual crystal structure, the difference map is characterized by a flat topography whose only features are minor and random undulations caused by errors of observation. If the proposed structure deviates in any way from the actual structure, the difference map reveals the nature of the deviation by a topography characteristic of the deviation. It follows that the proposed structure ought to be modified in such a way as to produce a nearly featureless difference map. In addition to this characteristic property, difference maps have another advantage. When the proposed and actual structures are nearly the same, the series termination errors between observed (3.13) and calculated (3.15) electron density will be virtual zero. For this reason, accurate values of the atomic coordinates can be derived from them.

The planar projection defined in (3.14) is simpler in computation both for the number of reflections included and the number of points to be computed. It is useful for confirming and making corrections to the initial set of atomic coordinates as well as locating the atoms not included in the preliminary structure factor calculations. For complicated structures, however, planar projections may be insufficient to reveal the details of the structure. In this case, three dimensional electron density and difference syntheses, particularly the latter, are much more effective in finding new atomic positions. This method has been applied in investigating the structure of $ReCl_2(acac)[P(C_6H_5)_3]_2$ and $ReOCl_2(acac)P(C_6H_5)_3$. Since the number of light atoms was relatively small in the structure of $ReCl_2(acac)_2$, planar projections revealed clearly all the light atom postions which has not been found from the Patterson function (see below).

3.3 Patterson Function

The basic problem in x-ray structure determination is to determine the phase of the structure factors and Patterson function is such a method. Patterson function P(u,v,w) is defined such that:

$$P(u,v,w) = V \int_0^1\int_0^1\int_0^1 \rho(x,y,z)\ \rho^*\ (x+u,y+u,z+w)\ dx\ dy\ dz \qquad (3.17)$$

where x and u, y and v, z and w are respectively fractional coordinates along the three major crystallographic axes. From (3.9),

$$\rho^*\ (x+u,y+v,Z+w) = \frac{1}{V} \sum_{h'}\sum_{k'}\sum_{\ell'=-\infty}^{\infty} F^*\ (h'k'\ell')\exp\ 2\pi i[h'(x+u)+k'(y+v)+\ell'(z+w)]$$

$$= \frac{1}{V} \sum_{h'}\sum_{k'}\sum_{\ell'=-\infty}^{\infty} F^*\ (h'k'\ell')\exp\ 2\pi i(h'x+k'y+\ell'z).$$

$$\exp\ 2\pi i\ (h'u+k'v+\ell'w) \qquad (3.18)$$

Substituting (3.9) and (3.18) into (3.17)

$$\rho(u,v,w) = \frac{1}{V} \int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_\ell\sum_{h'}\sum_{k'}\sum_{\ell'=-\infty}^{\infty} F(hk\ell)F^*(hk\ell)\exp\ -2\pi i(hx+ky+\ell z)\cdot$$

$$\exp\ (h'x+k'y+\ell'z)\ \exp\ 2\pi i\ (h'u+k'v+\ell'w)\ dxdydz$$

$$= \frac{1}{V} \int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_\ell\sum_{h'}\sum_{k'}\sum_{\ell'=-\infty}^{\infty} F(hk\ell)F^*(hk\ell)\ \exp\ -2\pi i\ [(h-h')x+(k-k').$$

$$y+(\ell-\ell')\ z]dxdydz$$

The above integral has non-zero value if h'=h, k'=k and ℓ'=ℓ and when this condition is satisfied, then:

$$\rho(u,v,w) = \frac{1}{V} \sum_h\sum_k\sum_{\ell=-\infty}^{\infty} F(hk\ell)\ F^*\ (hk\ell)\ \exp\ 2\pi i(hu+kv+\ell w) \qquad (3.19)$$

The product F(hkℓ) F*(hkℓ) is used as a Fourier coefficient to take advantage of the fact that it is always real and positive and can be obtained directly from the intensity, corrected for Lorentz, polarization and absorption factors.

The significance of the Patterson function can be seen from its definition (3.17). The value of $\rho(u,v,w)$ is proportional to the product of $\rho(x,y,z)$ and $\rho^*(x+u,y+v,z+w)$ or for a structure containing two atoms i and j separated by a vector (u,v,w):

$$\rho(u,v,w) = Mn_i n_j \tag{3.20}$$

where M is the multiplicity which arises from symmetry related atoms; n_i and n_j are numbers of electrons from atoms i and j, respectively.

3.4 Least Squares Refinement

In structural analysis, a set of observed structure factors are obtained from the intensities on one hand and a set of calculated structure factors F_c's are obtained from the proposed model on the other hand. The correctness of the structure is indicated by some function of the differences between $|F_o|$ and $|F_c|$, such a function which is called the R-factor or residue index and may be expressed in one of the following forms:

$$R_1 = \frac{\Sigma\big||F_o| - |F_o|\big|}{\Sigma |F_o|}$$

or

$$R_2 = \left[\frac{\Sigma\omega\ (|F_o| - |F_c|)^2}{\Sigma\omega F_o^{\,2}}\right]^{1/2} \tag{3.21}$$

R_1 and R_2 are called unweighted and weighted agreement indices respectively. ω is the weight given to each reflection and is based on the reliability of the intesity measurement. There are two kinds of weight that have been used in the present work: the unit weight where $\omega=1$, and the $^1/\sigma$ weight where σ is the standard deviation of the measured F_o.

It would be understandable that for a proposed structure that was correct, all the $|F_c|$ would be close to $|F_o|$. The situation often faced is that, from information of the Fourier synthesis, we can locate roughly the positions of atoms but the numerical value of the temperature factors is obtained with difficulty by these methods. If R_i is the indicator of correctness of the structure, we would like to improve our structure model by minimizing R_i through some process. According to Legendre's principle (203) which states that for a set of linear functions:

$$P_1 = C_{11}x_1 + C_{12}x_2 + \dots\dots\dots\dots + C_{1m}x_m + E_1$$

$$P_2 = C_{21}x_2 + C_{22}x_2 + \dots\dots\dots\dots + C_{2m}x_m + E_2$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$$

$$P_n = C_{n1}x_1 + C_{n2}x_2 + \dots\dots\dots\dots + C_{nm}x_m + E_n$$

and in general:

$$E_n = P_n - \sum_{j=1}^{m} C_{nj}x_j \qquad 3.22)$$

where $\sum_{j=1}^{m} C_{nj}x_j$ is a known function, P_n is the measured value derived from observation and liable to accidental error, E_n is the discrepancy between them, the best value for x_i's will be those which make the sum of the squares of the discrepancies a minimum, i.e.

$$E^2 = E_1^2 + E_2^2 + \dots\dots\dots\dots + E_n^2$$

is a minimum. In other words, to improve the set of values of x_i, we can minimize E^2 if we identify F_o (hkℓ) with P_n in (3.22) and F_c(hkℓ) with $\sum_{j=i}^{m} C_{nj}x_j$, then minimizing E^2 is equivalent to minimizing R_2^2. F_c must, however, be expressed as a linear function of the parameters x_i, this can be approximated by taking the first two terms of the Taylor expansion since if x_i is in the neighbourhood of the real x_i and the difference between the two is quite small, the higher order derivatives can be neglected(204).

Let $x_i' = x_i + \Delta x_i$, then

$$F_c = \overline{F}_c + \sum_{i=1}^{N} \frac{\partial F_c}{\partial x_i} \Delta x_i \qquad (3.23)$$

This summation is over the N parameters we wish to refine, F_c is the calculated structure factor from the improved parameters x_i' and $\overline{F}_c$ is based on the old parameters x_is. For m reflections that are to be used in the refinement:

$$\frac{\partial E^2}{\partial x_j} = \frac{\partial}{\partial x_j} \sum_{i=1}^{m} (F_o(t) - F_c(t))^2 = (F_o(t) - \overline{F}_c(t) - \sum_{i=1}^{N} \frac{\partial F_c(t)}{\partial x_i} \Delta x_i)(-\frac{\partial F_c(t)}{\partial x_j}) = 0 \qquad (3.24)$$

The subscript t is the abbreviation of the index hkℓ and for simplicity, also represents t-th reflection during summation. If we substitute ΔF_t for $F_o(t) - F_c(t)$, and rearrange the above equation, then:

$$\sum_{i=1}^{m} \omega_t \sum_{t=1}^{N} \frac{\partial F_c(t)}{\partial x_i} \frac{\partial F_c(t)}{\partial x_j} \Delta x_i = \sum_{t=1}^{m} \omega_t \frac{\partial F_c(t)}{\partial x_j} \Delta F_t \qquad (3.25)$$

where ω_t is the weight used for t-th reflection, or:

$$\sum_{i=1}^{N} \sum_{t=1}^{m} \omega_t \frac{\partial F_c(t)}{\partial x_i} \frac{\partial F_c(t)}{\partial x_j} \Delta x_j = \sum_{t=1}^{m} \omega_t \frac{\partial F_c(t)}{\partial x_j} \Delta F_t \qquad (3.26)$$

The value of Δx_i can be found by inversion of the matrix $\omega_t \frac{\partial F_c(t)}{\partial x_j} \cdot \frac{\partial F_c(t)}{\partial x_i}$ by using a high speed digital computer. A least squares program known as MACLS written by J.S. Stephens for an IBM 7040 computer was used in refining the structures of $ReCl_2(acac)_2$. For structures of $ReCl_2(acac)\cdot[P(C_6H_5)_3]_2$ and $ReOCl_2(acac)P(C_6H_5)_3$, a modified sub-routine (next section) was inserted in the main program of MACLS in refinement. In the MACLS program, the parameters used in the refinement are the atomic positional parameters (x_i, y_i, z_i) and thermal parameters B_i (3.3) or B_{ij} (a maximum of six parameters per atom) (3.4). Since the F_o's obtained from the intensity (3.12) are not on an absolute scale, scaling factors for adjusting a set of F_o (one scale factor per layer line for photographic intensity data) to the same set of F_c are used as additional parameters for refinement.

In the process of actual refinement, scale factors are correlated with the temperature factors of all the atoms, since a small decrease in scale factors has nearly the same effect as a small increase in the overall temperature factor. In order to overcome this difficulty, Lipson and Cochran (201) suggested that during each major cycle of refinement, scale factors are kept fixed. This is followed by a minor refinement cycle involving only the scaling factor and an overall isotropic temperature factor applied to the current values of F_c, and therefore small. The correction found for the former is applied; and that found for the latter is ignored since the necessary changes will be made to the temperature factor parameters of individual atoms by the next major refinement cycle.

3.5 Rigid Body in Least Squares Refinement

Some groups of atoms of chemically well known configurations can be treated as possessing well defined symmetry in a molecule (e.g. benzene ring with D_{6h} symmetry). The treatment of this group as a rigid body may be considered as a fair approximation if the knowledge of the deviation from this symmetry is not essential. Even if the detailed information about this group is of interest, one still can use this method as an intermediate stage of refinement, since each atom in the group can be refined individually at a later stage.

The advantages of group refinement are manifold. First of all, the range of convergence to minimize R_i by shifting atomic parameters (positional and thermal) to the correct structure is much larger than in the conventional single atom refinement. This fact was tested and observed by Scheringer (205), Ibers (206), Dahl (207) and their coworkers. Because of this ability to make larger shifts correctly, it could be a great help when conventional least squares and Fourier method did not give accurate trial parameters. Another obvious advantage is that within a rigid group, because the relative positions are fixed, meaningless shifts cannot occur, as they often do in the single atom method(205,207, 208). Furthermore, because the number of parameters is reduced considerably, the order of the matrix to be computed is much lower thus saving computer time. For example, a phenyl-group requires at least twenty-four parameters to define six carbon atoms with individual isotropic temperature factors, however it requires only seven parameters (three translational, three rotational and one overall group temperature factor) to define the same group as a rigid unit. In refining the structure of $((C_6H_5)_4C_4OC_2H_5)_2Pd_2C\ell_2$ first by the single atom method and then by the group method, Dahl and Oberhansli (207) concluded by a comparison of the bond lengths and angles of chemically equivalent sets that in general, the rigid body refinement results in a decrease in the standard deviations of the varied parameters and one obtains considerably better internal agreement. The structure determination of thiophenechromium tricarbonyl,

($C_6H_4SCr(CO)_3$) (209), utilized the group refinement method in a disordered structure for which a single atom parameters least-square refinement was impossible.

The principle of the rigid body approach is to use three translational coordinates to define the origin of the rigid body. The centers of mass of the benzene rings were chosen in this work. An orthogonal coordinate system (A) of unit dimensions (in Angstrom) relative to the crystallographic system (a) was defined in the following way. $A_2 || a_2$, $A_1 \perp a_2$ in the plane consisting of a_1 and a_2, and $A_3 = a_1 \times a_2$. The orientation of the benzene rings was defined by three Eulerian angles (ϕ, θ, ψ)* corresponding to three successive rotations of this orthogonal system. The coordinates are transformed back to the crystallographic coordinate system with respect to the following expression (subscripts i=1, 2 and 3 represent x,y and z respectively).

$$x_{ci} = x'_{ci} + (g_{i1}x_{o1} + g_{i2}x_{o2} + g_{i3}x_{o3})/a_i \qquad (3.27)$$

where x_{ci}s and x_{oi}s are coordinates of the rigid body in the crystallographic and orthogonal systems respectively, and x'_{ci}s are the origin of the rigid body in the crystallographic system. g'_{ij}s are matrix elements of transformation which are functions of three Eulerian angles, a set of these with respect to the transformation to the triclinic system is listed in Table 3.1.

In practice, a subroutine is inserted in the program MACLS; the ordinary atoms are treated in the usually way. The atoms belonging to the rigid groups go to a special section, the three positional parameters are those for the center of gravity of the rigid body; the first three components

* Goldstein's (210) notation is used here.

TABLE 3.1

MATRIX ELEMENTS g_{ij}

$\cos\phi(\cos\psi\sin\gamma+\sin\psi\cos\gamma)$	$\cos\phi\sin\psi+\sin\phi\cos\theta\cos\psi$	$\sin\phi\cos\theta(\cos\psi\cos\alpha-a_{13}^{\dagger}\sin\psi$ $+a_{33}^{*}\sin\phi\sin\theta)$ $+\cos\phi(a_{13}\cos\psi+\sin\psi\cos\alpha)$
$-\sin\phi(\cos\psi\sin\gamma+\sin\psi\cos\gamma)$ $+\cos\phi\cos\theta(\cos\psi\cos\gamma-\sin\psi\sin\gamma)$	$\cos\phi\cos\theta\sin\psi-\sin\phi\sin\psi$	$-\sin\phi(a_{13}\cos\psi+\sin\psi\cos\alpha)$ $+\cos\phi\cos\theta(\cos\psi\cos\alpha-a_{13}\sin\psi)$ $+a_{33}\cos\phi\sin\theta$
$\sin\theta(\sin\psi\sin\gamma-\cos\psi\cos\gamma)$	$-\sin\theta\cos\psi$	$\sin\theta(a_{13}\sin\psi-\cos\psi\cos\alpha)$ $+a_{33}\cos\theta$

† $a_{13} = (\cos\beta-\cos\alpha\cos\gamma)/\sin\gamma$

* $a_{33} = [\sin^2\alpha-\{(\cos\beta-\cos\alpha\cos\gamma)/\sin\gamma\}^2]^{1/2}$

of the anisotropic temperature factors are used for the three Eulerian angles, the fourth for the overall temperature factor of the whole rigid group, the fifth is used for the distance from the center to each carbon atom in the benzene ring and is kept fixed (1.392 Å) (211). The sixth component is not used. Once a set of parameters of three translational, three rotational (Eulerian angles) and one overall temperature factor for the group are put in, the individual atomic coordinates can be generated according to (3.27). The contribution to the structure factors can then be summed according to the space group concerned. The derivatives of the structure factors with respect to the parameters can thus be derived, then the procedure of the least squares refinements can proceed in the way described in the last section.

The rigid body least squares refinement approach has been tested and successfully applied for a geometrically well defined subunit like a benzene ring with either an overall temperature factor (205,206,208,211-214) or individual temperature factors for each atom (207,215,216, 12-15). In some cases, the use of both conventional methods and the rigid body least squares refinement is possible but the latter is preferable since the results obtained are more meaningful. The removal of the constraint preserved in the rigid body approach allows the group to deviate from the ideal symmetry if the conventional least squares refinement is used. However, this does not imply that the deformation from ideal symmetry is real; it is probably the result of errors in the measured intensities.

The method described was used for the phenyl groups in $ReC\ell_2(acac)\cdot[P(C_6H_5)_3]_2$ and $ReOC\ell_2(acac)P(C_6H_5)_3$. No attempt was made to apply this method to the β-diketone group because it was unnecessary. The process of applying the rigid body least squares refinement to phenyl groups of the two structures was quite satisfactory. For the refinement of the above two structures, after locating the phenyl groups by Fourier methods, three or four major full-matrix refinements dropped R from about 0.3 to 0.1 yielding quite reasonable molecular geometries. For the structure of $ReC\ell_2(acac)[P(C_6H_5)_3]_2$, if the carbon atoms in the phenyl groups are refined individually, forty-eight atoms require at least 192 parameters (four parameters, three positional and one temperature factor per atom) plus scaling factors among layers and it would be very time consumming to carry out a full-matrix refinement for the IBM 7040 computer. For the structure $ReOC\ell_2(acac)P(C_6H_5)_3$, ordinary least squares refinement, though it appeared possible, would take a much longer time and the result probably may not be as satisfactory as applying the group refinement. The detailed process used for the refinement of these structures will be discussed in the following chapters.

CHAPTER 4

CRYSTAL STRUCTURE OF $ReC\ell_2(acac)_2$

4.1 Experiments

In the following three chapters, the crystal structures of $ReC\ell_2(acac)_2$ (present chapter), $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ (chapter 5), and $ReOC\ell_2(acac)P(C_6H_5)_3$ (chapter 6) are described. Most of the experimental parts are common, such as the preparation of the starting material for these three complexes, and the method of crystallization. Any such common feature will be described in detail in this chapter and then mentioned briefly in the later chapters.

4.1.1 Preparation

The starting material $ReOC\ell_2(OEt)(PPh_3)_2$ can be obtained from $KReO_4$ (3) through the following intermediate steps:

$$KReO_4 \xrightarrow[\text{conc. } HC\ell]{P(C_6H_5)_3 \text{ in } CH_3CO_2H} ReOC\ell_3\ [P(C_6H_5)_3]_2 \xrightarrow[\text{reflux}]{EtOH}$$

$$ReOC\ell_2(OEt)\ [P(C_6H_5)_3]_2$$

Using $ReOC\ell_2(OEt)\ [P(C_6H_5)_3]_2$ as the starting material, the preparation of the compounds $ReC\ell_2(acac)_2$, $ReC\ell_2(acac).[P(C_6H_5)_3]_2$ and $ReOC\ell_2(acac)P(C_6H_5)_3$ is shown schematically in Figure 4.1.

