

THE CRYSTAL STRUCTURE  
DETERMINATION  
OF  
 $[\text{Rh}(\text{f}_6\text{fos})_2][\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$

by

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B. Sc., University of Victoria, 1967

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF  
THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE  
in the Department  
of  
Chemistry

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SIMON FRASER UNIVERSITY

June, 1970

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Title of Thesis: The crystal structure determination of  
 $[\text{Rh}(\text{f}_6\text{fos})_2][\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$

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ABSTRACT

The crystal structure of di(1,2-bis(diphenylphosphino)hexafluorocyclopentene) rhodium(I) cis-dicarbonyl-dichloro rhodate(I),  $[\text{Rh}(\text{f}_6\text{fos})_2][\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$  has been determined from three-dimensional x-ray data collected by counter methods. Using full-matrix least-squares techniques, the structure was refined to a conventional R factor of 8.8% for the 1628 observed reflections. The salt crystallizes in the tetragonal space group  $I4_1/a$ . For eight formula units in a cell of dimensions  $a = 17.722(1)\text{\AA}$  and  $c = 36.773(4)\text{\AA}$  the calculated density is  $1.59\text{g/cm}^3$ . The density as measured by flotation was between  $1.60$  and  $1.63\text{g/cm}^3$ . Both of the chemically and crystallographically distinct rhodium atom environments possess crystallographic two-fold symmetry. In the case of each rhodium atom, the arrangement of coordinating atoms is approximately square planar. The two Rh-P distances are  $2.282(6)\text{\AA}$  and  $2.300(6)\text{\AA}$ , and the bite of the chelating ditertiary phosphine,  $\text{f}_6\text{fos}$ , as measured by the intra-ligand P-P distance is  $3.111(8)\text{\AA}$ .

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## ACKNOWLEDGMENTS

I am grateful to Dr. F.W.B. Einstein for his guidance and assistance in this work.

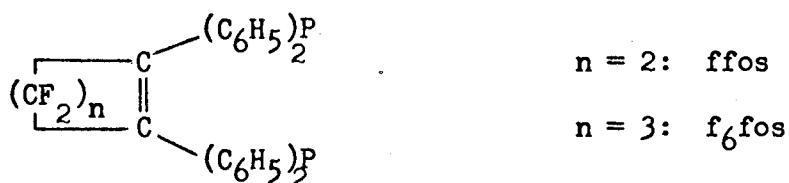
I would also like to thank Dr. W.R. Cullen for providing the crystals of  $[\text{Rh}(\text{f}_6\text{fos})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ .

## INTRODUCTION



As part of an investigation of transition metal compounds containing fluorocarbon-bridged ditertiary phosphines and arsines as ligands (2,13,14, 22-25), reactions between these ligands and chlorodicarbonyl rhodium dimer were studied. The intention was to prepare neutral complexes of the type, (diphosphine)Rh(CO)Cl, which are products of symmetric cleavage of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ , and these products were to be examined to ascertain their ability to undergo oxidative addition.

It has been found (?), however, that the ligands ffos and  $f_6\text{fos}$  do



not cleave  $\text{Rh}(\text{CO})_2\text{Cl}_2$  symmetrically as does the saturated hydrocarbon-bridged diphosphine, 1,2-bisdiphenylphosphinoethane. Rather, the cleavage is unsymmetric as with the reaction of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with the unsaturated hydrocarbon-bridged diphosphine, 1,2-bisdiphenylphosphinoethylene, and yields salts containing cations of the type  $[\text{Rh}(\text{diphosphine})_2]^+$ .

As well as confirming that the reaction between  $f_6\text{fos}$  and chlorodicarbonyl rhodium dimer occurs via unsymmetric cleavage of the dimer, this work reveals certain features (see page 38) of the cation which have implications for work on other compounds containing the  $f_6\text{fos}$  ligand.

The crystal structure of  $[\text{Rh}(f_6\text{fos})_2][\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$  described in this thesis was determined by the techniques of single crystal x-ray diffraction. These techniques and the instruments used are very commonly used in x-ray crystal structure determinations and will not be described here\*; instead, the emphasis is on a critical analysis of results.

\* One good book describing the practical side of a crystal structure determination is Stout and Jensen(1).

**EXPERIMENTAL**

Crystals were kindly provided by Dr. W.R. Cullen and their preparation is described elsewhere (2). The sample received was a mixture of two different kinds of crystals. The majority were small needles (of the order of 0.1 mm.) and the smaller fraction were crystals of the type whose structure determination is described here.