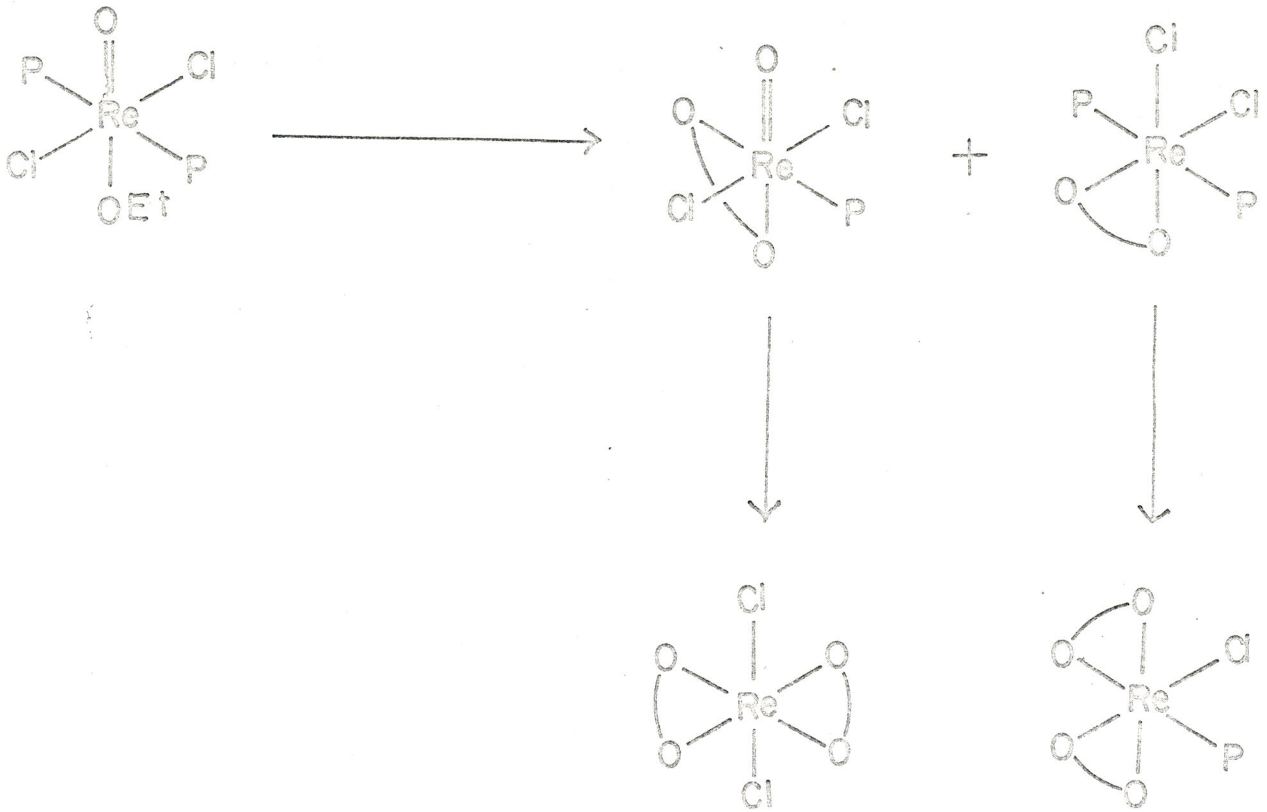


Figure 4.1
Preparation of $ReCl_2(acac)_2$,
$ReCl_2(acac)$ $P(C_6H_5)_{3\ 2}$ and
$ReOCl_2(acac)P(C_6H_5)_3$

A. Oxotrichlorobis(triphenylphosphine)rhenium(V)

$ReOC\ell_3[P(C_6H_5)_3]_2$ has three possible geometrical isomers (Figure 1.1A). The isomer used for preparing the three β-diketone complexes was the yellow isomer in which it was assumed that the two triphenylphosphine groups were in the trans position, and at right angles to the Re=O group. This is based on a comparison with the isomer of $ReOC\ell_3(PEt_2C_6H_5)_2$ for which the structure has been determined (9).

The yellow isomer was prepared as follows (3): a boiling solution of triphenylphosphine (5 g) in ethanol (10 ml.) was added to a boiling solution of perrhenic acid (1 g) and concentrated hydrochloric acid (1 ml.) in ethanol (10 ml.), and the mixture boiled for 3-5 minutes. The yield was about 80%.

B. Oxodichloroethoxobis(triphenylphosphine)rhenium(V) (3)

A suspension of $ReOC\ell_3[P(C_6H_5)_3]_2$ (2 g) in ethanol was boiled for about 2 hours. The purple crystals, which were produced, were collected, washed thoroughly with ethanol and dried (40°/0.1 mm.), giving the product.

C. Dichlorobis(2,4-pentanedionato)rhenium(IV)

$ReC\ell_2(acac)_2$ was prepared according to the procedure of Grove et al. (1) for $Re_2(acac)_4C\ell_4$. A solution of green $ReOC\ell_2(OEt)[P(C_6H_5)_3]_2$ (4.28 g) in acetylacetone (40 ml.) was refluxed for 50 hours and cooled. The product was dissolved in dichloromethane and reprecipitated from chloroform by adding light petroleum (b.p. 30-40°C) as microcrystals. Found: C, 26.6%; H, 3.1%; Cℓ, 16.1%. $C_{10}H_{14}C\ell_2ORe$ requires C, 26.4%; H, 3.1%; Cℓ, 15.6%[+]. Satisfactory molecular weight determinations were

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[+] All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

not possible because of the low solubility in organic solvents.

4.1.2 Crystallization

The three β-diketone complexes prepared according to the methods described above and in chapters 4 - 6, are microcrystalline and too small to be used for single crystal x-ray diffraction purposes.

None of the three compounds had very great solubility in any common solvent like water, alcohols, acetone, halogenated hydrocarbons (e.g. CH_2Cl_2, $CHCl_3$ and CCl_4), aromatic hydrogen carbon and petroleum ethers, although they did have fair solubility in dichloromethane, chloroform and benzene. Attempts to grow crystals from a single solvent by evaporation at room temperature were unsuccessful; such crystals as were obtained were of poor quality because they stuck to the wall of the vessel and were difficult to remove.

Greater success was obtained by crystallizing from mixed solvents. The material was dissolved in the solvent in which it had the greatest solubility, and the solution was then mixed with the other solvent in which the material was less soluble. The latter solvent, preferably has a higher boiling point than the former. The reason for this is that the first solvent having the lower boiling point, will have the higher vapor pressure at any given temperature, and will thus evaporate more readily. Thus the residual solution will become enriched in the poorer solvent and the material will be precipitated slowly, forming good crystals. Crystals up to 3-4 cm. in its longest dimension have been obtained. The crystals were separated from the solution by filtration.

Good single crystals of $\mathrm{ReC\ell_2(acac)_2}$ were obtained from one of the following solvents mixtures:

a) benzene with either $\mathrm{CC\ell_4}$, petroleum ether (80-100°C) or ethyl acetate;

b) methylene chloride with $\mathrm{CC\ell_4}$;

c) acetone alone or with anhydrous ethanol, methanol, cyclohexane, petroleum ether (80-100°C) or ethyl acetate;

d) chloroform with toluene.

The crystal used for x-ray studies was obtained from the slow evaporation of a benzene-carbon tetrachloride mixture kept in an oven slightly above room temperature. The crystals were orange, plate-like and quite large (0.2 x 0.7 x 1 mm^3 average). The crystals of $\mathrm{ReC\ell_2(acac)_2}$ obtained from the above method were usually transparent under microscopic examination. They lacked mechanical strength and could not be cut perpendicular to the largest face.

4.1.3 X-Ray Studies

Several crystals were examined under a polarizing microscope, and a crystal (0.6 x 0.15 x 0.4 mm^3) showing sharp extinction was chosen for structural studies. It was mounted along the direction of the longest dimension. Preliminary examination of the crystal showed they had × triclinic symmetry and it proved easier to study the structure using a cell of symmetry $I\bar{1}$, with twice the volume of the more conventional unit cell of symmetry $P\bar{1}$ since this gave interaxial angles close to 90°. Hereafter we use the subscript d for the centered cell. The two cells were related by the transformation:

$$\begin{pmatrix}\underline{a}\\ \underline{b}\\ \underline{c}\end{pmatrix} = \begin{pmatrix}0 & 1 & 0\\ 1/2 & 1/2 & 1/2\\ \bar{1} & 0 & 0\end{pmatrix}\begin{pmatrix}\underline{a}\\ \underline{b}\\ \underline{c}\end{pmatrix}_d \quad \text{OR} \quad \begin{pmatrix}\underline{a}\\ \underline{b}\\ \underline{c}\end{pmatrix}_d = \begin{pmatrix}0 & 0 & \bar{1}\\ 1 & 0 & 0\\ \bar{1} & 2 & 1\end{pmatrix}\begin{pmatrix}\underline{a}\\ \underline{b}\\ \underline{c}\end{pmatrix}$$

Accurate parameters were obtained by calibrating the $(hk0)_d$ and $(h0\ell)_d$ photographs by superposition of reflections from a TiO_2 (rutile): a=4.5929 and c=2.9593Å (217). The density of $ReC\ell_2(acac)_2$ was found to be 2.18 $gm\text{-}ml^{-1}$ by floating a few crystals in a tetrabromoethane-carbon tetrachloride mixture. This density requires one molecule in the primitive cell. The crystal data are listed in Table 4.1.

Intensity data of layers $\ell_d = 0, 1, 2, 3, 4$ and $k_d = 0, 1, 2, 3$ were recorded photographically by the integrated precession method. MoKα radiation (218) and Zr filter were used for all intensity data recording. Each layer was photographed four times using exposures of 1, 2, 4 and 8 integrating cycles (each cycle takes 144 minutes). The intensity of each reflection was measured using a Joyce-Loebl microdensitometer.

Standard errors were assigned to each reflection according to the methods of Ibers (219) and Hughes (220). The assignment depended on the number of measurements available and the agreement among different measurements for the same intensity on a scaled basis. The weight $1/\sigma^2$ was used throughout the least squares refinements. The intensity of each reflection was corrected for Lorentz and polarization effects. Absorption corrections were not applied mainly because correction factors could not be obtained. Examination of the ratio of calculated and

TABLE 4.1

CRYSTAL DATA FOR $ReC\ell_2(acac)_2$

(e.s.d.'s are enclosed in parentheses)

Parameter	Units	Centered Cell	Primitive Cell
a	Å	7.429(6)	8.032(4)
b	Å	8.032(4)	8.344(6)
c	Å	11.596(8)	7.429(6)
α	°	84.5(1)	118.1(2)
β	°	89.5(2)	92.4(2)
γ	°	87.6(2)	55.5(2)
Vol.	$Å^3$	688.0	344.0
M		455.34	455.34
D_{meas}	$g.cm^{-3}$	2.18(2)	2.18(2)
D_{calc}	$g.cm^{-3}$	2.20	2.20
Z	cm^{-1}	2	1
$\mu(MoK_\alpha)$		90.1	

Systematic absences for centered cell

$h + k + \ell = 2n + 1$

space group $I\bar{1}$

Systematic absence for true cell: none

space group $P\bar{1}$ (No 2, C_i^1)

observed structure factors along three reciprocal axes of the centered cell which were roughly coincident to the edges of parallelpiped of the crystal specimen used for x-ray studies did not reveal any systematic error that could have been caused by absorption. Although the maximum error caused by absorption could have been of the order of 10% in intensity, the average error would be less than 10%.

4.2 Solution and Refinement of the Structure

The centro-symmetric space group P$\bar{1}$ was assumed at the beginning unnecessary and was confirmed from the peak heights of the Patterson syntheses as well as from the later refinement of the structure. The low value for the final R factor would be an indication but not a proof, that the chosen space group is correct.

The scattering factors used for $C\ell$, O and C were taken from the International Tables (221) and Re was calculated by Cromer and Waber (222). The effects of anomalous scattering were included in the structure-factor calculations, the value of f' and f" for Re and $C\ell$, the real and imagined parts of the dispersion corrections to the atomic scattering factor, were those given by Cromer (223).

Since there is only one molecule per primitive cell, the unique rhenium atom, heaviest in the molecule in this case, must be placed at a special position, i.e. at the origin which is the center of symmetry for the primitive cell. The chlorine and oxygen atoms were located from the inspection of the Patterson functions projected on $(100)_d$ and $(010)_d$, and the remaining non-hydrogen atoms were found and confirmed from successive Fourier synthesis and least squares refinements. Further refinement was carried out by a full-matrix least squares procedure. When the value of R_2 had dropped to about 0.13, the individual isotropic thermal parameters were replaced by anisotropic ones. The refinement was terminated when the calculated shifts for the atomic coordinates were one-third or less of their estimated standard deviations. The final atomic parameters, positional and thermal, are collected in Table 4.2. The final values of 5 Fo and 5 Fc (in electrons) are recorded in Table 4.3 with indices respect to the primitive cell. The final value for R_1 for all the data is 0.076 while the value of R_2 is 0.070 for 1053 non-equivalent reflections. No peaks of magnitude greater than 1.5% of a Re peak could be detected in the three dimensional difference electron density maps.

4.3 Results and Discussion

Figure 4.2 shows one complete molecule. The bond lengths and bond angles are listed in Table 4.4 and the average dimensions of a rhenium acetylacetonate ring are shown in Figure 4.3.

The rhenium atom is at the origin of the unit cell, and the shortest Re-Re distance, i.e. about 8 Å, corresponds to two Re related by the centering. This distance negates the dimerization suggested by Grove et al. (1). For the monomer, cis and trans configurations are possible, but the centro-symmetric space group $P\bar{1}$, as concluded from the last section, would rule out the possibility of cis configuration for one molecule in a unit cell. The inner coordination around rhenium is a tetragonally distorted octahedron elongated along the Re-Cℓ direction. The bond length of Re-Cℓ is not significantly different from that observed

TABLE 4.2

ATOMIC PARAMETERS FOR $ReCl_2(acac)_2$ IN THE PRIMITIVE CELL (e.s.d's are enclosed in parentheses)

Atom	x	y	z
Re	0	0	0
Cℓ	0.2599(7)	0.0341(10)	0.0499(8)
O_1	0.2248(17)	-0.3212(19)	-0.0819(14)
O_2	0.0110(19)	-0.1191(21)	-0.3093(15)
C_1	0.3057(31)	0.4927(34)	-0.2680(24)
C_2	0.2630(30)	0.4835(30)	-0.4591(23)
C_3	0.1208(28)	-0.3271(29)	-0.4680(20)
C_4	0.4798(36)	0.2663(35)	-0.2826(32)
C_5	0.0815(35)	-0.3592(40)	0.3193(25)

TABLE 4.2 (continued)

Thermal, (anisotropic), $(\text{Å}) \times 10^4$

Atom	U_{11}†	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	352(7)	314(6)	308(4)	-58(3)	-41(2)	78(2)
Cℓ	482(34)	610(30)	720(26)	-143(17)	-82(12)	185(13)
O_1	296(80)	343(51)	314(42)	51(36)	-11(24)	71(21)
O_2	745(101)	544(65)	324(44)	-198(45)	-120(29)	132(24)
C_1	671(153)	628(107)	482(76)	-245(72)	-142(46)	187(42)
C_2	550(139)	408(84)	408(68)	-32(61)	-41(41)	121(34)
C_3	771(133)	420(81)	302(57)	-226(60)	-45(38)	64(29)
C_4	810(168)	467(95)	780(108)	-162(73)	-235(58)	201(48)
C_5	1520(204)	863(133)	440(74)	-546(90)	-300(54)	207(44)

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† These values were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where β_{ij}'s appear as a temperature effect $\exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \ldots)]$ in the structure factor expression and b_i are the reciprocal lattice vectors.

TABLE 4.3

OBSERVED AND CALCULATED STRUCTURE FACTORS (x 5)

UNRELIABLE REFLECTIONS ARE MARKED WITH THE SYMBOL (*).

[illegible]

Figure 4.2

The $ReCl_2(acac)_2$ Molecule

The numbering of the atoms corresponds to that in Tables 4.2, 4.4 and 4.5.

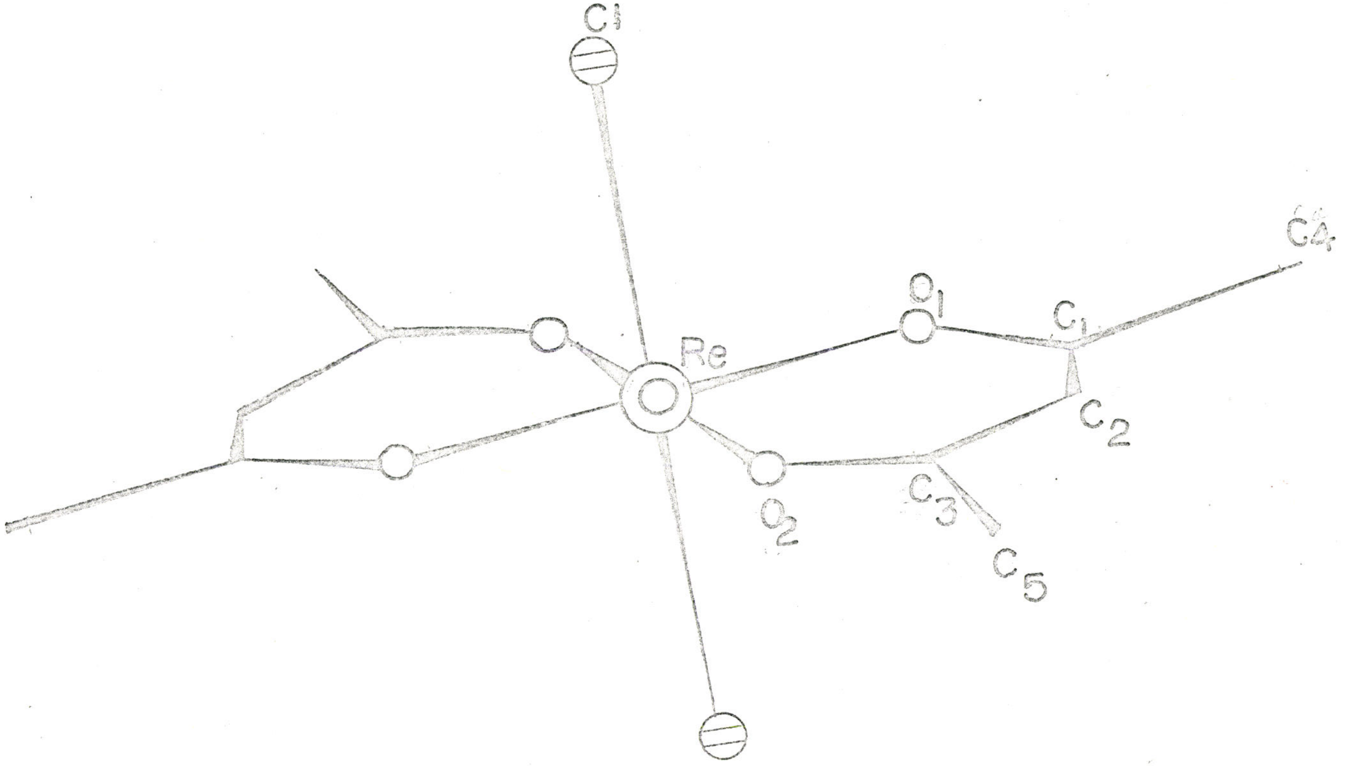

Figure 4·2 The $ReCl_2(acac)_2$ Molecule

TABLE 4.4

SELECTED BOND DISTANCES AND ANGLES IN $\mathrm{ReC\ell_2(acac)_2}$

(e.s.d.'s are enclosed in parentheses)

A. Bonded Distances (Å)

Re-Cℓ	2.326(8)		
$\mathrm{Re{-}O_1}$	1.972(12)	$\mathrm{C_1{-}C_2}$	1.424(27)
$\mathrm{Re{-}O_2}$	2.010(10)	$\mathrm{C_2{-}C_3}$	1.361(28)
$\mathrm{O_1{-}C_1}$	1.285(18)	$\mathrm{C_1{-}C_4}$	1.537(32)
$\mathrm{O_2{-}C_3}$	1.266(17)	$\mathrm{C_3{-}C_5}$	1.524(26)

B. Non-bonded Distances (Å)

$\mathrm{C\ell{-}O_1}$	3.034(21)	$\mathrm{C\ell{-}O_2}$	3.059(18)
$\mathrm{C\ell{-}O_1^1}$	3.065(13)	$\mathrm{O_1{-}O_2}$	2.796(19)
$\mathrm{C\ell{-}O_2}$	3.099(18)	$\mathrm{O_1{-}O_2}$	2.836(12)

C. Angles (°)

$\mathrm{C\ {-}Re{-}O_1}$	89.4(5)	$\mathrm{O_2{-}C_3{-}C_2}$	124.4(20)
$\mathrm{C\ {-}Re{-}O_2}$	90.9(5)	$\mathrm{O_1{-}C_1{-}C_4}$	115.1(19)
$\mathrm{O_1{-}Re{-}O_2}$	89.2(10)	$\mathrm{O_2{-}C_3{-}C_5}$	115.3(15)
$\mathrm{Re{-}O_1{-}C_1}$	127.1(12)	$\mathrm{C_1{-}C_2{-}C_3}$	124.4(20)
$\mathrm{Re{-}O_2{-}O_3}$	128.5(11)	$\mathrm{C_2{-}C_1{-}C_4}$	119.9(21)
$\mathrm{O_1{-}C_1{-}C_2}$	125.5(13)	$\mathrm{C_2{-}C_3{-}C_5}$	119.6(28)

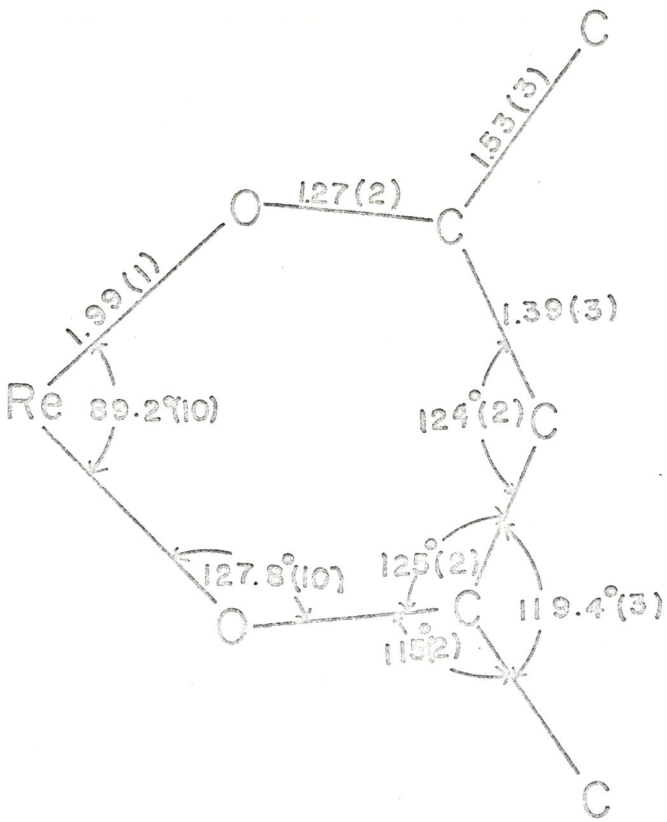

Figure 4.3

Average dimension of rhenium acetylacetone unit in $ReCl_2(acac)_2$

from other Re(IV)-Cℓ complexes (224-226). The Re-O (average 1.99(1)Å) bond lengths suggest that the Re-O bonds are single and are possibly slightly shorter than Cotton's calculated value for Re(V) single bond (2.04 A) (11). This is an indication that some multiple bonding may occur between the oxygen atom and metal atom. The O-Re-O and Cℓ-Re-O angles are very close to 90° (± 1°) required for the ideal tetragonal configuration around the metal. The O ... O distances within the chelate ring (2.80 A), are nearly equal to that between chelated rings (2.83 A). It is rather interesting to find that the approximate value of 2.8 A for O ... O distances exists in most metal-β-diketone complexes irrespective of the M-O bond length, being almost exactly twice the van der Waals radius for the oxygen atom. Almost no variation in the O ... O distance is found as the M-O bond length changes from 2.0 A (in this compound) to 2.4 A (in Ce(acac)$_4$) (121). Bond distances of the equivalent sets within the group differ only about 2σ in the extreme case. The average values of O-C, C-C (ring) and C-C (non-ring) are 1.28 A, 1.39 A and 1.53 A, respectively. The sum of angles around β-carbon atoms are within 0.7° of 360°, the value required for the planarity which would be expected if only sp^2 hybrid orbitals are used in the formation of the wave functions describing the bonds.

The equation of the least squares planes of OReO and OCCCO belonging to the ring part of the acetylacetonate group together with the orthogonal coordinates of the whole metal acetylacetonate unit and the displacement of each atom from the plane of OCCCO are listed in Table 4.5. The orthogonal coordinate system is the same as that defined in Sec. 3.5.

TABLE 4.5

BEST WEIGHTED LEAST SQUARES PLANES OF THE RHENIUM ACETYLACETONATE UNIT IN $ReCl_2(acac)_2$

Equation of Plane of the Form Ax+By+Cz=D

(Orthogonal Coordinate)†

Atoms	Plane No.	A	B	C	D
Re, O_1, O_2	1	0.6844	0.7142	-0.1465	0
O_1, O_2, C_1, C_2, C_3	2	0.7045	0.6830	-0.1929	0.081

Orthogonal Coordinates and Distances

of Atoms from Plane 2 (Å)

Atom	x	y	z	Distances from Plane 2
Re	6.621	8.3435	6.228	0.081
O_1	1.322	-1.372	-0.510	0.012
O_2	-0.557	0.139	-1.926	-0.007
C_1	1.478	-1.905	-1.669	-0.183
C_2	0.806	-1.507	-2.860	0.101
C_3	-0.153	-0.542	-2.915	0.003
C_4	2.601	-2.951	-1.760	-0.156
C_5	-0.846	0.244	-4.239	-0.056

---

† Defined in Section 3.5

Rhenium is slightly displaced (0.08Å) from the plane, the dihedral angle between this plane and the OReO plane is 3°5'. One of the methyl carbon atoms is displaced from the plane more (0.16 Å against 0.06 Å) than the other one. The crystal packing viewed along the *a* direction is shown in Figure 4.4.

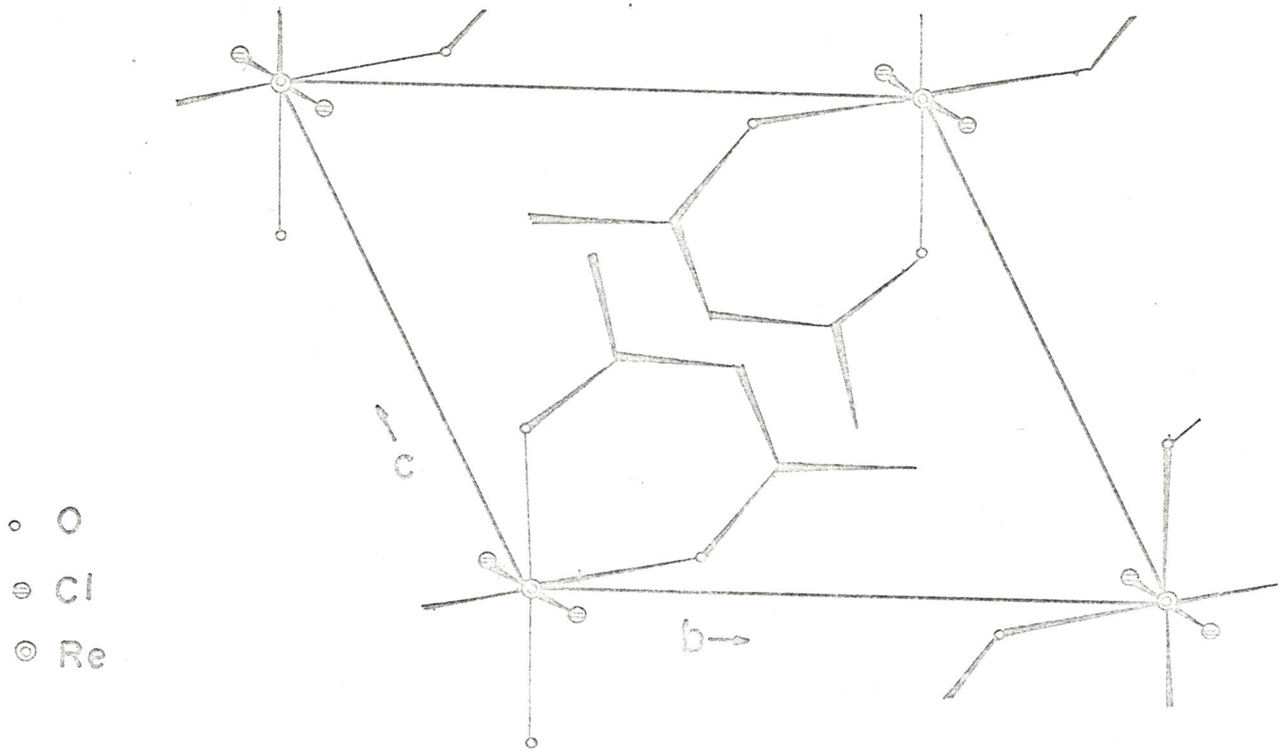

Figure 4.4

Structure of $ReCl_2(acac)_2$

projected down [100]

CHAPTER 5

CRYSTAL STRUCTURE OF $ReC\ell_2(acac)[P(C_6H_5)_3]_2$

5.1 Experiments

5.1.1 Preparation

$ReC\ell_2(acac)[P(C_6H_5)_3]_2$ was prepared by the method of Grove et al. (1). A solution of purple $ReOC\ell_2(OEt)$ $[P(C_6H_5)_3]_2$ (2 g) and pentane-2,4-dione (2 ml) in benzene (30 ml.) was boiled under reflux conditons for 6 hours, concentrated to 15 ml. and allowed to cool. The product was obtained as micro crystals, and was separated by filtration. The crystals were washed with a little benzene and diethyl ether. Calculated for $C_{41}H_{37}C\ell_2O_2P_2Re$ requires C, 55.9%; H, 4.2%; Cℓ, 8.1% and P, 7.0%. Found: C, 55.8%; H, 4.4%; Cℓ, 8.0% and P, 6.9%.

5.1.2 Crystallization

Single crystals were obtained according to the method described in Sec. 4.1. The material was dissolved in dichloro-methane and benzene mixture at about 2:1 volume ratio and evaporated slowly at room temperature. Crystals obtained by this method were orange plates.

5.1.3 X-Ray Studies

A crystal of $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ showing sharp extinction was cut out into a cylindrical shape with the dimensions 0.07 x 0.09 x 0.13 mm^3. The specimen was mounted parallel to the longest dimension ($\underline{c}^*$). The cell parameters were obtained from precession photographs of (Okℓ) and (h0ℓ) which has been calibrated with TiO_2 (rutile: a = 4.5929 and c = 2.9593 Å) (217). It was observed that h0ℓ reflections with ℓ = 2n + 1 and 0k0 reflections with k = 2n + 1 were systematically absent, and thus the monoclinic space group was uniquely determined as $P2_1/c$. The density of the crystal was determined by flotation, the liquids used in this case were carbon tetrachloride and bromoform. The density was 1.6 g. $ml.^{-1}$ for $ReCℓ(acac)(P(C_6H_5)_3)_2$, suggesting four molecules in a unit cell. The crystal data for $ReCℓ_2(acac)[PC_6H_5)_3]_2$ are listed in Table 5.1.

The intensity data for layers h = 0, 1, 2, 3, 4 and k = 0, 1, 2, 3, 4, 5, 6 were recorded photographically by the integrated precession method. MoKα (λ = 0.71069 Å) radiation and Zr filter were used for all intensity data recorded. Each layer was photographed three times using exposures of 2, 6 and 18 integrating cycles (1 cycle takes 144 minutes). The intensities of all reflections were measured with a Joyce-Loebl microdensitometer. The unobserved reflections were assigned an intensity equal to the minimum observed intensity in their region of reciprocal space. Standard errors, σ, were assigned in the same way described in Section 4.1. The measured intensities were corrected for Lorentz and polarization effects. Absorption corrections were not applied since the transmission factors (this is the ratio of the intensity which is diffracted to the intensity which would be diffracted if there were no absorption) various from 1.3 to 1.5 for extreme cases.

5.2 Solution and Refinements

The density together with the volume suggests that there are four molecules in the unit cell, this means that all atoms are in general

TABLE 5.1

CRYSTAL DATA FOR $ReCl_2(acac)[P(C_6H_5)_3]_2$

(e.s.d.'s are enclosed in parentheses)

Parameter	Unit	Value
a	Å	13.06(1)
b	Å	18.30(1)
c	Å	16.55(1)
β	°	112.7(2)
Vol	$Å^3$	3648
M		881
$D_{meas.}$	$g\text{-}cm^{-3}$	1.61(8)
$D_{calc.}$	$g\text{-}cm^{-3}$	1.60
Z		4
μ(MoKα)	cm^{-1}	37.9

Systematic absences	$ho\ell$, $\ell = 2n + 1$; OKO, $K = 2n + 1$
Space group	$P2_1/c - C_{2h}^5$

positions. Patterson syntheses projected on (100) and (010) were calculated. The coordinates of the Re atom were readily obtained. No information about the other atoms could be derived, however. Structure factors of the $0k\ell$ and $h0\ell$ layers were calculated using the Re positional parameters, the scale and the isotropic temperature factors for Re having been obtained from a Wilson plot(227). For this set of atomic positions $R_1 = 0.37$ and $R_2 = 0.39$. In all calculations of F_c, the atomic scattering factors tabulated in the International Tables (221) were used for Cl, P, O and C, and those of Cromer and Waber were used for Re (222). The effects of anomalous dispersion were included in F_c, the value of f' and f" for Re, Cl and P were those given by Cromer (223). A three-dimensional difference synthesis using the $h0\ell$ and $nk\ell$ ($n = 0$ to 4) reflection data were computed. Common reflections were averaged in this and later three-dimensional syntheses. Six atoms which formed an approximate octahedron surrounding Re could be observed. Of these, two peaks in cis positions were much smaller than the other four, and were assigned as position of two oxygen atoms of the chelated β-diketone group. It was not possible to distinguish between Cl and P peaks because the scattering powers are very close. Structure factors of $0k\ell$ and $h0\ell$ were computed based on the coordinates of Re, two O, and four Cℓ, (assuming P has the same scattering power as Cℓ at this stage). The successive Fourier electron density and difference syntheses on (100) and (010) did not reveal any information about the six phenyl groups though peaks corresponding to carbon atoms of the acetylacetone group could be resolved with the help of an assumed geometry. Structure factors of the [010] and [100] zones were then calculated based on the parameters of atomic coordinates of rhenium, the six ligand atoms directly bonded to the metal and five carbon atoms from the β-diketone group. Successive Fourier electron density and difference syntheses using the above data were computed but gave no more information. Then the structure factors of the observed reflections of ten upper layers ($hn\ell$ for $n = 1$ to 6 and $nk\ell$ for $n = 1$ to 4) were calcualted using the same atomic parameters and resulted in $R_1 = 0.27$ and $R_2 = 0.30$ for all the observed reflections. Unobserved reflections were not included in this calculation because it would be unnecessarily wasteful of computer time. A three-dimensional difference synthesis calculated using structure factors satisfying $F_o/F_c \leq 1.5$, about 2500 in all, allowed all the remaining light atoms other than hydrogen to be found. These also allowed the phosphorus atom to be distinguished from the $C\ell$ atoms since the two atoms identified as chlorine were more than 3.0 A away from any phenyl carbon atom. R_1 and R_2 dropped to 0.22 and 0.28 respectively for the observed reflections of all twelve layers as coordinates of all non-hydrogen atoms in an asymmetric unit were included in the structure factors calculation. At this stage, the three Eulerian angles of each phenyl group were calculated according to the inverse matrix of Table 3.1 and (3.27). In case the carbon atoms in the ring did not conform exactly to the D_{6h} symmetry, individual values of translational and rotational parameters were averaged.

The refinement of this structure was carried out by a special least squares program according to the principle described in section 3.5. Each phenyl group was treated as an atomic unit with D_{6h} symmetry. Six parameters were used to define the position of the ring; three to define a reference point of the ring, the center of the ring was chosen in this case, and the other three parameters corresponding to three Eulerian angles (210) defining the orientation of the ring. The overall isotropic temperature factors were assigned and refined one per rigid group. One cycle of the full-matrix least squares refinement dropped R_1 and R_2 to 0.15 and 0.20 respectively. Three successive cycles of refinement decreased both R_1 and R_2 to 0.083. At this stage common reflections were averaged between layers and unobserved reflections were given zero weight if $F_c < F_{min}$. Anisotropic temperature factors were introduced for all atoms except carbon. No attempt was made to locate hydrogen atoms in the crystal. The refinement was terminated when $R_1 = 0.078$ and $R_2 = 0.069$ for all 2818 independent reflections. For the last cycle of least squares refinement, the shift of the atomic positional and thermal parameters and scale factors were very small; all shifts in the parameters were less than one sixth of the standard deviation. A three dimensional difference synthesis did not give any peak higher than 1.3 e/A^3.

The positional, thermal and group parameters derived from the last cycle of least-squares refinement are present in Table 5.2. together with the corresponding standard deviations in these parameters derived from the inverse matrix. The corresponding positional parameters of the group carbon atoms are presented in Table 5.3. The final values of 10 F_o and 10 F_c (in electrons) are given in Table 5.4.

5.3 Result and Discussion

Figure 5.1 shows one complete molecule and Figure 5.2 shows the crystal packing projected down b. Principle intramolecular distance and

TABLE 5.2

POSITIONAL, THERMAL AND RIGID GROUP PARAMETERS
FOR $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ (e.s.d.'s are enclosed in parentheses)

Atom	x	y	z	Thermal (isotropic) B (A^2)
Re	0.2820(5)	0.14652(3)	0.21635(4)	-
$C\ell_1$	0.2435(4)	0.0285(2)	0.2564(3)	-
$C\ell_2$	0.3577(3)	0.1971(3)	0.3591(3)	-
P_1	0.0925(3)	0.1864(2)	0.1974(3)	-
P_2	0.4719(3)	0.1070(2)	0.2388(3)	-
O_1	0.3142(9)	0.2422(5)	0.1722(6)	-
O_2	0.2183(8)	0.1135(5)	0.0887(6)	-
C_1	0.2996(14)	0.2598(10)	0.0929(11)	3.7(3)
C_2	0.2627(14)	0.2135(10)	0.0225(10)	3.4(3)
C_3	0.2199(13)	0.1476(10)	0.0192(9)	3.0(3)
C_4	0.3362(17)	0.3399(12)	0.0835(13)	5.8(5)
C_5	0.1671(15)	0.3994(11)	0.4374(12)	4.4(4)

TABLE 5.2 (continued)

Thermal (Aniostropic), $(\mathring{A})^2 \times 10^4$

Atom	U_{11} †	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	300(4)	280(4)	293(3)	-8(2)	63(1)	-5(2)
$C\ell_1$	461(25)	317(20)	491(23)	9(13)	91(10)	16(9)
$C\ell_2$	389(23)	478(25)	361(21)	-9(13)	67(9)	-53(10)
P_1	292(22)	212(21)	324(19)	27(12)	65(9)	-1(8)
P_2	381(28)	303(22)	348(23)	13(13)	96(11)	-30(9)
O_1	429(64)	252(54)	446(63)	46(34)	130(27)	-5(24)
O_2	282(55)	244(49)	390(55)	1(32)	76(23)	-23(23)

† These vales were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{11}$ where β_{ij}'s appear as a temperature effect through $\exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \ldots)]$ in the structure factor expression and b_i are the reciprocal lattice vectors.