Crystal Data:  $[\text{Rh}(\text{f}_6\text{fos})_2] [\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$ , formula weight 1421.20, is tetragonal, space group  $I4_1/a$  (identified unambiguously from Laue group  $4/m$  and systematic absences).  $a = b = 17.722(1)\text{\AA}$ ,  $c = 36.773(4)\text{\AA}$ ,  $V = 11,815\text{\AA}^3$ ,  $1.60 < D_m < 1.63\text{g/cc.}$  (as measured by flotation\*),  $z = 8$ ,  $D_x = 1.59\text{g/cc.}$ ,  $F(000) = 5664$  and  $\mu(\text{Mo-K}\alpha) = 8.2\text{ cm.}^{-1}$ .

X-ray Data Collection: Weissenberg photographs of the zones  $h0l$ ,  $hll$ ,  $h2l$ ,  $h3l$  and  $h4l$  using  $\text{Cr-K}\alpha$  radiation, together with precession photographs of the zones  $hk0$  and  $h0l$  using  $\text{Mo-K}\alpha$  radiation, showed absences for  $hkl$  with  $h+k+l = \text{odd}$  missing, for  $00l$  with  $l = 4n+2$  missing and for  $hk0$  with  $h = \text{odd}$  missing.

All counter data were collected using a crystal mounted along its "b" axis. The crystal was in the shape of a slightly tetragonally distorted octahedron. Distension was in the "c" direction of the crystal, so that from apex to apex in that direction the distance would be about  $0.21(\pm 0.01\text{ mm.})$  were one of the apices not chipped off. In the "b" apical

\*Crystals separated from the crystal mixture by hand and slightly smaller than that used for counter data collection were found to sink very slowly in  $\text{CCl}_4$  ( $\rho = 1.60\text{g/cc.}$ ) and to float just beneath the surface in concentrated aqueous KI solution ( $\rho = 1.63\text{g/cc.}$ , maximum density for concentrated aqueous KI solution).

(not-distended) direction, the dimension of the crystal was about 0.18mm. Cell dimensions were determined by least-squares from high-angle reflections measured on a Picker four-circle automated diffractometer ( $\lambda = 0.70926\text{\AA}$ , unfiltered Mo-K $_{\alpha}$  radiation was used to obtain cell dimensions at 19°C). The errors were estimated from the internal consistency obtained.

Reflection intensities for the unique set of data were measured using a Picker four-circle diffractometer equipped with our own semi-automation. Zirconium filtered Mo-K $_{\alpha}$  radiation was measured by a scintillation detector with pulse-height analysis. The take-off angle was  $1.1^{\circ}$  and a symmetrical  $\theta$ - $2\theta$  scan of  $1.6^{\circ}$  width was used. Background was measured by stationary counts lasting 12 seconds on either side of the  $1.6^{\circ}$  scans. The stationary counts were subtracted from the scanned intensity for each reflection. Any net intensity which was less than two standard deviations (ie.,  $2\sigma$ ;  $\sigma = \sqrt{N}$ , and N is the sum of counts obtained for the scan plus two background counts) was coded as unobserved. Unobserveds are denoted by a minus sign in the  $F_{\text{obs}}$  columns in Table I. Of the 2934 intensities recorded in the range  $0 < 2\theta < 40$ , 1628 were observed. Three measurements for each of two standard reflections were taken at intervals ranging from  $1\frac{1}{2}$  to 5 hours. The average of these six measurements changed by about  $\pm 5\%$  during the data collection.

Because of the large size of the unit cell care had to be exercised in order to recognize cases of scans overlapping more than

Table 1. Measured and calculated structure factors

A dense grid of numbers and labels, likely a data table or index. The table contains numerous columns and rows of numerical data, with some labels like 'L 10' and 'L 15' interspersed. The text is oriented vertically on the page.



one reflection, and some effort was made to correct for this effect. It appeared that no serious errors of this type remained, since there were no large deviations of  $F_o$  from  $F_{calc}$  at the end of the refinement to enable detection of such an effect. This effect was observed particularly along the  $c^*$  axis and at low values of  $2\theta$  (length of  $c \approx$  twice the length of  $a$ ).

Lorentz and polarization factors were applied and structure factors calculated in the usual way. No correction for absorption was made since the small size and the shape of the crystal suggested that this correction would be small. Furthermore, the variation of intensity due to absorption was calculated to be no more than 5% (with an estimated error in this percentage of  $\pm 2\%$  due to uncertainty in the crystal size measurements).