TABLE 5.2 (continued)

Group	x_c	y_c	z_c	ϕ	θ	ψ	B $(\mathring{A})^2$
P_1R_1	-0.0745(6)	0.1443(4)	0.0011(5)	74.3(3)	-104.0(4)	265.6(4)	4.1(2)
P_1R_2	-0.0140(6)	0.1213(4)	0.3292(5)	42.5(3)	76.5(4)	193.2(5)	4.1(2)
P_1R_3	0.0329(7)	0.3573(5)	0.2056(5)	-2.6(4)	11.4(4)	107.9(5)	4.6(2)
P_2R_1	0.6349(6)	0.0570(4)	0.4362(4)	87.2(3)	68.3(4)	231.8(4)	3.7(1)
P_2R_2	0.5001(7)	-0.0417(5)	0.1429(5)	5.2(2)	325.0(5)	49.4(5)	5.2(2)
P_2R_3	0.5976(6)	0.2347(5)	0.1771(5)	337.0(5)	47.6(4)	65.0(6)	4.3(2)

†x_c, y_c and z_c are the fractional coordinates of the ring centers, ϕ, θ and ψ (in degrees) are three Eulerian angles were defined in Section 3.5. The rings are numbered so that C_{i4}(i=1, 2, 3, 4, 5 and 6) is attached to P; C_{i1} is para to C_{i4}

TABLE 5.3

DERIVED POSITIONAL PARAMETERS FOR CARBON ATOMS IN RIGID GROUP

Group	Atom	x	y	z
P_1R_1	C_{11}	-0.1432[+]	0.1252	-0.0840
	C_{12}	-0.1182	0.1983	-0.0622
	C_{13}	-0.0495	0.2174	0.0230
	C_{14}	-0.0059	0.1634	0.0863
	C_{15}	-0.0309	0.0903	0.0645
	C_{16}	-0.0996	0.0712	-0.0207
P_1R_2	C_{21}	-0.0575	0.0968	0.3890
	C_{22}	0.0562	0.1082	0.4158
	C_{23}	0.0997	0.1327	0.3559
	C_{24}	0.0294	0.1458	0.2693
	C_{25}	-0.0843	0.1344	0.2426
	C_{26}	-0.1278	0.1099	0.3025
P_1R_3	C_{31}	0.0042	0.4306	0.2048
	C_{32}	-0.0611	0.3769	0.2208
	C_{33}	-0.0324	0.3036	0.2217
	C_{34}	0.0616	0.2840	0.2065
	C_{35}	0.1269	0.3377	0.1904
	C_{36}	0.0982	0.4110	0.1896

[+] These are fractional coordinates and have been obtained with the restriction that intra-ring C-C bonded distances are C-C = 1.39 Å; the e.s.d.'s in these coordinates have not been extimated, however, they could be derived from e.s.d.'s given in group parameters listed in the preceding page.

TABLE 5.3 (continued)

P_2R_1	C_{41}	0.7040	0.0467	0.5208
	C_{42}	0.7295	0.1078	0.4821
	C_{43}	0.6604	0.1281	0.3975
	C_{44}	0.5678	0.0873	0.3516
	C_{45}	0.5403	0.0262	0.3903
	C_{46}	0.6094	0.0058	0.4749
P_2R_2	C_{51}	0.5124	-0.1063	0.1032
	C_{52}	0.6024	-0.0769	0.1721
	C_{53}	0.5901	-0.0123	0.2118
	C_{54}	0.4878	0.0230	0.1826
	C_{55}	0.3977	-0.0064	0.1136
	C_{56}	0.4100	-0.0710	0.0739
P_2R_3	C_{61}	0.6515	0.2898	0.1508
	C_{62}	0.6141	0.3028	0.2177
	C_{63}	0.5602	0.2478	0.2440
	C_{64}	0.5437	0.1797	0.2035
	C_{65}	0.5811	0.1667	0.1366
	C_{66}	0.6350	0.2217	0.1103

TABLE 5.4.1

OBSERVED AND CALCULATED STRUCTURE FACTORS (x 10)

K	L	|FOBS|	FCALC
		H = 0	
0	2	3916	4513
0	6	1697	1548
0	12	985	435
0	16	938	841
1	2	1675	1689
1	3	474	556
1	5	937	913
1	7	2000	1800
1	9	843	778
1	11	463	457
2	1	2650	4402
2	2	1000	1017
2	3	2278	2126
2	6	432	417
2	7	859	868
2	10	331	351
2	11	1066	935
2	13	949	928
2	15	1015	939
2	16	307	326
3	1	824	1007
3	2	1342	1288
3	4	843	765
3	5	2085	2042
3	8	697	698
3	9	1797	1652
3	10	503	543
3	12	576	651
4	0	3467	3370
4	1	1551	1649
4	2	1011	1803
4	3	432	469
4	4	1041	1131
4	9	370	326
4	10	837	861
4	12	801	781
4	15	662	676
5	2	1021	1313
5	4	1766	1736
5	5	449	447
5	6	2207	2201
5	12	816	816
6	0	1573	1650
6	1	1727	1756
6	2	2035	2100
6	3	1274	1235
6	4	1125	1153
6	5	1347	1270
6	7	346	241
6	9	462	451
6	10	783	721
6	13	607	617
6	15	752	761
6	16	527	535
7	2	585	495
7	3	2006	2043
7	4	337	339
7	5	1748	1678
7	6	672	635

K	L	|FOBS|	FCALC
1	4	317	265
1	6	306	273
1	7	1261	1248
1	9	355	474
2	-10	436	411
2	-9	2351	2251
2	-7	2312	2171
2	-5	2750	2678
2	-3	2475	2417
2	5	2249	2220
2	6	1153	1244
2	7	1463	1233
2	8	432	440
2	9	1436	1351
2	11	911	864
2	13	571	565
3	-15	1675	1422
3	-14	456	412
3	-12	434	420
3	-11	1730	1522
3	-7	562	661
3	-6	2539	654
3	-3	1012	1172
3	-2	1481	1392
3	-1	3056	2731
3	1	2173	2140
3	2	1150	1130
3	3	1672	1612
3	4	918	971
3	6	1362	1155
3	13	1120	1067
4	-16	347	363
4	-12	354	475
4	-10	1483	1443
4	-8	2114	2093
4	-6	1721	1910
4	-5	1485	1387
4	-4	1573	2028
4	-2	1334	1452
4	0	1276	1262
4	2	1012	958
4	3	1000	933
4	4	782	725
4	6	1682	1670
4	8	1563	1577
4	10	1249	1167
4	11	353	334
4	13	375	421
4	14	383	411
5	-14	1403	1252
5	-10	1479	1351
5	-8	602	703
5	-4	810	1005
5	-3	611	677
5	-2	920	923
5	-1	1547	1445
5	0	2362	2346
5	2	1800	1765
5	3	361	337
5	4	1730	1654
5	5	377	334
5	12	810	820

TABLE 5.4.1
(continued)

TABLE 5.4.2

UNOBSERVED AND CALCULATED STRUCTURE FACTORS (x 10)

Figure 5.1

The $ReCl_2(acac)[P(C_6H_5)_3]_2$ Molecule

The numbering of the atoms corresponds to that in Tables 5.2, 5.3, 5.5 and 5.7.

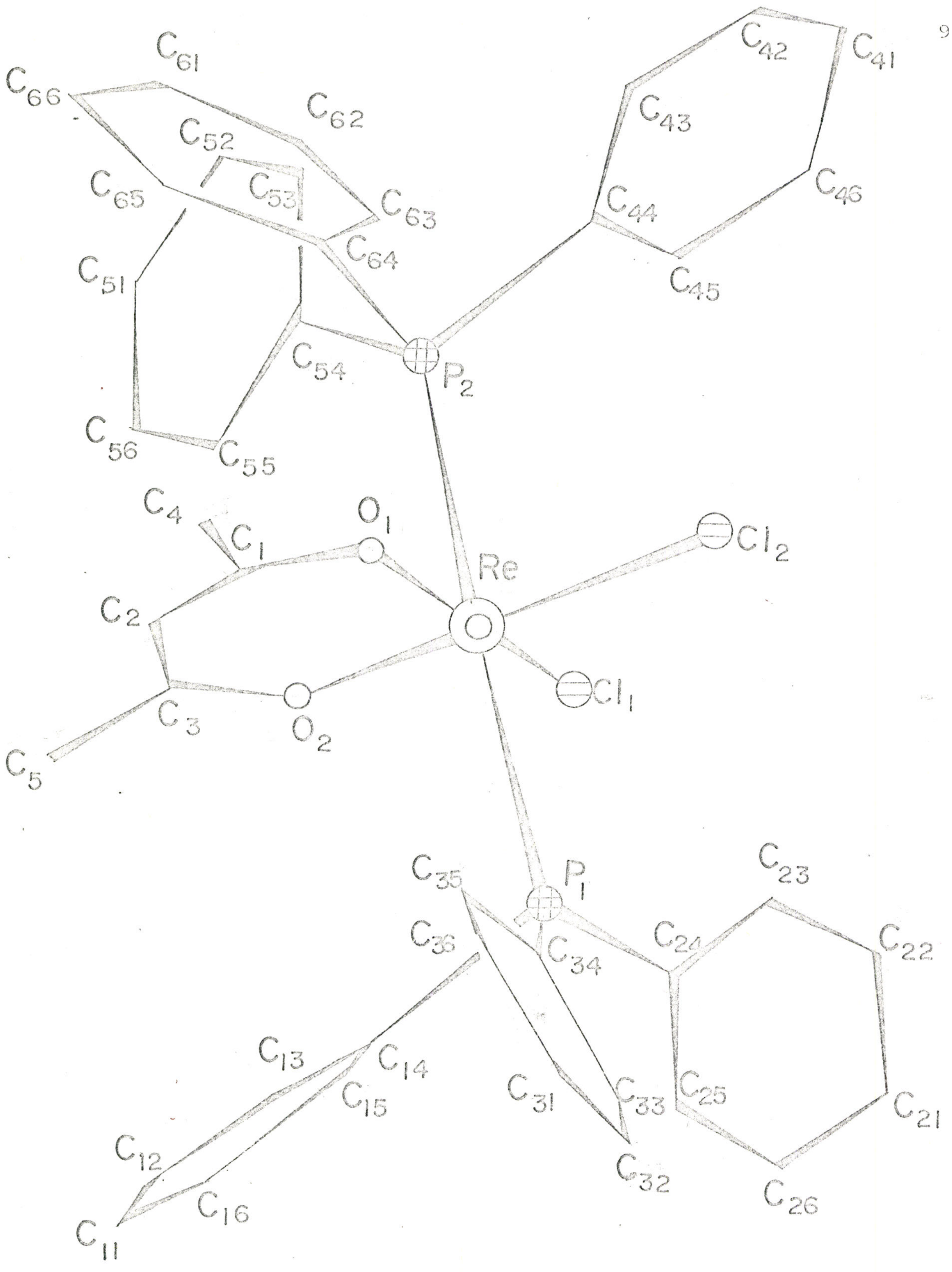

Figure 5·1 The $ReCl_2(acac)[P(C_6H_5)_3]_2$ Molecule

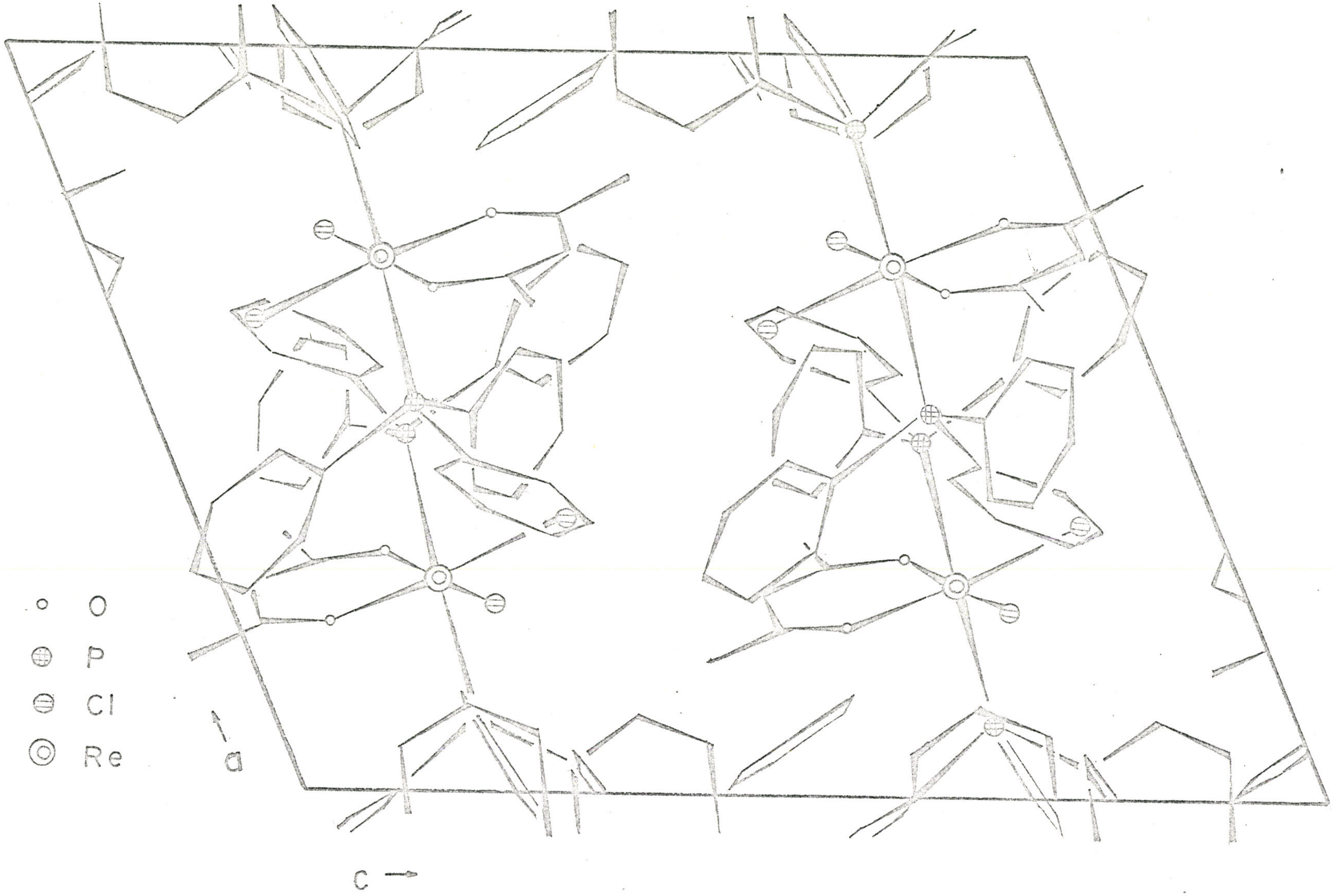

Figure 5.2

Structure of $ReCl_2(acac)[P(C_6H_5)]_2$

projected down [010]

angles and their estimated standard deviations are given in Table 5.5. The interatomic distances from different molecules appear to be normal, the shortest ones are about 3.4 Å (C_4-C_{46} 3.35 and $C\ell_1$-C'_{41} 3.41 Å), all the other distances are more than 3.5 Å which equals or exceeds the sum of the van der Waals radii.

The configuration of the molecule can be seen in Figure 5.1. The trans P-Re-P arrangement exists in the geometrical isomer (B-I, Figure 1.1) which is most closely related to the starting material, $ReOC\ell_2(OEt)[P(C_6H_5)_3]_2$, in which P-Re-P is also trans. The reaction mechanism involved will be discussed in Chapter 7.

The ligands which surround the rhenium atom form an octahedron which is distorted as a result of the difference in bond length between Re-O , Re-Cℓ and Re-P. The two Re-Cℓ distances both are 2.369(4) Å and close to the 2.33 Å found in $ReC\ell_2(acac)_2$. These also agree well with the 2.353 A in $K_2ReC\ell_6$ (228), 2.35 Å in $(TH)_2ReC\ell_6$ (TH = p-toluidinium group) (225) and 2.38 Å in $K_4(Re_2OC\ell_{10}).H_2O$ (226). The Re-P bond lengths of 2.474(5) Å and 2.482(4) Å are longer than the M-P distance for most second and third row transition metals (12) but agree well with those found in other Re compounds containing triphenylphosphine or diethyl phenylphosphine groups. These distances are listed in Table 5.6. Re-O distances of 2.00(1) Å and 2.04(1) Å agree well with the 1.97 Å and 2.01 Å found in $ReCl_2(acac)_2$.

Bond distances and angles in the acetylacetone group agree well with many metal acetylacetonates, as can be seen from Table 2.5. The equation of the best weighted least squares plane of OReO and OCCCO, the orthogonal coordinates (Å) of the metal acetylacetonate unit, together

TABLE 5.5

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

IN $ReCl_2(acac)[P(C_6H_5)_3]_2$ (e.s.d.'s are enclosed in parentheses)

A. Bonded Distances (Å)

$Re-Cl_1$	2.369(4)	C_3-C_2	1.353(25)
$Re-Cl_2$	2.369(4)	C_1-C_4	1.567(30)
$Re-P_1$	2.482(4)	C_3-C_5	1.528(23)
$Re-P_2$	2.464(5)	P_1-C_{14}	1.840†
$Re-O_1$	2.004(11)	P_1-C_{24}	1.845
$Re-O_2$	2.041(9)	P_1-C_{34}	1.849
O_1-C_1	1.293(22)	P_2-C_{44}	1.830
O_2-C_3	1.315(20)	P_2-C_{54}	1.850
C_1-C_2	1.349(24)	P_2-C_{64}	1.847

B. Non-bonded Distances (Å)

Cl_1-Cl_2	3.569(6)	Cl_2-O_1	3.035(11)
Cl_1-P_1	3.421(6)	P_1-O_1	3.245(13)
Cl_1-P_2	3.423(7)	P_1-O_2	3.163(12)
Cl_1-O_2	3.086(11)	P_2-O_1	3.136(11)
Cl_2-P_1	3.469(5)	P_2-O_2	3.288(9)
Cl_2-P_2	3.347(7)	O_1-O_2	2.774(13)

† The error of P-C bond distances is estimated to be less than 0.02A and that of Re-P-C, C-P-C and P-C-C angles listed in the following page are less than 1.5°.