**STRUCTURE SOLUTION**

From the unsharpened Patterson function it was possible to assign approximate positions on the two-fold axis to two crystallographically distinct rhodium atoms, and also to one other atom which was temporarily assumed to be a chlorine atom. One cycle of least-squares on four atoms including the three above as well as one misplaced chlorine atom yielded a conventional R factor of 46.2%. These two rhodiums later proved to be the rhodiums of the cation and anion. The remainder of the structure was filled in as prominent features of successive difference maps and good chemical sense dictated.

With all the non-hydrogen atoms allowed appropriate coordinates and isotropic thermal parameters, the structure was refined to a conventional R factor of 11.5% (weighted R, 12%). It was inferred from prominent features of a difference map at this point that the fluorine atoms were vibrating anisotropically. After two cycles of least-squares, varying anisotropic parameters for the fluorines, the R factor dropped to 9.8% (weighted R, 10.1%). Prominent features of a difference map at this stage pointed to the possibility that the anion was vibrating anisotropically. The R factor after two cycles of least-squares varying anisotropic parameters for the anion had dropped to 9.4% (weighted R, 9.7%).

Up to this point all observed reflections had received unit weights. Unobserveds were not included in the least-squares refinement (ie., they were effectively given zero weight). After refinement involving weights which were the reciprocals of the variances

of  $F_{\text{obs}}$ , the R factor dropped to 9.2% (weighted R, 11.1%).\*

The R factor dropped to its final value of 8.8% (weighted R, 10.5%) after four changes had been made: (i) anomalous dispersion corrections (3) were applied to the rhodium scattering factor curve; (ii) the cationic rhodium atom was allowed to "go anisotropic"; (iii) the phosphorus scattering factor curve was employed, in the calculations, for phosphorus atoms which had been mistakenly given chlorine scattering power; and (iv) the carbon (C(6)) at the extreme end of the fluorocarbon moiety of the  $f_6\text{fos}$  ligand was allowed to go anisotropic. It seemed there was a suggestion of anisotropy for this carbon in the difference map at that stage. The value for R of 8.8% signified a reasonable point at which to discontinue the refinement for a large problem which involved a large amount of computing time.

In the last cycle of least-squares refinement all elements of the full-matrix were varied except for the atomic parameters of atoms C(16)-C(21). These parameters were varied in the previous cycle. Final positional and thermal parameters are listed in Table II.

A final difference Fourier contained no peaks larger than  $0.86 \text{ e}/\text{\AA}^3$ , which corresponds to about 29% of the height of the broad peak that was found for the carbonyl group. A peak of  $0.86 \text{ e}/\text{\AA}^3$  was found about  $2.3\text{\AA}$  away from the anionic rhodium atom.

There was also a peak of substantial height remaining in the final difference map about  $1.49\text{\AA}$  from the cationic carbon atom farthest from the rhodium of the cation. It is in a position roughly corresponding to the position a fluorine atom would be expected to

\*The weighting scheme used is described in appendix D.

Table II. Final positional and thermal parameters with standard deviations.

Atoms with isotropic thermal parameters:

Atom	x	y	z*	B (in Å <sup>2</sup> )
P(3)	0.0865(3)	0.8454(3)	0.1410(2)	3.23(14)
P(4)	0.1025(3)	0.6707(3)	0.1440(2)	3.45(14)
C(9)	0.2516(14)	0.8404(15)	0.1316(7)	4.8(5)
C(13)	0.2677(15)	0.7059(15)	0.1339(7)	5.3(6)
C(14)	0.1857(11)	0.7295(11)	0.1370(5)	2.8(4)
C(15)	0.1802(11)	0.8027(11)	0.1362(5)	3.1(5)
C(16)	0.0956(13)	0.8939(13)	0.1842(6)	4.4(5)
C(17)	0.0619(14)	0.9635(15)	0.1886(7)	5.5(6)
C(18)	0.0646(18)	0.9973(18)	0.2246(9)	8.0(8)
C(19)	0.0986(17)	0.9580(17)	0.2528(9)	7.5(7)
C(20)	0.1305(16)	0.8907(16)	0.2473(8)	6.7(7)
C(21)	0.1319(14)	0.8556(14)	0.2119(8)	5.3(6)
C(22)	0.0852(12)	0.9136(12)	0.1047(6)	3.8(4)
C(23)	0.0535(14)	0.8903(13)	0.0733(7)	5.0(6)
C(24)	0.0548(16)	0.9382(16)	0.0414(8)	7.0(7)
C(25)	0.0861(15)	1.0079(15)	0.0454(7)	6.1(6)
C(26)	0.1156(15)	1.0326(15)	0.0768(8)	6.1(6)

# Here and throughout this thesis, standard deviations are indicated by brackets. For example, for 3.23(14), the standard deviation is 0.14.