TABLE 5.5 (continued)

C. Angles (°)

Cl_1-Re-Cl_2	97.4(2)	Re-P_2-C_{44}	116.7
Cl_1-Re-P_1	89.7(2)	Re-P_2-C_{54}	117.9
Cl_1-Re-P_2	90.0(2)	Re-P_2-C_{64}	110.1
Cl_1-Re-O_1	174.8(3)	C_{14}-P_1-C_{24}	103.8
Cl_1-Re-O_2	88.5(3)	C_{24}-P_1-C_{34}	99.8
Cl_2-Re-P_1	91.3(1)	C_{34}-P_1-C_{14}	102.2
Cl_2-Re-P_2	87.5(1)	C_{44}-P_2-C_{54}	100.9
Cl_2-Re-O_1	87.5(3)	C_{54}-P_2-C_{64}	105.7
Cl_2-Re-O_2	174.1(3)	C_{64}-P_2-C_{44}	104.1
P_1-Re-P_2	178.7(1)	P_1-C_{14}-C_{13}	121.0
P_1-Re-O_1	92.1(3)	P_1-C_{14}-C_{11}	176.3
P_1-Re-O_2	88.2(3)	P_1-C_{14}-C_{15}	118.9
P_2-Re-O_1	88.4(3)	P_1-C_{24}-C_{23}	116.9
P_2-Re-O_2	93.1(3)	P_1-C_{24}-C_{21}	174.1
O_1-Re-O_2	86.6(4)	P_1-C_{24}-C_{25}	122.9
Re-O_1-C_1	128.2(10)	P_1-C_{34}-C_{33}	119.9
Re-O_2-C_3	128.8(8)	P_1-C_{34}-C_{31}	175.1
O_1-C_1-C_2	126.2(15)	P_1-C_{34}-C_{35}	119.8
O_2-C_3-C_2	123.1(2)	P_2-C_{44}-C_{43}	123.7
O_1-C_1-C_4	113.7(14)	P_2-C_{44}-C_{41}	175.8
O_2-C_3-C_5	110.8(16)	P_2-C_{44}-C_{45}	116.2
C_2-C_1-C_4	120.0(16)	P_2-C_{54}-C_{53}	119.3
C_2-C_3-C_5	126.2(14)	P_2-C_{54}-C_{51}	178.0
Re-P_1-C_{14}	109.7	P_2-C_{54}-C_{55}	120.7
Re-P_1-C_{24}	118.2	P_2-C_{64}-C_{63}	119.7
Re-P_1-C_{34}	120.8	P_2-C_{64}-C_{61}	179.7
		P_2-C_{64}-C_{65}	120.3

TABLE 5.6

COMPARISON OF Re-P BOND DISTANCES

(e.s.d.'s are enclosed in parentheses)

Compound	Bond Lengths (Å)	Ref.
$ReOCl_3(PEt_2Ph)_2$	2.45	9
	2.48	
$ReNCl_2(PEt_2Ph)_3$	2.490(5)	12
	2.442(4)	
	2.469(5)	
$ReNCl_2[P(C_6H_5)_3]_2$	2.448(2)	13
$ReCl_3(NC_6H_4OCH_3).P(Et_2C_6H_5)_2$	2.470(1)	14
$ReCl_3(NC_6H_4COCH_3)P(Et_2C_6H_5)_2$	2.457(4)	14
	2.461(4)	
$ReCl_3(NCH_3)P[C_6H_5)_2Et]_2$	2.482(7)	15
	2.486(7)	
$ReCl_2(acac)[P(C_6H_5)_3]$	2.482(4)	
	2.469(5)	
$ReOCl_2(acac)(C_6H_5)_3$	2.436(4)	

with the value of displacement from the plane of OCCCO are presented in Table 5.7. The dihedral angle between these two planes is 5.7° which is slightly larger than that found in $ReC\ell_2(acac)_2$ (3.1°). Re is displaced from the OCCCO plane by about 0.15 A as are the two methyl carbon atoms, one by about 0.12 A and the other by about 0.16 A. Bond distances of the equivalent sets within this group do not differ by more than 1.5σ in the extreme case. The average values of O-C, C-C (ring) and C-C (non-ring) are 1.30 A, 1.35 A and 1.55 A respectively. The sum of angles around the β-carbon atoms are within 0.1° of 360°, the value required for the planarity which would be expected if only sp^2 hybrid orbitals are used in the formation of the wave functions describing the bonds.

The bond lengths and angles for two triphenylphosphine groups are also normal, the P-C distances and C-P-C angles are within the range that has been observed in a number of complexes of triphenylphosphine. Since the phenyl groups in the present case were treated as a group least squares refinement (Sec. 3.5), the test of the correctness of this approach in addition to P-C distance and C-P-C angles would be the P-C-C (ortho) and P-C-C (para) angles. The ideal value for the former should be 120° which is the necessary condition for the carbon atom bonded to P having sp^2 hybrid bonds. P is expected to be coplanar with the phenyl group, so the value for P-C-C (para) angle should be 180°. As listed in Table 5.5, the agreement for P-C-C (ortho) angles are within 4° and that for P-C-C (para) angles are within 6°, so the use of the group least-squares method of refinement would appear to be justified.

TABLE 5.7

WEIGHTED LEAST SQUARES PLANES OF THE RHENIUM ACETYLACETONATE UNIT IN $ReC\ell_2(acac)[P(C_6H_5)_3]_2$

Equation of Plane of the Form Ax+By+Cz=D

(Orthogonal Coordinate)[†]

Atoms	Plane No.	A	B	C	D
Re, O_1, O_2	1	0.9362	-0.3379	0.0965	1.568
O_1, O_2, C_1, C_2, C_3	2	0.9104	-0.3698	0.1871	1.571

Orthogonal Coordinates and Distances

of Atom from Plane 2 (A)

Atom	x	y	z	Distances from Plane 2
Re	2.302	2.681	3.581	0.154
O_1	3.004	4.432	2.850	0.020
O_2	2.286	2.077	1.468	-0.004
C_1	3.320	4.754	1.537	-0.038
C_2	3.278	3.940	0.372	0.032
C_3	2.749	2.701	0.268	-0.010
C_4	3.858	6.222	1.382	-0.115
C_5	-0.611	1.841	-1.036	-0.157

[†] Defined in Section 3.5

CHAPTER 6

CRYSTAL STRUCTURE OF $ReOC\ell_2(acac)P(C_6H_5)_3$

6.1 Experiments

6.1.1 Preparation

$ReOC\ell_2(acac)P(C_6H_5)_3$ was prepared from $ReOC\ell_2(OEt)[P(C_6H_5)_3]_2$ on various occasions. A purple solution of $ReOC\ell_2(OEt)[P(C_6H_5)_3]_2$ (2 g) and acetylacetone (2 ml.) in benzene (50 ml.) was boiled until it turned bright green (about 1 min.) and then poured into light petroleum ether (b.p. 40-60°, 400 ml.). The mixture was stirred vigorously and the precipitate allowed to settle. If the supernatant liquid was still appreciably green, it was decanted and set aside, green crystals of the compound separating; these were hand-picked from some orange material. The chemical analysis was as follows: Found: C, 43.1%, H, 4.2%, P, 5.0% and Cℓ, 11.3%. $C_{23}H_{22}C\ell_2O_3PRe$ requires C, 43.5%; H, 3.5%; P, 4.8% and Cℓ, 11.1%.

6.1.2 Crystallization

Appropriate single crystals were obtained by the method described in Sec. 4.1. The compound was crystallized from the mixture of methylene chloride and petroleum ether (80-100°C). Crystals obtained from this solvent mixture were usually twinned or fern-like with small crystals grouped around the main axis. If the temperature of crystallization was maintained constant at about 0°C, non-twinned plate-like crystals were obtained suitable for x-ray diffraction purpose.

6.1.3 X-ray Studies

Two crystals were cut from a large crystal chosen because it had sharp extinctions and optical homogenity when examined through a polarizing microscope. Crystal I with the dimensions 0.09 x 0.10 x 0.12 mm^3 was mounted along its longest dimension which turn out to parallel c*. Intensity data of layers h= 0, 1, 2, 3, 4 and k = 0, 1, 2, 3 were recorded for this crystal. Crystal II with the dimensions 0.09 x 0.14 x 0.11 mm^3 was mounted along its longest dimension parallel to b*. Intensity data of the layer hk0 were recorded from this crystal. All the above intensity data were recorded photographically by the integrating precession method. MoKα (λ = 0.71069 A) radiation and a Zr filter were used for all intensity data recorded. Each layer was photographed three times using exposures of 2, 6 and 18 integrating cycles (1 cycle takes 144 minutes). The intensities of all reflections were measured with a Joyce-Loebl microdensitometer. The unobserved reflections were assigned an intensity equal to the minimum observed intensity in that region of reciprocal space. Standard errors were assigned in the way described in Section 4.1. The measured intensities were corrected for Lorentz and polarization effects. Absorption corrections were not applied since the transmission factors vary from 1.5 to 1.8 and therefore the extreme error of 10% would be introduced. Of course, the average error would be substantially lower.

Accurate cell parameters were determined from 0kℓ and hk0 precession photographs which were calibrated with a diffraction pattern of TiO_2 (rutile) single crystal (a = 4.5929(5) and c = 2.9593 A (217)) and the β-angle was measured from the spindle reading. The density was determined by the flotation method using a solvent mixture of tetrabromoethane and carbon tetrachloride. The measured value was 1.75 ± 0.04 $g.cm^{-3}$ and using the lattice parameters in Table 6.1 we conclude that there are two molecules in the primitive cell. The crystal was found to have triclinic symmetry with no extinction condition. In the initial stages, the centro-symmetric group $P\bar{1}$ was assumed and this was confirmed later as described in the next section. The crystal data are listed in Table 6.1.

6.2 Solution and Refinements

The Patterson function projected on (100) and (010) planes showed large peaks attributable to Re-Re vectors and three rhenium-ligand vectors (two chlorines and one phosphorous). Based on the coordinates of Re and three Cℓ atoms (the phosphorous atom was initially treated as a chlorine atom), the structure factors of $h0\ell$ and $0k\ell$ reflections were calculated, giving $R_1 = 0.34$ and $R_2 = 0.38$. The parameters of scale and isotropic temperature factors were obtained from a Wilson plot (227). In all calculations of F_c, the atomic scattering factors tabulated in the International Tables (221) were used for Cℓ , P, O and C, and those of Cromer and Waber used for Re (222). The effects of anomalous dispersion were included in F_c; the value of f' and f" for Re, Cℓ and P were those given by Cromer (223). Fourier electron density and difference syntheses of (100) and (010) did not disclose the positions of oxygen or carbon atoms. The three dimensional intensity data from different layers were scaled based on these atomic parameters, and a three-dimensional Patterson function was calculated. Peaks corresponding to three rhenium ion-oxygen atom vectors were found. The peak heights corresponding to Re-Cℓ and/or Re-P showed the predicted peak heights for $P\bar{1}$ symmetry without any splitting as might be expected if the space group

TABLE 6.1

CRYSTAL DATA FOR $ReOCl_2(acac)P(C_6H_5)_3$

(e.s.d.'s are enclosed in parentheses)

Parameter	Units	Value
$\underline{a}$	Å	11.023(8)
$\underline{b}$	Å	9.360(7)
$\underline{c}$	Å	13.817(8)
α	°	71.2(1)
β	°	64.1(2)
γ	°	65.9(1)
Vol	$Å^3$	1158
$\underline{M}$		634.54
D_{meas}	$g-cm^{-3}$	1.76(4)
D_{calc}	$g-cm^{-3}$	1.82
Z		2
μ(MoKα)	cm^{-1}	57.55

Systematic absences	None
Space Group	$P\bar{1}$ (No. 2 C_i^1)

were P1 but nearly P$\bar{1}$, supporting the choice of centro-symmetric space group P$\bar{1}$. Structure factors of Okℓ and hOℓ data were calculated, and successive Fourier difference synthesis showed positions of five carbon atoms of the acetylacetonate group and the anisotropic thermal motion of the Re. One cycle of full matrix least squares refinement of all known positional and thermal (anisotropic for Re only) parameters of the three dimensional data brought R_1 to 0.24 and R_2 to 0.26. The scale factors were adjusted before this major cycle refinement. Successive three dimensional Fourier difference syntheses located all eighteen phenyl carbon atoms and the P was assigned from the proximity of carbon atoms of the phenyl groups. At this stage, $R_1 = 0.17$ and $R_2 = 0.21$. The least squares refinement was then carried out by the special method described in Section 3.5. The three Eulerian angles of each phenyl group were calculated from the inverse matrix listed in Table 3.1 and (3.27). These values were averaged in case the geometry was different from D_{6h} symmetry. One cycle of full matrix least squares refinement of all scale and atomic parameters, positional and thermal (anisotropic for Re only), brought R_1 down to 0.13 and R_2 to 0.15. Three successive cycles of refinement dropped R_1 to 0.089 and R_2 to 0.084. Unobserved reflection were given zero weight in the refinement if $F_c < F_{min}$ and ligand atoms (i.e. non-carbon and non-hydrogen atoms) were given anisotropic temperature factors. No attempt was made to locate hydrogen atom positions. The refinement was terminated at $R_1 = 0.082$ and $R_2 = 0.070$ for 2759 non-equivalent reflections, the magnitudes of parameter shifts were small, all parameters were shifted about 0.12σ or less. A three dimensional Fourier difference synthesis did not reveal any peaks higher than 1.4 e/Å^3.

The positional, thermal and group parameters derived from the last cycle of least squares refinement are presented in Table 6.2 along with the corresponding standard deviations of these parameters as derived from the inverse matrix. The corresponding positional parameters of the group carbon atoms are presented in Table 6.3. The final values of 10 F_o and 10 F_c (in electrons) are given in Table 6.4.

6.3 Result and Discussion

Figure 6.1 shows one complete molecule and Figure 6.2 shows the crystal packing projected down the b axis. Principal intramolecular distances and angles and their estimated standard deviations are given in Table 6.5. The intermolecular distances appear to be normal, the shortest ones are about 3.4 A ($C\ell_2 \ldots C'_1$, 3.38 A and $O_3 \ldots C'_4$ and $O_3 \ldots C'_5$ are both 3.40 A) which are fairly close to the sum of the van der Waals radii of atoms and groups (methyl and aromatic carbon) (134).

The configuration of the molecule can be seen in Figure 6.1, this corresponds to the isomer B-I shown in Figure 1.1 in which the Cℓ-Re-Cℓ is close to linear. The molecule is closely related to the starting material $ReOC\ell_2(OEt)[P(C_6H_5)_3]_2$ where the Cℓ-Re-Cℓ group is also linear. If an OEt group is replaced by one carbonyl oxygen and one of two P atoms by another carbonyl oxygen, we would obtain the configuration of the present compound.

The two Re-Cℓ distances of 2.337(3) Å and 2.373(4) Å are approximately the same as those found in $ReC\ell_2(acac)_2$ (2.33(1) Å) and $ReC\ell_2(acac)\cdot[P(C_6H_6)_3]_2$ (2.37(1) Å) and in fair agreement with values found for other rhenium compounds mentioned in the last chapter but consistently shorter

TABLE 6.2

POSITIONAL, THERMAL AND RIGID GROUP PARAMETERS FOR $ReOCl_2(acac)P(C_6H_5)_3$ (e.s.d.'s are enclosed in parentheses)

	Positional			Thermal (isotropic)
Atom	x	y	z	B (Å^2)
Re	0.19882(6)	0.25742(7)	0.16857(4)	-
Cl_1	-0.0322(4)	0.2665(6)	0.2923(3)	-
Cl_2	0.4132(4)	0.2070(4)	0.0245(2)	-
P	0.3240(4)	0.1463(4)	0.2984(2)	-
O_1	0.2179(9)	0.0220(11)	0.1799(6)	-
O_2	0.1132(10)	0.2922(12)	0.0579(8)	-
O_3	0.1938(9)	0.4369(11)	0.1770(7)	-
C_1	0.7772(18)	0.0508(19)	0.8876(13)	5.1(3)
C_2	0.1766(17)	0.0393(18)	0.0289(11)	4.9(3)
C_3	0.1311(17)	0.1916(19)	0.0057(12)	5.0(3)
C_4	0.7481(20)	0.2248(19)	0.8552(13)	5.7(4)
C_5	0.0739(18)	0.2808(19)	0.9061(13)	5.9(4)

TABLE 6.2 (continued)

Thermal (anisotropic), $(\mathring{A}^2) \times 10^4$

Atom	U_{11}[†]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	456(4)	489(4)	424(3)	-55(1)	75(1)	-78(1)
$C\ell_1$	485(21)	1310(40)	718(25)	-152(13)	-59(9)	-204(13)
$C\ell_2$	527(20)	585(16)	396(16)	-99(9)	-29(8)	-54(7)
P	401(18)	435(18)	358(16)	-51(9)	-48(7)	-57(7)
O_1	468(55)	644(57)	268(41)	-156(26)	11(19)	-52(19)
O_2	529(60)	673(63)	768(67)	-58(29)	-130(26)	-170(26)
O_3	410(54)	566(54)	501(51)	-84(24)	-86(21)	-100(20)

[†] These values were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where β_{ij}'s appear as a temperature effect through $\exp[-(\beta_{11}h^2+2\beta_{12}hk+\ldots)]$ in the structure factor expression and b_i are the reciprocal lattice vectors.

TABLE 6.2 (continued)

	$x_c^{\dagger}$	y_c	z_c	ϕ	θ	ψ	B ($\mathring{A}^2$)
R_1	0.6131(8)	0.2258(8)	0.2138(5)	151.8(5)	223.9(4)	191.2(5)	5.1(1)
R_2	0.5764(7)	0.2350(8)	0.6517(5)	10.5(3)	249.8(4)	116.5(5)	5.3(1)
R_3	0.1502(9)	0.2725(9)	0.5264(6)	95.6(5)	121.2(4)	219.4(5)	6.7(2)

$\dagger$ x_c, y_c and z_c are the fractional coordinates of the ring centers, ϕ, θ and ψ (in degrees) are three Eulerian angles were defined in Section 3.5. The rings are numbered so that C_{i4}(i=1, 2 and 3) is attached to P; C_{i1} is para to C_{i4}

TABLE 6.3

DERIVED POSITIONAL PARAMETERS FOR CARBON ATOMS IN RIGID GROUP

R_1	x	y	z
C_{11}	0.7399[†]	0.2577	0.1767
C_{12}	0.7204	0.1237	0.2552
C_{13}	0.5936	0.0918	0.2922
C_{14}	0.4863	0.1939	0.2509
C_{15}	0.5058	0.3279	0.1725
C_{16}	0.6326	0.3598	0.1354
R_2			
C_{21}	0.5321	0.4006	0.6323
C_{22}	0.6403	0.3180	0.5516
C_{23}	0.6846	0.1524	0.5709
C_{24}	0.6208	0.0694	0.6711
C_{25}	0.5125	0.1520	0.7518
C_{26}	0.4682	0.3175	0.7325
R_3			
C_{31}	0.0728	0.3322	0.6227
C_{32}	0.2111	0.3347	0.5664
C_{33}	0.2885	0.2750	0.4701
C_{34}	0.2276	0.2128	0.4301
C_{35}	0.0893	0.2103	0.4864
C_{36}	0.0119	0.2700	0.5828

[†] These are fractional coordinates obtained with the restriction that C-C bonded distances are C-C=1.392 Å; the error of the coordinates was not estimated, however, it could be derived from errors given in group parameters listed on the preceeding page.

TABLE 6.4.1

OBSERVED AND CALCULATED STRUCTURE FACTORS (x 10)

UNRELIABLE REFLECTIONS ARE MARKED WITH THE SYMBOL (X).