\* The positional coordinates x,y and z are fractions of the unit cell edges a,b and c respectively.

Atoms with isotropic thermal parameters (continued):

Atom	x	y	z	B
C(27)	0.1180(12)	0.9838(13)	0.1082(6)	4.2(5)
C(28)	0.1192(11)	0.6300(11)	0.1878(5)	3.3(4)
C(29)	0.0778(13)	0.6591(12)	0.2155(6)	4.2(5)
C(30)	0.0896(16)	0.6330(15)	0.2529(8)	6.4(7)
C(31)	0.1469(15)	0.5802(15)	0.2592(7)	5.6(6)
C(32)	0.1834(15)	0.5480(15)	0.2305(7)	6.0(7)
C(33)	0.1739(13)	0.5739(13)	0.1951(6)	4.2(5)
C(34)	0.1158(12)	0.5955(12)	0.1114(6)	3.5(5)
C(35)	0.0993(13)	0.5211(13)	0.1184(7)	4.6(5)
C(36)	0.1097(16)	0.4621(16)	0.0920(8)	6.3(7)
C(37)	0.1318(18)	0.4832(19)	0.0585(9)	7.6(8)
C(38)	0.1444(17)	0.5575(17)	0.0499(8)	7.1(7)
C(39)	0.1381(15)	0.6146(15)	0.0767(7)	5.7(6)

Atoms with anisotropic thermal parameters:

Atom	x	y	z
Rh(1)	0.0	0.75	0.1410(1)
Rh(2)	0.0	0.25	0.0389(1)
C(6)	0.3089(15)	0.7783(16)	0.1330(9)
F(5)	0.3286(15)	0.7797(14)	0.1716(9)
F(7)	0.3761(10)	0.7863(10)	0.1225(7)
F(8)	0.2668(8)	0.8977(9)	0.1546(5)

Atoms with anisotropic thermal parameters(continued):

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
F(10)	0.2598(8)	0.8713(10)	0.0981(4)
F(11)	0.2912(10)	0.6580(13)	0.1538(10)
F(12)	0.2849(10)	0.6871(19)	0.0986(8)
Cl(40)	0.0888(7)	0.2277(10)	-0.0059(4)
C(41)	0.0752(22)	0.2417(25)	0.0756(10)
O(42)	0.1116(15)	0.2408(19)	0.0932(9)

Anisotropic thermal parameters(continued):

Atom	$U_{11}^*$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Rh(1)	0.0350(16)	0.0377(18)	0.0425(14)	-0.0008(14)	0.0	0.0
Rh(2)	0.085(3)	0.088(3)	0.093(3)	-0.0053(24)	0.0	0.0
C(6)	0.047(18)	0.085(22)	0.13(3)	-0.009(15)	-0.017(18)	0.023(19)
F(5)	0.160(23)	0.174(23)	0.25(3)	0.072(19)	-0.114(23)	-0.052(21)
F(7)	0.065(12)	0.089(12)	0.29(3)	0.002(9)	0.072(16)	0.027(16)
F(8)	0.054(10)	0.103(13)	0.133(15)	-0.028(9)	0.019(9)	-0.029(11)
F(10)	0.047(9)	0.140(15)	0.103(14)	-0.029(9)	0.016(9)	0.046(11)
F(11)	0.049(12)	0.143(19)	0.41(4)	0.007(12)	-0.018(17)	0.160(24)
F(12)	0.053(12)	0.34(4)	0.26(3)	0.028(18)	0.002(15)	-0.20(3)
Cl(40)	0.136(9)	0.298(18)	0.171(11)	-0.068(11)	0.023(9)	-0.086(12)
C(41)	0.09(3)	0.094(24)	0.08(3)	-0.026(24)	-0.001(20)	0.005(22)
O(42)	0.084(22)	0.124(21)	0.16(3)	-0.002(18)	-0.020(17)	-0.021(23)

\*U's are in  $\text{\AA}^2$ .