H	K	|FOBS|	FCALC
L = 0			
0	4	1035	1073
[illegible]	[illegible]	[illegible]	[illegible]

TABLE 6.4.1
(continued)

[illegible]

TABLE 6.4.2

UNOBSERVED AND CALCULATED STRUCTURE FACTORS (x 10)

		|FOBS|	FCALC
H	K		L = 0
0	3	54	142
1	8	81	-45
2	7	77	55
2	9	82	-47
3	8	80	-46
3	10	81	46
4	-8	81	53
4	-6	81	-120
5	-7	82	41
5	-5	79	-53
5	5	69	61
5	7	77	-101
5	9	82	6
6	-4	79	33
6	2	63	-110
6	4	68	63
6	6	75	20
6	8	81	30
7	3	70	-47
9	-4	82	17
9	-2	82	-36
9	2	79	-130
9	4	79	100
9	6	81	-78
10	-3	81	36
10	-1	83	37
10	1	83	-23
10	3	82	-61
10	5	83	73
10	7	83	31
11	0	84	5
11	2	84	17
11	6	84	-77
12	1	82	-30
K	L		H = 0
1	-9	105	-14
1	-6	90	16
1	-3	66	-93
1	6	86	-3
1	12	113	-109
3	-5	97	-52
7	-6	113	90
7	2	104	103
8	-5	115	-16
8	1	111	-17
9	3	115	147
9	6	116	-38
9	8	116	-132
10	1	117	4
10	4	117	26
10	5	115	-150
10	-1	115	-112
10	-2	114	71
K	L		H = 1
-10	-2	114	-55
-10	1	114	62
-10	2	114	113
-9	-5	111	176

		|FOBS|	FCALC
-9	-4	110	24
-9	-1	110	-143
-9	4	113	-160
-9	5	113	-41
-8	-8	110	-8
-8	3	107	-115
-8	4	109	113
-7	-4	98	-10
-7	5	106	118
-6	-8	103	43
-6	7	106	64
-6	9	110	123
-6	10	112	-147
-5	-10	104	46
-5	8	105	-62
-4	-8	97	41
-4	6	93	72
-3	-10	104	-101
-3	-7	91	72
-3	8	94	71
-3	11	109	-23
-1	11	106	23
0	12	109	46
1	-10	106	-94
2	-9	103	126
2	12	107	58
3	-10	108	-58
3	8	89	-7
4	-9	107	34
4	12	107	-156
5	-7	103	5
5	8	93	71
7	10	106	-125
8	-5	109	-131
8	-3	105	-6
8	3	97	64
8	6	102	-130
8	9	107	92
9	6	106	143
10	0	112	-6
10	2	111	147
10	3	111	-104
K	L		H = 2
-9	-8	123	32
-9	-2	117	25
-9	2	119	-123
-9	5	122	161
-9	3	120	-120
-8	-10	122	-138
-8	4	122	6
-8	-6	115	-133
-8	2	112	-40
-8	3	114	179
-8	5	118	140
-8	6	120	-132
-7	-5	107	40
-7	-2	107	86
-7	4	109	-102
-7	7	117	-12
-6	5	105	-80
-5	-11	117	-136
-5	-8	108	-85
-5	7	107	-158

		|FOBS|	FCALC
-4	-10	114	-100
-4	-4	85	-93
-4	2	78	-106
-4	5	91	-49
-3	-8	103	119
-2	-10	113	89
-2	8	97	-47
-2	11	113	-146
-1	-15	125	-113
-1	-8	102	72
-1	13	120	-169
0	-4	68	-172
0	11	109	114
1	-8	104	-151
2	-10	116	92
2	-7	100	9
4	-4	88	65
4	-1	69	-164
4	3	89	175
5	-3	89	157
5	6	92	-17
5	12	113	-30
6	-4	101	14
6	8	97	-33
7	-3	104	-54
8	-12	117	-65
8	-3	122	69
8	-4	113	-14
8	11	116	-101
9	-5	120	35
9	-3	116	90
9	0	110	-37
9	3	107	132
9	6	109	40
9	9	115	73
10	-4	122	-20
10	-3	121	-115
10	-1	114	105
10	2	113	-59
10	4	115	-164
10	5	115	82
10	8	118	-112
K	L		H = 3
-9	-5	127	-169
-9	-3	125	48
-9	-2	124	210
-9	-1	126	94
-9	0	124	-84
-9	1	125	-149
-9	2	126	-168
-9	3	127	-10
-9	4	124	138
-8	-5	121	-148
-8	-2	116	81
-8	4	122	88
-8	6	124	-165
-7	-9	127	-51
-7	-6	117	43
-7	5	111	-5
-7	6	120	71
-7	8	126	120
-6	-8	119	-50
-6	4	104	-93

		|FOBS|	FCALC
-6	7	117	74
-5	-3	94	73
-4	-11	127	-1
-4	-8	112	155
-4	-5	96	-97
-4	-2	83	8
-4	1	79	-97
-4	10	119	-65
-3	-6	97	14
-3	9	109	-41
-2	-11	126	-48
-2	-8	108	-12
-2	-5	86	111
-2	10	111	-53
-1	-6	92	-2
0	-11	125	-66
0	-9	108	-101
0	10	102	-103
0	13	122	81
2	-8	112	25
4	-8	118	20
4	-2	72	21
4	13	119	136
5	-7	116	-142
5	8	89	61
7	-4	111	-42
7	-1	97	-106
7	2	89	-115
7	5	90	18
7	8	100	-55
8	-5	121	80
8	-3	113	135
8	0	102	-46
8	4	97	-143
8	6	101	-35
8	9	116	172
8	10	114	-77
9	-3	120	-168
9	2	108	95
9	5	107	-25
9	8	113	23
9	11	127	-65
K	L		H = 4
-8	-3	139	90
-8	-5	144	174
-8	-2	138	-190
-8	-1	137	-177
-8	1	137	191
-8	0	137	53
-8	4	143	-153
-8	5	145	-154
-8	6	148	15
-7	-1	127	175
-7	-4	143	-16
-7	5	136	73
-6	-3	121	-97
-6	0	116	-120
-6	-9	147	-30
-6	-6	133	-80
-6	3	120	-88
-6	6	131	-21
-5	-8	138	144
-5	-4	116	93

		|FOBS|	FCALC
-5	7	127	-121
-4	-9	141	63
-4	-6	121	140
-4	-3	103	-43
-4	6	111	76
-4	9	131	-118
-3	4	86	-47
-3	10	131	30
-2	-6	111	-17
-2	6	84	-79
-2	9	115	126
-1	10	117	86
1	10	105	8
1	13	136	-16
2	-7	121	106
2	-6	110	-85
3	-8	134	32
3	-5	103	140
3	10	102	-79
4	-9	145	-56
5	-5	119	-94
5	7	80	44
6	-4	119	-37
7	-2	115	-37
7	1	100	64
7	4	96	-16
7	7	103	78
8	-9	158	-43
8	-8	155	-100
8	-7	151	-49
8	-6	146	127
8	-1	120	-133
8	2	109	132
8	5	108	-35
8	8	117	34
9	-2	134	41
9	1	123	-40
9	4	118	-4
10	-3	146	95
10	-1	139	29
10	2	131	-135
10	3	130	157
10	5	129	101
10	8	134	-22
H	L		K = 0
1	12	90	46
2	-7	80	70
2	5	61	54
3	1	48	-45
5	-2	72	-154
7	-7	91	88
7	-4	87	-34
7	2	76	76
7	8	82	30
8	-2	87	74
8	4	82	-43
8	7	84	16
9	-6	90	54
9	3	87	-157
9	6	87	74
10	-4	90	-41
10	7	91	139
11	6	93	6

		|FOBS|	FCALC
12	2	92	-45
11	1	93	-156
12	1	91	-113
H	L		K = 1
-11	-8	138	-67
-11	-7	135	98
-11	-5	137	56
-11	-2	138	55
-11	-1	139	141
-11	2	140	-132
-10	-12	139	-19
-10	3	139	49
-10	5	139	134
-9	-7	127	-85
-9	-4	124	145
-9	4	137	60
-9	5	128	-85
-8	-12	136	-110
-8	-11	133	83
-8	-8	124	-99
-8	-2	117	-13
-8	3	129	125
-8	4	132	-152
-8	5	135	-151
-8	6	137	-81
-8	10	134	-96
-8	11	127	-87
-7	-13	136	-38
-7	-7	116	-100
-7	-6	109	167
-7	5	130	-133
-6	-14	138	-43
-6	-11	129	96
-6	-8	116	-97
-6	-5	103	149
-6	7	132	5
-5	-9	118	170
-5	-6	102	9
-5	6	123	-175
-4	-10	123	46
-2	8	120	72
-2	11	135	-146
-1	10	128	197
-1	13	139	75
0	6	96	-3
1	-10	130	-94
2	-4	85	11
4	-8	129	-133
4	10	118	8
5	13	133	-16
8	9	117	-137
8	6	111	140
9	11	127	2
9	-5	137	7
9	-2	124	-117
9	1	121	95
9	7	119	175
9	10	127	102
10	-6	139	-1
10	-3	137	-14
10	0	130	-23
10	9	120	11

		|FOBS|	FCALC
H	L		K = 2
-10	-2	138	8
-10	1	142	-80
-10	2	145	54
-10	4	149	38
-9	-12	166	-65
-9	-9	138	25
-9	-6	131	-46
-9	-3	129	-44
-9	0	133	-35
-9	3	141	-31
-9	5	146	-130
-8	-10	137	48
-8	-7	127	-65
-8	-4	121	-119
-8	-1	122	-51
-8	2	130	-40
-8	5	141	42
-7	-11	138	-75
-7	-8	125	-23
-7	-2	112	36
-6	2	113	-43
-5	1	99	20
-4	-6	107	-79
-4	3	99	91
-4	6	120	-17
-3	-10	129	-63
-3	8	127	-12
-3	2	81	-115
-2	-11	136	-146
-2	-8	115	-47
-2	10	135	89
-1	-6	97	-96
0	10	127	142
1	12	137	58
2	-10	139	92
2	-7	118	9
2	-4	85	-171
3	-8	130	25
3	13	138	-5
4	-7	128	106
5	-6	121	-85
5	-2	96	184
6	0	93	-110
6	12	130	39
7	-4	126	129
7	-1	109	22
7	8	107	-157
7	11	125	-34
8	-2	123	-111
8	7	109	-80
9	-3	135	36
9	0	122	-130
9	6	113	1
9	11	130	76
10	-4	144	60
10	-3	141	114
10	-2	137	112
10	-1	134	-152
10	4	121	59
11	0	138	17
11	4	130	-95
11	6	129	-28
11	9	133	45

		|FOBS|	FCALC
12	0	145	158
12	1	143	106
12	2	141	9
12	7	137	187
H	L		K = 3
-9	-10	130	-103
-9	-7	122	52
-9	-4	118	-85
-9	-2	118	-146
-9	-1	119	161
-9	2	126	-67
-8	5	122	42
-7	-10	123	-80
-7	-9	119	83
-7	-7	111	66
-7	-4	103	24
-7	2	110	-54
-6	-8	111	127
-6	-5	98	98
-6	1	98	67
-6	4	110	47
-5	-9	113	21
-5	-6	97	161
-5	-3	86	-45
-5	6	113	21
-4	-10	118	30
-4	-4	81	-42
-3	-9	111	-41
-3	0	60	-18
-3	6	97	14
-1	-8	103	71
-1	-5	70	-31
-1	7	87	72
-1	10	115	-101
0	-6	84	-52
0	9	100	-120
1	8	87	-7
5	-6	112	-75
5	-3	87	-88
5	9	87	37
6	2	65	-1
6	11	105	67
7	6	79	50
7	10	100	89
8	-4	118	-99
8	2	89	-11
8	11	109	96
9	-5	129	36
9	-2	115	-4
9	1	101	-55
9	4	95	-53
10	-4	130	73
10	-3	126	-79
10	-2	122	-95
10	0	114	-61
10	5	102	-76
10	6	102	42
10	9	108	0
11	-1	125	86
11	2	115	-67

Figure 6.1

The $ReOCl_2(acac)P(C_6H_5)_3$ Molecule

The numbering of the atoms corresponds to that in Tables 6.2, 6.3, 6.5 and 6.7.

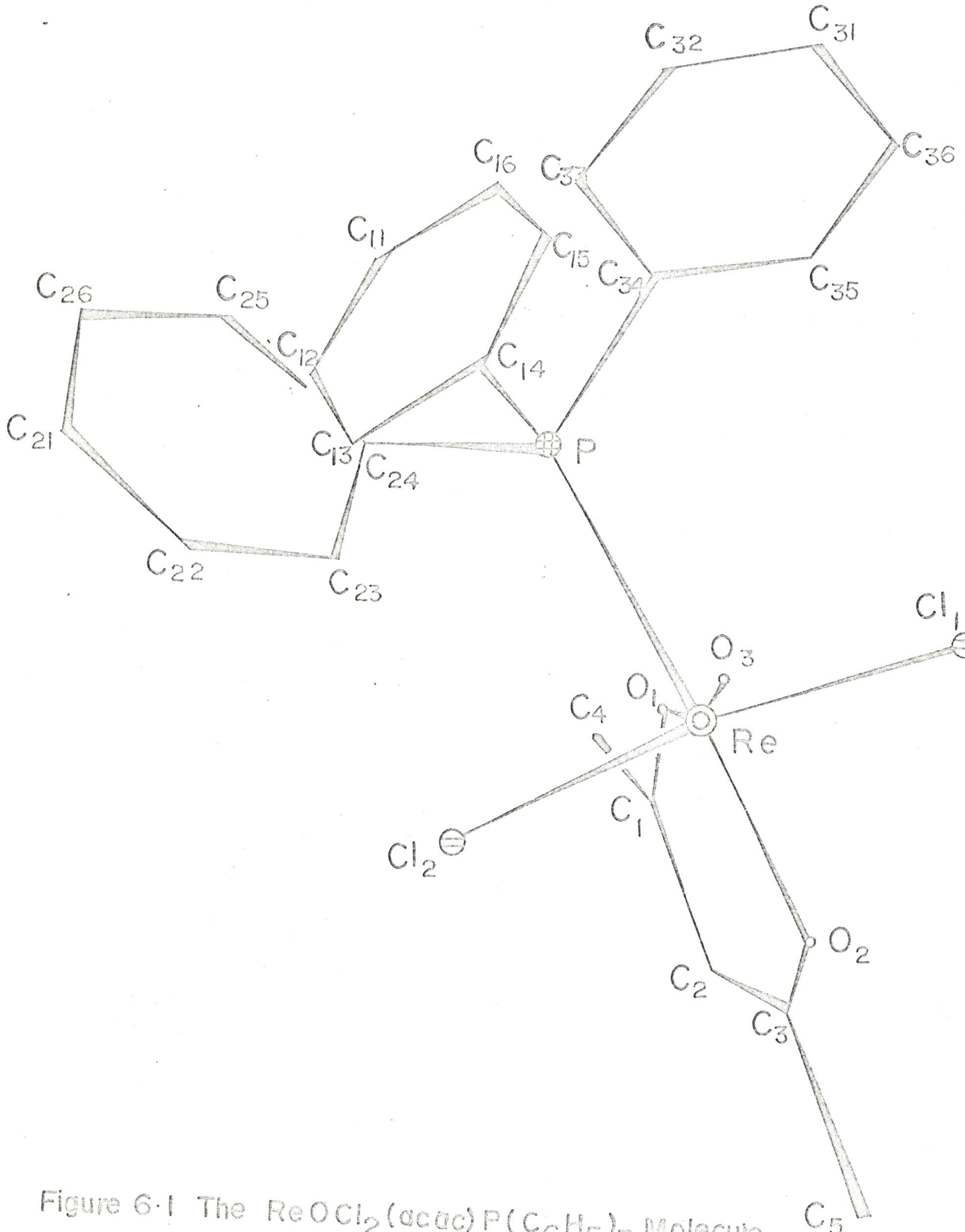

Figure 6·1 The $ReOCl_2(acac)P(C_6H_5)_3$ Molecule

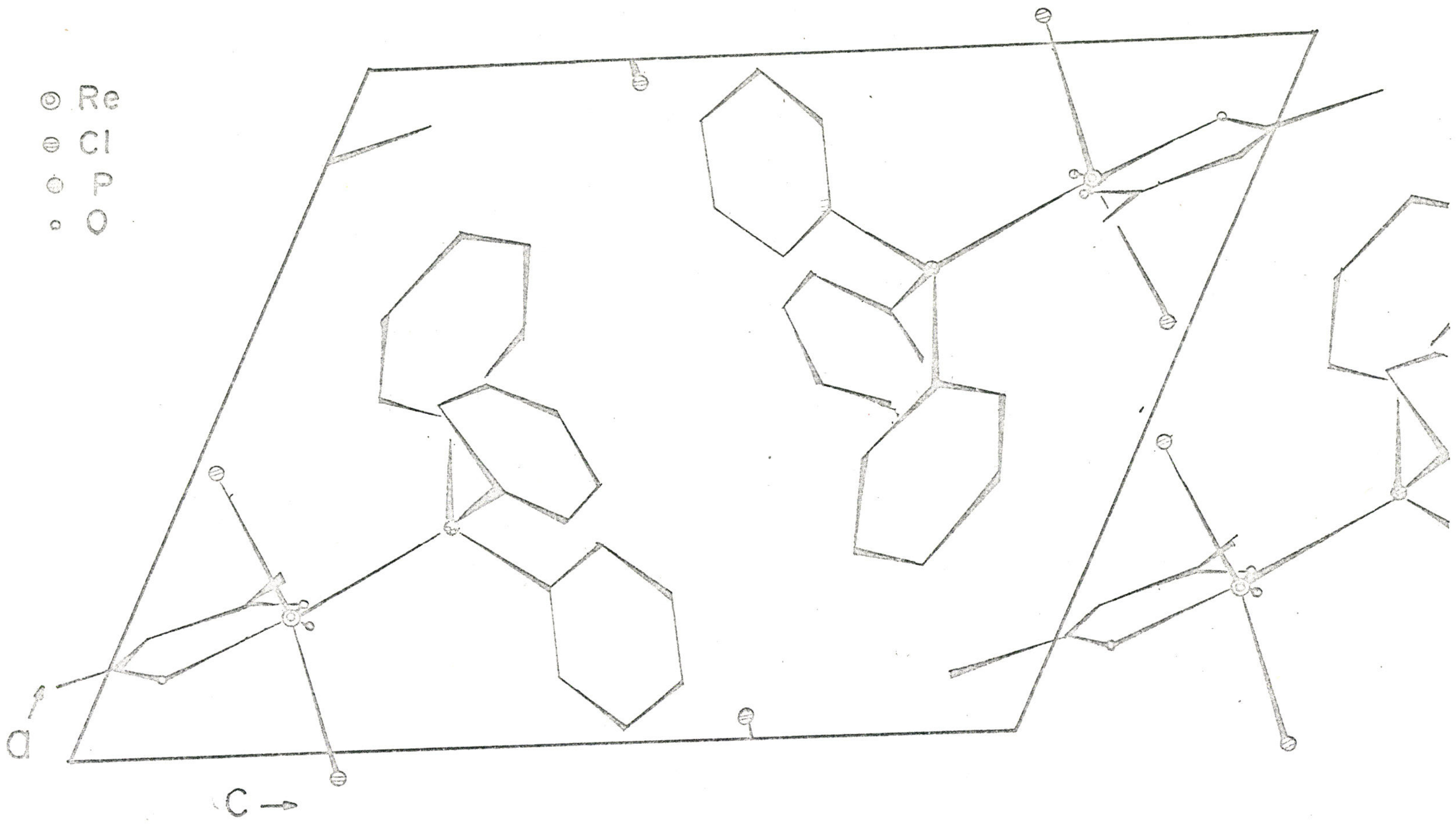

Figure 6.2

Structure of $ReOCl_2(acac)P(C_6H_5)_3$ projected down [100]

TABLE 6.5

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES IN $ReOCl_2(acac)P(C_6H_5)_3$

(e.s.d.'s are enclosed in parentheses)

A. Bonded Distance (Å)

$Re-Cl_1$	2.373(4)	C_1-C_2	1.250(24)
$Re-Cl_2$	2.337(3)	C_2-C_3	1.283(21)
Re-P	2.436(4)	C_1-C_4	1.470(22)
$Re-O_1$	2.086(11)	C_3-C_5	1.599(26)
$Re-O_2$	1.998(13)	$P-C_{14}$	1.815†
$Re-O_3$	1.698(12)	$P-C_{24}$	1.814
O_1-C_1	1.294(25)	$P-C_{34}$	1.836
O_2-C_3	1.268(25)		

B. Non-bonded Distances (Å)

Cl_1-P	3.648(6)	Cl_2-O_2	2.928(12)
Cl_1-O_1	2.959(9)	Cl_2-O_3	3.044(9)
Cl_1-O_2	2.918(10)	$P-O_1$	3.062(13)
Cl_1-O_3	3.048(12)	$P-O_3$	2.861(9)
Cl_2-P	3.393(4)	O_1-O_2	2.663(12)
Cl_2-O_1	2.992(10)	O_2-O_3	3.000(20)

† The error of P-C band distances is estimated to be less than 0.02 Å, and that of, the Re-P-C, C-P-C and P-C-C angles listed on the following page are less than 1.5°

TABLE 6.5 (continued)

Angles (°)

Cl_1-Re-Cl_2	163.9(3)	O_1-C_1-C_4	114.5(15)
Cl_1-Re-P	98.7(2)	C_2-C_1-C_4	127.4(22)
Cl_1-Re-O_1	82.9(3)	O_2-C_3-C_5	110.0(10)
Cl_1-Re-O_2	83.3(4)	C_2-C_3-C_5	121.4(22)
Cl_1-Re-O_3	97.1(4)	Re-P-C_{14}	113.7
Cl_2-Re-P	90.6(1)	Re-P-C_{24}	112.7
Cl_2-Re-O_1	84.9(2)	Re-P-C_{34}	116.0
Cl_2-Re-O_2	84.6(3)	C_{14}-P-C_{24}	104.2
Cl_2-Re-O_3	96.6(3)	C_{14}-P-C_{34}	103.0
P-Re-O_1	84.9(3)	C_{24}-P-C_{34}	106.2
P-Re-O_2	165.7(1)	P-C_{14}-C_{11}	178.2
P-Re-O_3	85.6(4)	P-C_{14}-C_{13}	118.8
O_1-Re-O_2	81.4(3)	P-C_{14}-C_{15}	121.2
O_1-Re-O_3	170.4(10)	P-C_{24}-C_{21}	177.9
O_2-Re-O_3	108.2(5)	P-C_{24}-C_{23}	121.9
Re-O_1-C_1	132.1(5)	P-C_{24}-C_{25}	118.1
Re-O_2-C_3	127.6(13)	P-C_{34}-C_{31}	176.3
O_1-C_1-C_2	117.6(10)	P-C_{34}-C_{33}	120.5
O_2-C_3-C_2	128.4(15)	P-C_{34}-C_{35}	119.4
C_1-C_2-C_3	127.5(22)		

than other Re(V)-Cℓ distances listed in Table 6.6. The Re-P length, 2.436(4) A is in fair agreement with the 2.469(5) A found in $ReC\ell_2(acac)\cdot[P(C_6H_5)_3]_2$ and other Re complexes containing phosphines as ligands. The references are cited in Chapter 5. The metal-carbonyl oxygen distances (2.086(11) A and 1.998(13) A) appeared to be significantly different. The lower value shown by the oxygen cis to the oxo group is in fair agreement with those found in $ReC\ell_2(acac)_2$ (1.97(1) and 2.01(1) Å) and $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ (2.00(1) A and 2.04(1) A) but the Re-O distance (2.09(1) A) for the oxygen trans to the oxo group is longer than any listed above and as the magnitude of difference of the two Re-O bonds is more than 7σ (σ = 0.012 A) appears to be significant. The longer M-O bond which is trans to the oxo group would be the result of the strong Re-O (oxo) bonding where π-bonding exists, and which is postulated to weaken the trans Re-ligand bond (3,4). The same effect is observed in some other Re(V) complexes containing oxo (9-11) and nitrido (12-15) ligands. The Re-O (oxo) bond length is 1.698(12)Å which, allowing for the large errors involved, the standard deviation agrees well with the value 1.60(5)Å found in $ReOC\ell_3\cdot(PEt_2C_6H_5)_2$ (9) and 1.73(6)Å found in $(C_6H_5)_4As\cdot(ReBr_4O(CH_3CN)$ (11) and $(C_2H_5)_4N(ReBr_4O(H_2O))$ (10). The short Re-O(oxo) bond length, the Re out of the equatorial plane by 0.02 A,and the longer M-ligand bond trans to the oxo group are features in good agreement of observations noted for other Re(V)-oxo complex as well as $ReNC\ell_2[PEt_2C_6H_5]_3$ and appears to be the result of strong π-bonding between the metal and the oxo oxygen.

---

* The error is about 0.04 - 0.06Å as estimated in reference (12).

TABLE 6.6

Re(V)-Cℓ BONDED DISTANCES (e.s.d.'s are enclosed in parentheses)

Compound	Bond Lengths (Å)	Ref.
$\mathrm{ReOC\ell_2(acac)P(C_6H_5)_3}$	2.373(4)	
	2.337(3)	
$\mathrm{ReOC\ell_3(P(C_2H_5)_2C_6H_5)_2}$	2.47*	9
	2.41	
	2.43	
$\mathrm{ReNC\ell_2(P(C_2H_5)_2C_6H_5)_3}$	2.45	12
	2.56*	
$\mathrm{ReC\ell_3(NC_6H_4OCH_3)(P(C_2H_5)_2C_6H_5)_2}$	2.43*	14
	2.42	
$\mathrm{ReC\ell_3(NC_6H_4COCH_3)(P(C_2H_5)_2C_6H_5)_2}$	2.41*	14
	2.40	
	2.43	
$\mathrm{ReC\ell_3(NCH_3)(P(C_6H_5)_2(2H_5))_2}$	2.41*	15
	2.41	
	2.43	

* At the position trans to O or N.

The β-diketone group is slightly different from that in $ReC\ell_2$·(acac)$_2$ and $ReC\ell_2$(acac)[$P(C_6H_5)_3$]$_2$ not only in the non-equivalence of the metal-carbonyl oxygen bonds but that the OReO angle of 81.4° is the smallest among these three structures. The cause appears to be the short Re ... oxo bond; thus the cis carbonyl oxygen is pushed down away from the equatorial plane to lengthen the interatomic distance between the oxo and cis carbonyl oxygen. Therefore, this carbonyl oxygen is twisted slightly from the "normal" poistion towards the other carbonyl oxygen. This effect would decrease the OMO angle as well as the O ... O distance. The strain cannot be relieved by the movement of O_3 (oxo) since this is already constrained by non-bonded interactions with other ligands.

Equation of the best weighted least squares planes of the OReO and the OCCCO, together with the orthogonal coordinates and the distances of displacement from the OCCCO plane of the Re-AcAc unit are listed in Table 6.7. The dihedral angle between two planes is 17.1° which is much larger than that found in $ReC\ell_2$(acac)$_2$ (35°) and $ReC\ell_2$(acac)[$P(C_6H_5)_3$]$_2$ (5.9°) and close to the value 17° observed in VO(acac)$_2$ (192) and 17.7° in VO(Phacac)$_2$ (196). The two vanadyl β-diketonates are chemically closely related to the present compound in the sense all contain oxo- and β-diketone groups, so some similarity would be expected between them. The two methyl groups may be considered as coplanar with the OCCCO plane since the magnitude of displacement from this plane is quite small (0.008A and 0.019A), less than twice the displacement of the number of atoms contained in the plane. As a result of the larger dihedral angle compared with the other two rhenium acetylacetonates in the series, the metal atom is 0.45 A out

TABLE 6.7

BEST WEIGHTED LEAST SQUARES PLANES OF THE RHENIUM ACETYLACETONATE UNIT IN $ReOCl_2(acac)P(C_6H_5)_3$

Equation of Plane of the Form Ax+By+Cz=D

(Orthogonal Coordinate)[†]

Atom	Plane No.	A	B	C	D
Re, O_1, O_2	1	0.7017	0.0343	-0.3116	0.5832
O_1, O_2, C_1, C_2, C_3	2	0.7854	0.2727	-0.5556	1.662

Orthogonal Coordinates and Distances

of Atom from Plane 2 (A)

Atom	x	y	z	Distances from Plane 2
Re	2.749	4.056	2.074	0.4518
O_1	2.992	1.998	2.213	0.0010
O_2	1.396	3.486	0.712	-0.0059
C_1	2.741	1.028	1.382	0.0035
C_2	1.905	1.291	0.355	-0.0105
C_3	1.344	2.409	0.070	0.0120
C_4	3.280	-2.801	1.781	-0.0077
C_5	0.326	2.542	-1.155	0.0189

[†] Defined in Section 3.5

of the plane which is much larger than the 0.08Å found in $ReC\ell_2(acac)_2$ and 0.15Å in $ReC\ell_2(acac)\ [P(C_6H_5)_3]_2$. As has been mentioned, the two C-C (ring) bonds should be considered as equivalent since the difference of 0.036A is less than 2σ (σ = 0.025A). The two C-C (non-ring) bonds (1.470(22)A and 1.599(26)A) thought differing by 0.12Å (5σ), are still in the range of bond lengths of this type of bond found in metal-β-diketone complexes. Consider the range of the C-C (non-ring) bond lengths found in $Y(acac)_3 \cdot 3H_2O$ (193) as an example. This varies from 1.46(3)Å to 1.70(3)Å. So the difference in the present compound probably does not have any chemical meaning. The sum of the angles subtended at two β-carbon atoms is close to 360° (within 0.5°), the condition required for the planarity which would be expected if only sp^2 hybrid orbitals are used.

The P-C distances and the C-P-C angles of the present compound are within the range found in a number of metal complexes containing triphenylphosphine as a ligand. The P-C-C (ortho) angles are close to 120° (within 2°) and P-C-C (para) are close to 180° (within 4°), indicating that the phenyl groups are not misplaced by the method of group refinement.

CHAPTER 7

DISCUSSION AND CONCLUSION

7.1 Inner Coordination of the Three Rhenium-acetylacetonate Complexes

For the compounds $ReC\ell_2(acac)_2$, $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ and $ReOC\ell_2(acac)P(C_6H_5)_3$, the inner coordinations around rhenium are all distorted octahedra. The distortion, however, is different from compound to compound. This can be seen from bond angles of L-Re-L' (L and L' are ligand atoms directly bonded to rhenium) for these three complexes listed in Table 4.4, 5.5 and 6.5; these angles are close to 90° if they are in neighbouring positions or nearly 180° if they are at opposite corners of the octahedron around rhenium atom. The distortion can also be seen from the intramolecular non-bonded distances between neighbouring ligand atoms. In fact, since these lengths are the edges of the octahedron these distortions can be seen easily. For comparison, these non-bonded distances of compounds $ReC\ell_2(acac)_2$, $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ and $ReOC\ell_2(acac)P(C_6H_5)_3$ are listed in Table 7.1.

A) $ReC\ell_2(acac)_2$

As has been stated in Chapter 4, the inner coordination around the rhenium atom is an octahedron tetragonally distorted by the difference of bond lengths and character between Re-Cℓ and Re-O. The bond angles subtended at the rhenium atom by two ligand atoms are either close to 90° (within 1°) if they are at the neighboring corners of the octahedron or exactly linear because of the symmetry of inversion if they are at the

TABLE 7.1

INTRAMOLECULAR NON-BONDED DISTANCES (Å) IN $ReCl_2(acac)_2$, $ReCl_2(acac)[P(C_6H_5)_3]_2$ AND $ReCl_2(acac)P(C_6H_5)_3$ (e.s.d.'s are enclosed in parentheses)

	$ReCl_2(acac)_2$	$ReCl_2(acac)[P(C_6H_5)_3]_2$	$ReOCl_2(acac)P(C_6H_5)_3$
Cl...P		3.421(6)	3.648(6)
		3.423(7)	3.393(4)
		3.469(5)	
		3.347(7)	
Cl...O(carbonyl)	3.034(21)	3.086(11)	2.959(9)
	3.065(13)	3.035(11)	2.918(10)
	3.099(18)		2.992(10)
	3.059(18)		2.928(12)
Cl...O(oxo)			3.084(12)
			3.044(9)
P...O(carbonyl)		3.245(13)	3.062(13)
		3.163(12)	
		3.136(11) 3.288(9)	
P...O(oxo)			2.861(9)
O...O(carbonyl... carbonyl)	2.796(19) (intraring)	2.774(13)	2.663(12)
	2.836(12) (interring)		
O...O(carbonyl...oxo)			3.000(20)

opposite corners. The edges of this distorted octahedron which is formed by non-bonded distances between neighbouring ligand atoms are very close for chemically equivalent sets. Thus, the four Cℓ ... O distances are only different by 2σ (σ = 0.02 A). The O ... O distance is 2.80 A within the acetylacetone group and 2.84 A between neighbouring acetylacetone groups; though they are not chemically equivalent the lengths are still close.

B) $ReC\ell_2(acac)[P(C_6H_5)_3]_2$

The distortion of the octahedron in $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ is slightly different from $ReC\ell_2(acac)_2$. In addition to the distortion caused by the difference of bond distance among Re-Cℓ, Re-P and Re-O, further distortion is observed in the sense that some angles subtended at the rhenium atom by neighbouring ligands are not as close to right angles as that observed in $ReC\ell_2(acac)_2$; the $C\ell_1$-Re-$C\ell_2$ angle is 97.4° and the O_1-Re-O_2 angle is 86.6°. The two Re-P bond directions are nearly co-linear (178.7°) and perpendicular to the plane containing the ligand atoms $C\ell_1$, $C\ell_2$, O_1 and O_2 and rhenium as well. It should be pointed out that the cis configuration of the two chlorine atoms in the present compound is different from other rhenium-chlorine complexes having the cis configuration for two chlorine atoms. The reason is that in other compounds the Cℓ-Re-Cℓ angles are either restricted by symmetry or are influenced by multiple bonds. For $L_2ReC\ell_6$ (L = K (228) and p-toluidinium (225)), the Cℓ-Re-Cℓ angle of 90° would be expected because of the octahedral symmetry. For the Re(V) oxo (9-11), nitrido (12) and imino (14, 15) complexes, because of the Re-O and Re-N multiple bonds, the

Cℓ atom cis to the oxygen or nitrogen atom is displaced towards the Cℓ atom trans to the O or N atom. This makes the angles Cℓ (cis to N or O)-Re-Cℓ (trans to N or O) less than 90°. If the two chlorine atoms are both cis to N or O in the above cases the Cℓ-Re-Cℓ angle is close to 180°. In the present compound, the two chlorine atoms are not restricted by any high order symmetry nor influenced by any Re-N or Re-O multiple bonds. They may be considered as chemically equivalent because their relative positions in the molecule are similar. The two chlorine atoms in the present compound are free to push apart and 97° for the Cℓ-Re- Cℓ angle has been observed. The Cℓ ... Cℓ separation in the present compound is 3.6 A which is very close to the sum of the van der Waals radii. It should be noted that the averaged cis Cℓ ... O distance is equal to that found in $ReC\ell_2(acac)_2$. This would imply that the lengthening of the Cℓ ... Cℓ distance does not really shorten the Cℓ ... O separation.

C) $ReOC\ell_2(acac)P(C_6H_5)_3$

For the complex $ReOC\ell_2(acac)P(C_6H_5)_3$, the weighted best least-squares plane of Re and ligands are listed in Table 7.2, Rhenium is surrounded by a distorted octahedron which can be found from figures listed in Tables 7.1 and 7.2. The neighbours of the oxo group (i.e. $C\ell_1$, $C\ell_2$, P and O_2) are nearly coplanar, but the central metal, rhenium atom is about 0.2 A out of plane towards the oxo direction which means that the angles subtended at the central metal by the oxo group and its cis neighbours are always greater than 90°. A similar phenomenon has been observed in the structure of $ReOC\ell_3[P(C_2H_5)_2C_6H_5]_2$. (9)

TABLE 7.2

BEST WEIGHTED LEAST SQUARES PLANES OF Re AND LIGAND ATOMS IN $\mathrm{ReOC\ell_2(acac)P(C_6H_5)_3}$

Equation of Plane of the Form Ax+By+Cz=D

(Orthogonal Coordinate)[†]

Atom	Plane No.	A	B	C	D
Cl_1,Cl_2,P,O_2	1	-0.1511	0.9878	-0.0656	3.227
Re,Cl_1,Cl_2,P,O_2	2	-0.1408	0.9878	-0.0660	3.278
Cl_1,Cl_2,O_1,O_3	3	0.7042	0.0509	0.7082	3.593
Re,Cl_1,Cl_2,O_1,O_3	4	0.7042	0.0504	0.7082	3.595
P,O_1,O_2,O_3	5	0.6745	0.0396	-0.7372	0.5105
Re,P,O_1,O_2,O_3	6	0.6742	0.0402	-0.7375	0.5064

Distances of Atoms from Planes (Å)

Atom	1	2	3	4	5	6
Re		0.2045	-0	0.0146		-0.0187
Cl_1	0.0087	-0.0437	-0.1752	-0.1788		
Cl_2	0.0093	-0.0406	-0.1754	-0.1791		
P	-0.0072	-0.0583			0.0416	0.0454
O_1			0.1820	0.1793	-0.0447	-0.0412
O_2	-0.0108	-0.0619			0.0451	0.0506
O_3			0.1686	0.1641	-0.0421	-0.0362

[†] Defined in Section 3.5

and a series of nitrogen complexes where the oxygen is replaced by nitrogen or an imido group; $ReCl_2N[P(C_2H_5)_2(C_6H_5)]_3$ (12) and $ReCl_3X[P(C_2H_5)\cdot(C_6H_5)_2]_2$ (X=p-$NC_6H_4OCH_3$ and p-$NC_6H_4COCH_3$ (14) and NCH_3 (15)).

For the intramolecular non-bonded distances between the ligand atoms, Cl_1 and Cl_2 are nearly equidistant from ligand atoms O_1, O_2 and O_3 but not from P since the $Cl_1 \cdots P$ distance is about 0.25 Å longer than $Cl_2 \cdots P$. The longer $Cl_1 \cdots P$ distance might be caused by an interaction of Cl_1 with a phenyl group attached to the phosphorous atom since the shortest $Cl_1 \cdots C$ distance is 3.29 Å ($Cl_1 \cdots C_{35}$) which is comparable to the 3.17 Å of the $Cl_2 \cdots C(C_{15})$ in the present complex. Based on the positions of C_{35} and C_{15} and the assumed geometry of the phenyl group, the locations of hydrogen atoms bonded to these two carbon atoms were estimated. The $Cl \cdots H$ distances calculated in this way are 2.49 Å for $Cl_1 \cdots H$ (the H atom bonded to C_{35}) and 2.89 Å for $Cl_2 \cdots H$ (the H bonded to C_{15}). The shorter $Cl_1 \cdots H$ distance might fairly indicate that the longer $Cl_1 \cdots P$ distance than that of $Cl_2 \cdots P$ is purely to relieve the interaction between the Cl_1 atom and the hydrogen atom bonded to C_{35}. Both the above $Cl \cdots H$ distances are certainly shorter than 3.0 Å, the sum of the van der Waals radii for Cl and H. It can be rationalized now that the longer $Cl_1 \cdots P$ distance compared to $Cl_2 \cdots P$, is caused by interaction of the chlorine atoms with the phenyl rings. The average $Cl \cdots O$ (carbonyl) distance of 2.95 Å is about 0.11 Å shorter than the average value found in $ReCl_2(acac)_2$ (3.06(2) Å) and $ReCl_2$ (acac) $[P(C_6H_5)_3]_2$ (3.06 (1) Å). The $Cl \cdots O$(oxo) distances (3.04(1) and 3.08(1) Å) are comparable to the value of 3.0 Å found for $N \cdots Cl$(cis) in $ReNCl_2(P(C_2H_5)_2\cdot C_6H_5]_3$ (12) and $Re\,Cl_3(NCH_3)\,[P(C_6H_5)_2C_2H_5]_2$ (15) after correction for the difference of the van der Waals radius of N and O.