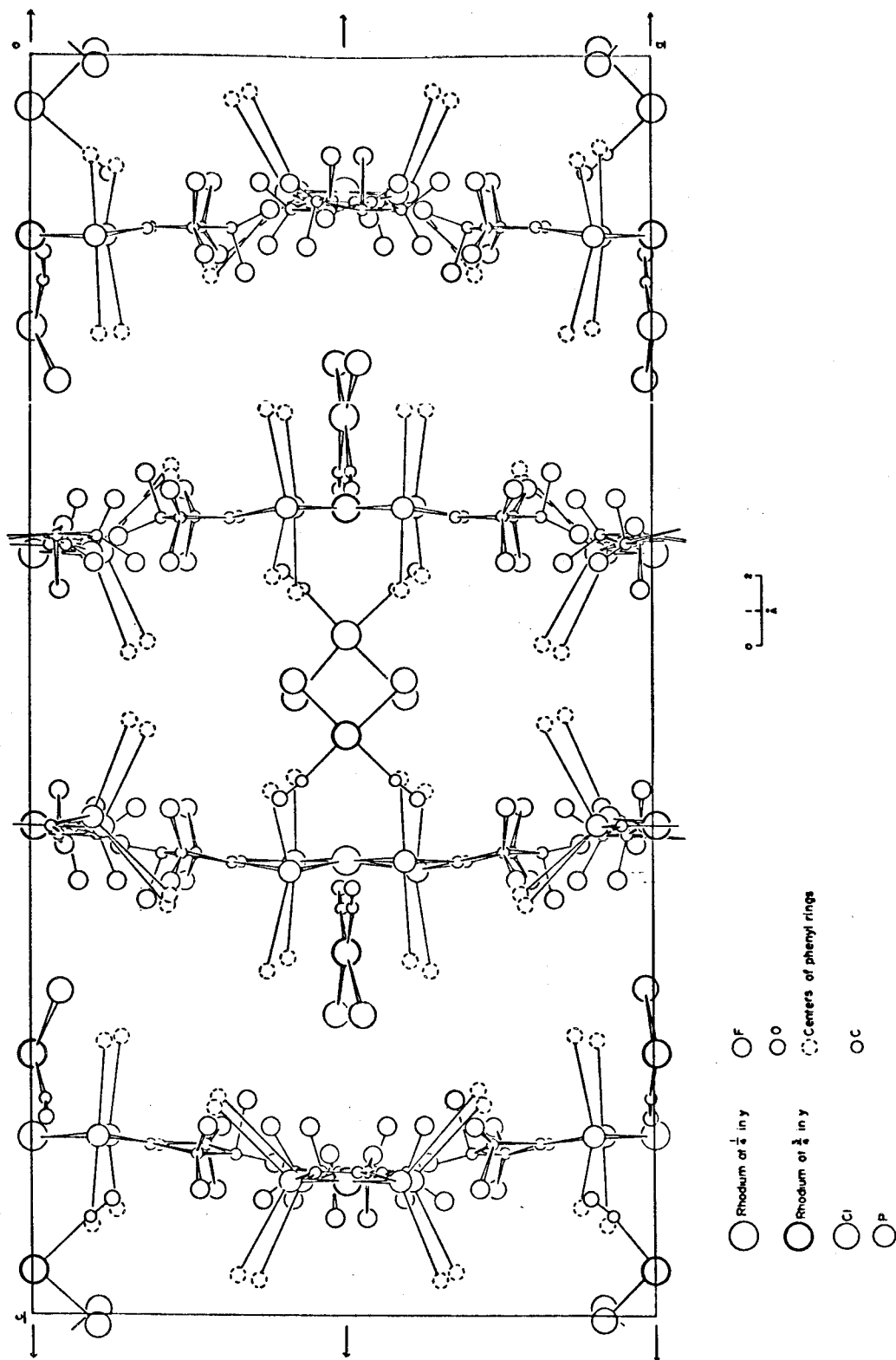
take for another conformation of the fluorocyclopentenyl ring. This together with the unreasonable anisotropic motion of the fluorocarbon fluorine atoms led us to consider the possibility of disorder involving another conformation of the fluorocyclopentenyl ring. Such a conformation, if it exists, would probably occur less frequently in the crystal structure than the one which was refined. However, no refinement involving two conformations of the ring was carried out as such further investigation would have required an unwarranted amount of computer time.

The function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the discrepancy factor R was  $\sum (||F_o| - |F_c||) / \sum |F_o|$ . The weighted R was  $\sqrt{(\sum w ||F_o| - |F_c||)^2 / \sum w F_o^2}$ .

Scattering factors used were those tabulated in "International Tables for X-ray Crystallography"(4).



figure 1. The crystal structure of  $[\text{Rh}(\text{f}_6\text{fos})_2][\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$  ---packing diagram.