As it can be seen from Table 7.2, ligand atoms O_1, O_2, O_3 and P and the rhenium atom are nearly coplanar. The bond distances of these ligand atoms around the Re atom as well as the intramolecular non-bonded distances are presented in Figure 7.1. The $O_1 \cdots P$ distance (3.062(13) Å) is about 0.15 Å shorter than the averaged value found in $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ and the 2.66 Å of the $O_1 \cdots O_2$ (intra-ring carbonyl oxygen atoms) is about 0.12 Å shorter than that found in both $ReC\ell_2(acac)_2$ and $ReC\ell_2(acac)[P(C_6H_5)_3]_2$. This might be the result of the very short Re-O(oxo) bond, which in turn would cause very short non-bonded distances between the oxo oxygen and its cis neighbouring ligands unless considerable angular distortion from 90° occurred. To prevent any very short intramolecular non-bonded distances, two effects have been observed: (1) cis ligands bend away from the direction of the multiple bond of Re-O or Re-N, making the angles subtended at the central metal by the oxo group and its cis neighbours greater than 90° as stated at the beginning of this section. This would shorten the non-bonded distance between ligands cis to the oxo group and the ligand trans to the oxo group, unless further distortion occurred. (2) Another effect has been found in that the metal-ligand (trans to the oxo group) distance has been lengthened considerably as mentioned in Chapter 5. However, the non-bonded distances between ligands in the presence of the Re-O or Re-N multiple bonds are about 0.1-0.2 Å shorter than the compounds free of this multiple bond. This conclusion can be found directly from Table 7.1. One exception is that the non-bonded distance between oxo oxygen and its

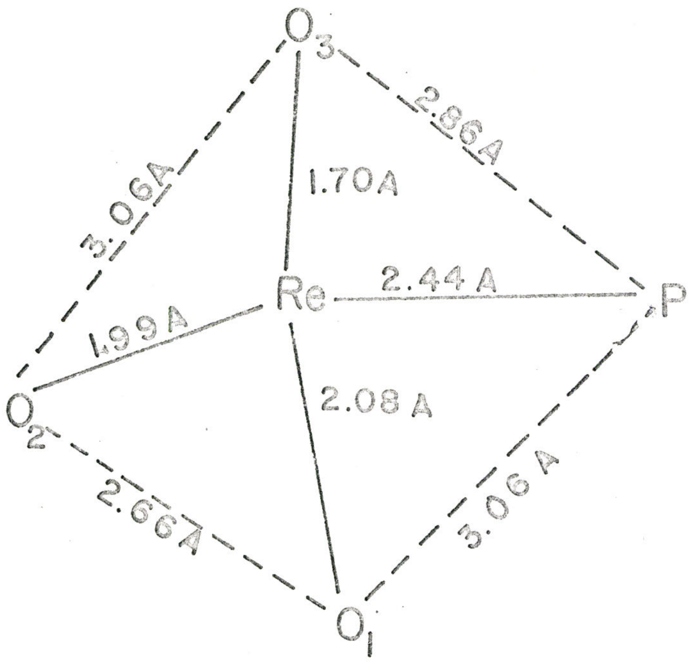

Figure 7.1

Intramolecular distance of ligand atoms O_1; O_2, O_3 and P around Re atom in $ReOCl_2(acac)P(C_6H_5)_3$

cis carbonyl oxygen is longer than the 2.8 Å value usually found for the oxygen···oxygen non-bonded distance. However, a similar effect has been observed in VO(acac)$_2$ (192) and VO(bzac)$_2$ (196) in which the distances between carbonyl···oxo oxygen atoms are all longer than 2.8 Å , the sum of the van der Waals radii for two oxygen atoms. The longer oxo···carbonyl oxygen distance in these three metal-β-diketone complexes would suggest that the repulsive force in the region normal to the direction of the M-O multiple bond is much larger than the van der Waals interaction. APParently, high electron density is distributed there, associated with the strong metal-oxygen multiple bond (229). It should be noted that the distances between intra-ring carbonyl oxygen atoms in the vanadium compounds are less than 2.8 Å , as was observed in our compound, and the distances between inter-ring oxygen atoms are very short; the shortest one is 2.56(1) Å found in VO(bzac)$_2$. It appears that these very short intramolecular non-bonded distances are a consequence of the strong multiple metal oxygen bonds from their neighbouring atom.

If the above explanation holds for the long O_3-O_2 distance we would expect the P···O_3 distance to have the same value or be longer than P···O_1. As can be seen from Figure 7.1, this is not so. The P···C_3(oxo) (2.86(2) Å) distance is about 0.2 Å shorter than P···O_1(carbonyl)(3.061 (13) Å). This fact cannot be satisfactorily explained at present and there is no closely related compound that can be used for comparision,perhaps there is some weak interaction between the P and O (oxo) atoms. There is some indication that such an interaction does occur. The preparation of $ReCl_2(acac)_2$, using $ReOCl_2(acac)P(C_6H_5)_3$ as starting material, gives a nearly quantitative yield of $OP(C_6H_5)_3$ (230). The intermediate step for this reaction is probably the one that will be illustrated in Figure 7.3 (A).

7.2 Reaction Mechanism

The structures of the compounds $ReCl_2(acac)[P(C_6H_5)_3]_2$, $ReOCl_2(acac)\cdot P(C_6H_5)_3$ and $ReCl_2(acac)_2$ have been determined by x-ray crystal structure analysis. This has provided us with some information about the reaction mechanism involved in preparing these compounds.

Theoretical treatment in interpreting the reaction mechanism for a substitution reaction of an octahedral inorganic compound is based on two processes, dissociation (S_N1) and displacement (S_N2) reactions (231). The former would involve five coordination as its intermediate step and the latter would involve seven coordination as its intermediate step. For five fold coordination, two geometrical configurations are common, the trigonal bipyramid and tetragonal pyramid. For seven coordination a number of possibilities exist (231), but two main configurations are the pentagonal bipyramid and trigonal biprism. Since the geometrical configuration of the product is the same when the reaction route is through either the pentagonal bipyramid or the trigonal biprism (231), the displacement process is usually discussed in terms of the model of the pentagonal bipyramid. The reason for doing so is that it is easier to visualize the stereochemical changes that take place.

For any possible geometrical intermediate, there are two possible positions for the entering group relative to the departing ligand. Either the entering group adds at a position adjacent to that of the departing ligand (cis attack) or opposite to that of the departing ligand (trans attack).

The only direct information from the crystal structure analysis is the geometrical configuration of those products or stable intermediates which were examined. The amount of information which one has about the reaction mechanism is obviously limited. In the reactions under discussion it is not possible to say whether reactions were S_N1 or S_N2, but one can infer the nature of the intermediates in the reactions. With this limitation the reaction mechanism for the formation of compounds $ReOC\ell_2(acac)P(C_6H_5)_3$, $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ and $ReC\ell_2(acac)_2$ will be described briefly in the following sections.

(A) $ReOC\ell_2(acac)P(C_6H_5)_3$ and $ReC\ell_2(acac)[P(C_6H_5)_3]_2$ These two compounds can be prepared either from $ReOC\ell_2(OEt)[P(C_6H_5)_3]_2$ or $ReOC\ell_3[P(C_6H_5)_3]_2$. In either case, one of the carbonyl oxygen atoms would be expected to substitute for the ligand trans to the oxo group since it is weakly bonded to the rhenium atom (3,4). Then the second oxygen atom of the acetylacetone group can replace either a triphenylphosphine group as observed for $ReOC\ell_2(acac)P(C_6H_5)_3$ or the oxo group as observed for $ReC\ell_2(acac)[P\cdot(C_6H_5)_3]_2$. As we have indicated, for the substituting reaction of inorganic octahedral complexes, two routes are possible; cis attack and trans attack. From the results of crystal structural analysis, it has been found that, the carbonyl oxygen atom substitutes for a triphenylphosphine group by cis attack (Chapter 6) and substitutes for the oxo group by trans attack (Chapter 5). These reactions are shown in Figure

7.2 (A) and 7.2 (B) for the formation of $ReOC\ell_2$ (acac) $P(C_6H_5)_3$ and $ReC\ell_2$ (acac)$[P(C_6H_5)_3]_2$ respectively.

(B) $ReC\ell_2$ $(acac)_2$ This compound can be prepared either from $ReOC\ell_3[P(C_6H_5)_3]_2$ or $ReOC\ell_2(acac)P(C_6H_5)_3$, the latter may be considered as an intermediate for the formation of $ReC\ell_2(acac)_2$ if $ReOC\ell_3[P(C_6H_5)_3]_2$ is used as the starting material. Using $ReOC\ell_2(acac)P(C_6H_5)_3$ as the starting material, two processes have been tried successfully: (1) react with sodium acetyl-acetonate and (2) react with concentrated acetylacetone at high temperature (230). In the latter process, triphenylphosphine oxide can be isolated, two intermediate stages are possible; either triphenylphosphine oxide is eliminated before substituting the second acetylacetone group, as shown in Figure 7.3 (A) or triphenylphosphine oxide is still bonded to rhenium through the Re-O single bond as that shown in Figure 7.3 (B). It is not possible on the basis of this work to say which process is more probable.

In addition to $ReC\ell_2(acac)_2$, $ReO(acac)_2C\ell$ (230) has been isolated from the reaction of $ReOC\ell_2(acac)P(C_6H_5)_3$ with acetylacetone at low temperatures. The configuration and the reaction mechanism involved are not known but from the example of $ReC\ell_2(acac)_2$, we think that the route of cis attack is more probable. The possible reaction mechanism for the formation of $ReOC\ell(acac)_2$ is shown in Figure 7.4. According to the route of cis eliminate attack, the configuration for this compound would be that shown in Figures 7.4 where $C\ell$ is cis to the oxo ligand in $ReOC\ell(acac)_2$.

Figure 7.2

Possible Reaction Mechanism for the Formation of

(A) $ReOCl_2(acac)P(C_6H_5)_3$ and

(B) $ReCl_2(acac)[P(C_6H_5)_3]_2$

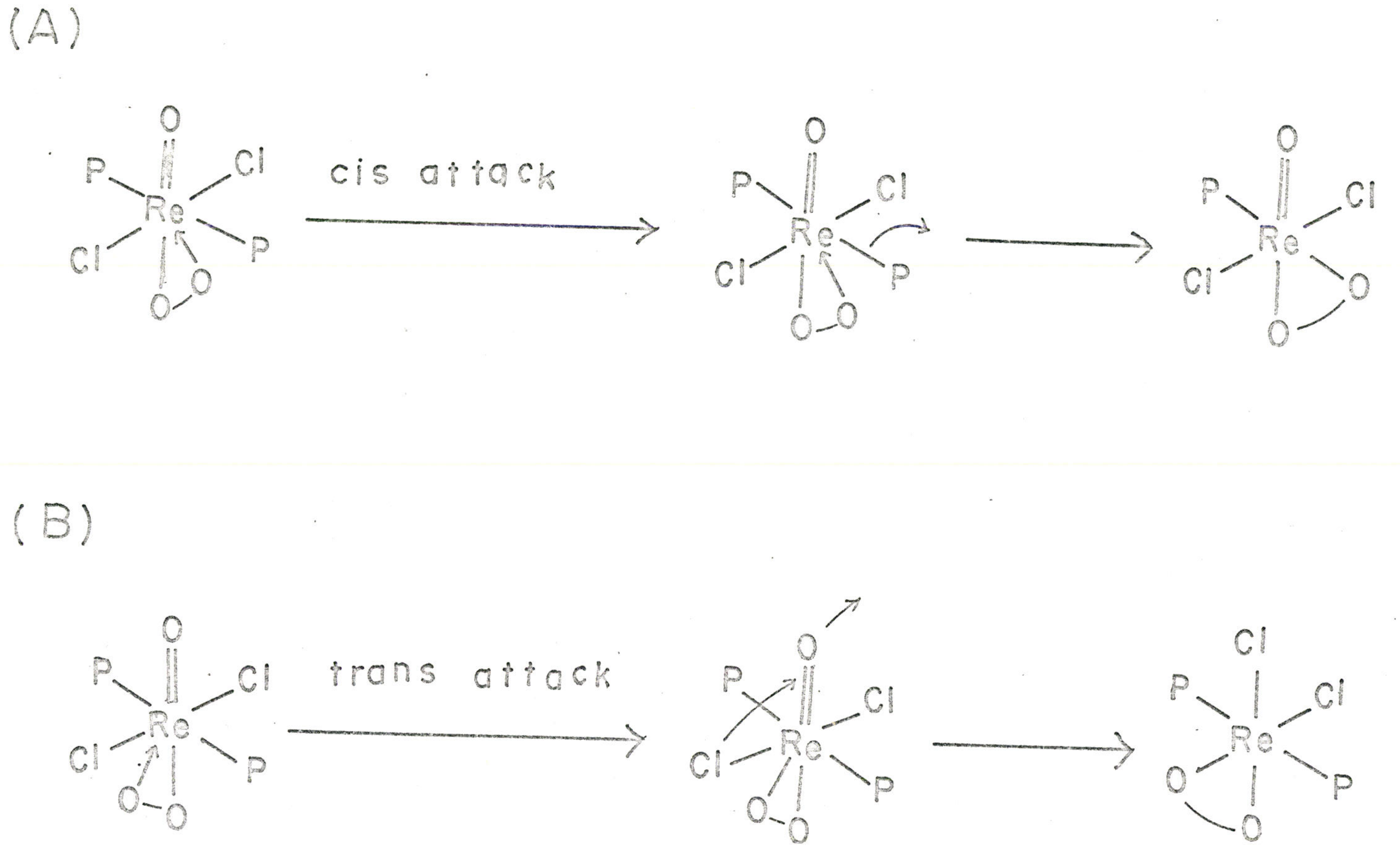

Figure 7.2

Figure 7.3

Possible Reaction Mechanism of the Formation of $ReCl_2(acac)_2$ from $ReOCl_2(acac)P(C_6H_5)_3$

(A) Involving the formation of $OP(C_6H_5)_3$ as a by-product

(B) Four-coordinated intermediate around rhenium

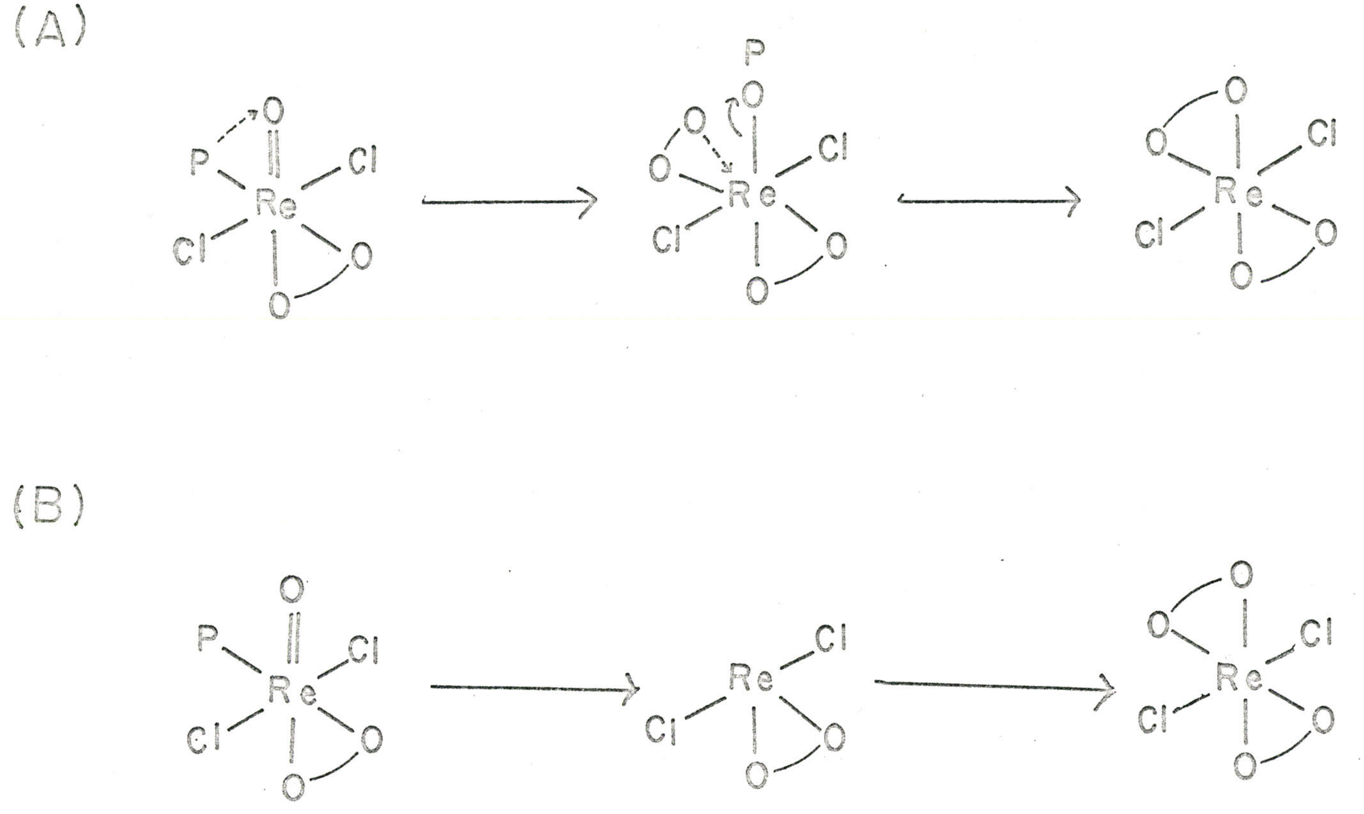

Figure 7.3

Figure 7.4

Suggested Reaction Mechanism for the Formation of ReOCl(acac)$_2$ with Its Configuration According to (C)

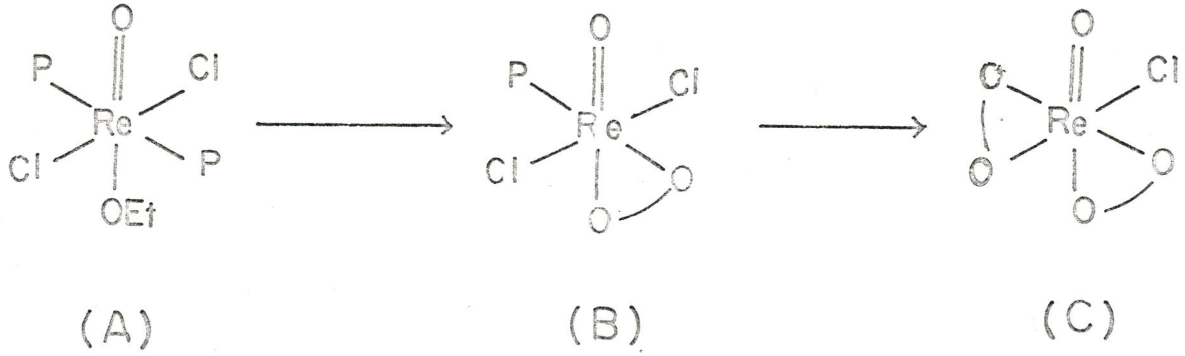

Figure 7.4

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