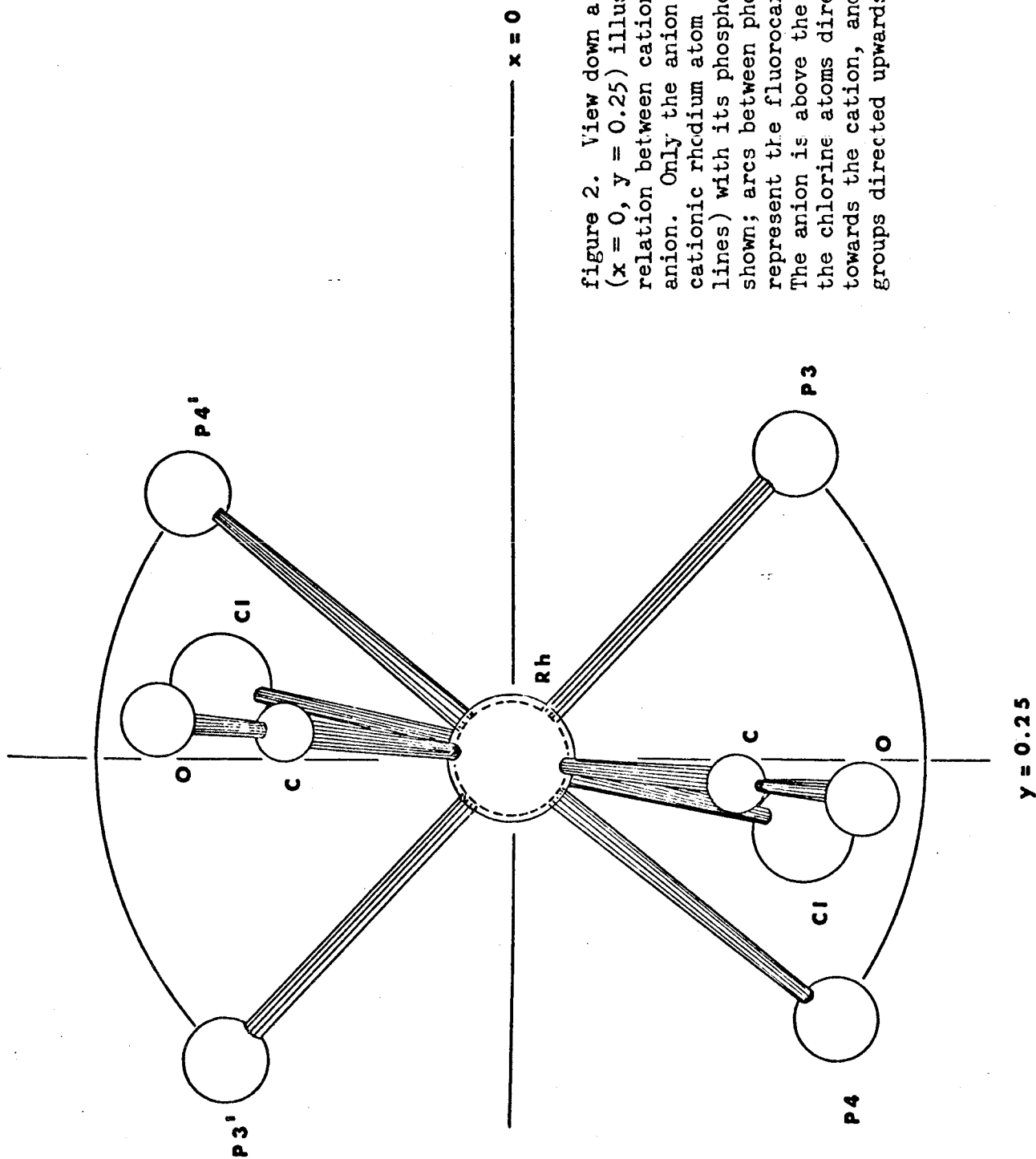


Figure 2. View down a two-fold axis ( $x = 0$ ,  $y = 0.25$ ) illustrating the relation between cation and adjacent anion. Only the anion and the cationic rhodium atom (in dashed lines) with its phosphorus atoms are shown; arcs between phosphorus atoms represent the fluorocarbon bridge. The anion is above the cation, with the chlorine atoms directed down towards the cation, and carbonyl groups directed upwards.

**DISCUSSION**

### A. Crystal Structure

The crystal structure of  $[\text{Rh}(\text{f}_6\text{fos})_2][\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$  contains  $[\text{Rh}(\text{f}_6\text{fos})_2]^+$  ions and  $[\text{cis-Rh}(\text{CO})_2\text{Cl}_2]^-$  ions packed together in a body-centred tetragonal lattice (see figure 1). The asymmetric unit contains half a cation and half an anion. All rhodium atoms are on two-fold special positions so that both cation and anion possess crystallographic two-fold symmetry. The disposition of coordinating atoms about the rhodium in both cation and anion is approximately square planar. Cation and anion are so packed together that the chlorines of the anion are directed toward the adjacent cation, as illustrated in figure 2. The chlorine atoms of the anion, which are separated from the cationic rhodium by a distance of  $5.23(1)\text{\AA}$ , are directed away from the P(3) and P(3)' atoms and towards the P(4) and P(4)' atoms. This is accommodated by a twist in the cation such that the P(4) and P(4)' atoms are depressed relative to the anion above them apparently in favour of the anion chlorine atoms<sup>#</sup>. Consequently the cation is not superposable on its mirror image; this means there are two distinct enantiomorphs\* in the crystal lattice, related to each other by either a centre of symmetry or a glide plane operation.

The anion also has adopted a twist in the form of a tetrahedral distortion. The oxygen atoms of the carbonyl groups are  $0.32(3)\text{\AA}$  on either side of the plane of the rhodium and two chlorine atoms.

### B. The Anion

Substantiating the presence of the  $[\text{cis-Rh}(\text{CO})_2\text{Cl}_2]^-$  anion is the ir

<sup>#</sup>The z-coordinate of P(3) is  $-0.1410(2)$ , of Rh(1) is  $-0.1410(1)$  and of P(4) is  $-0.1440(2)$ .

\*At least, there are two predominant enantiomorphs; there may be disorder involving other conformations.

spectrum(2) whose two carbonyl stretching frequencies closely resembled the carbonyl stretching frequencies of other compounds containing this same anion (5,6).

Though the presence of this anion is certain, not all the atomic parameters are certain. The C-O bond distance ( $0.91(3)\text{\AA}$ ) is too short to believe since C-O distances are usually  $1.1\text{\AA}$  (7-10,19). Furthermore, in two other cases (11,20) where carbonyl groups are trans to chlorine atoms in rhodium complexes, the C-O distances are  $1.18\text{\AA}$  (average value) and  $1.098(13)\text{\AA}$ . Thus to the extent that the C-O bond distance is not feasible, the atomic coordinates for the carbon and oxygen are in question. That these coordinates are questionable is also indicated by the high correlation coefficients between them.\* Between the x-coordinate of the carbon atom and the z-coordinate of the oxygen atom the correlation coefficient is 0.54 and between the z-coordinate of the carbon atom and the x-coordinate of the oxygen atom the correlation coefficient is 0.52 (see Table VII). No other correlation coefficient between positional parameters of different atoms is greater than 0.30. A possible reason for these high correlation coefficients for the carbon and oxygen is mentioned on page 34. However, the Rh-C-O angle is reasonable:  $177(6)^\circ$ , and linear within experimental error.

The Rh-Cl distance corrected for thermal motion is  $2.35(1)\text{\AA}^\#$  which is similar to values obtained ( $2.36\text{\AA}$  (average value) , and

\*A correlation coefficient shows the interdependence of parameters in the refinement. It is defined for the parameters i and j as  $\delta_{ij} = b_{ij} / \sqrt{b_{ii} b_{jj}}$  where  $b_{ij}$  is the  $ij^{\text{th}}$  element of the inverse matrix of the least-squares procedure.

$\#2.31(1)\text{\AA}$  was the value for the Rh-Cl distance before correction for thermal motion.

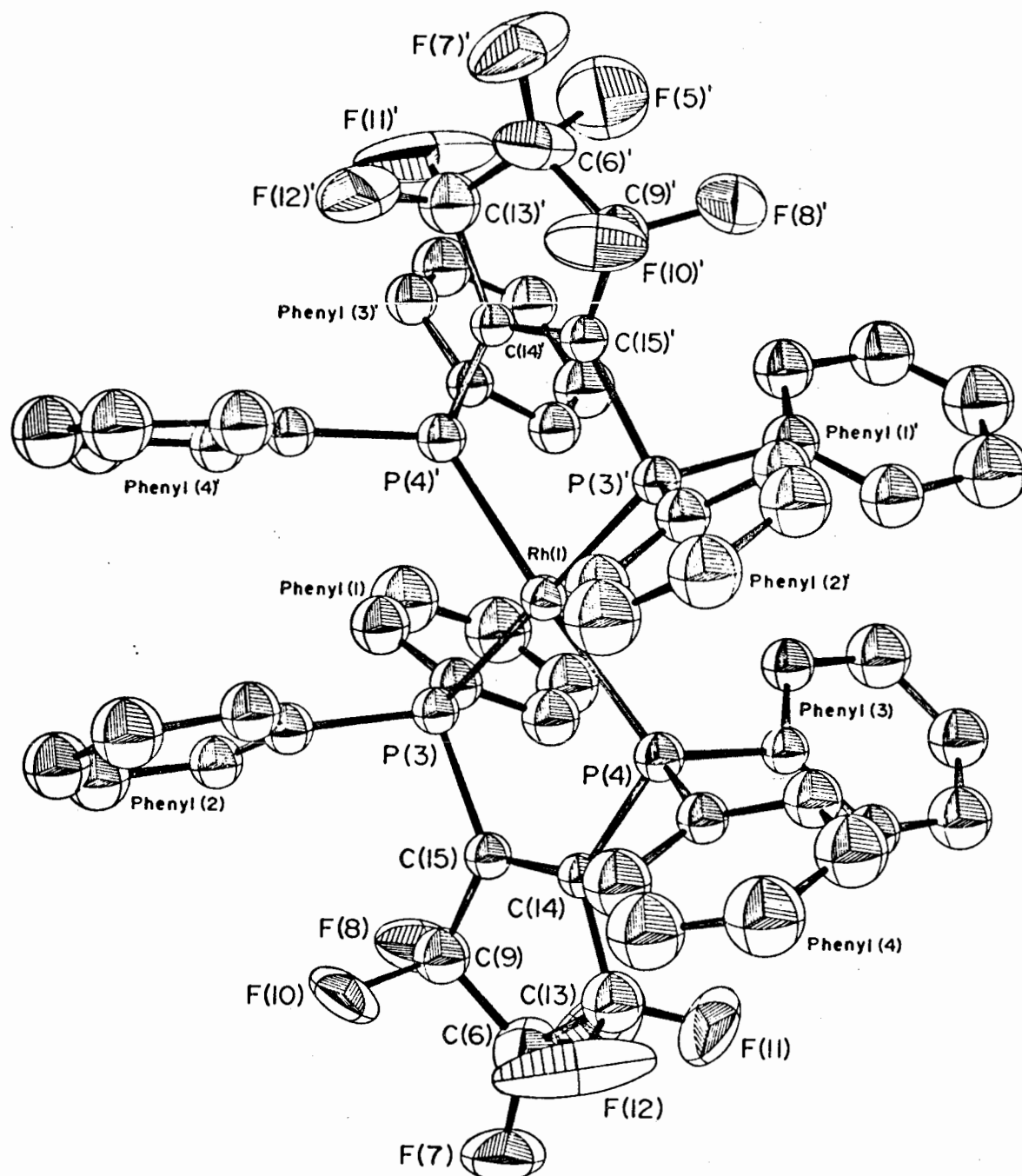


figure 3. Thermal ellipsoid plot of the cation  $[\text{Rh}(\text{f}_6\text{fos})_2]^+$

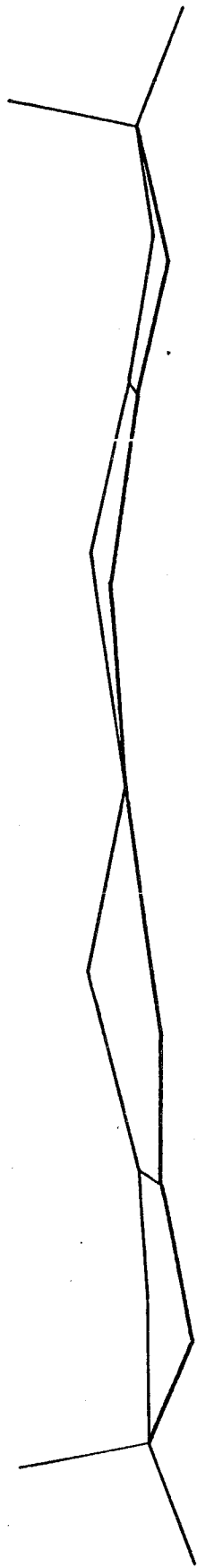


figure 4. Diagram featuring ring conformations of the cation. Lines protruding from the extreme ends of the cation indicate the approximate orientations of C-F bonds.

2.372(3)Å) for other rhodium complexes where a chlorine atom is trans to a carbonyl group (11,20).

### C. The Cation

The cation  $[\text{Rh}(\text{f}_6\text{fos})_2]^+$  (figure 3) contains two crystallographically identical  $\text{f}_6\text{fos}$  ligands. The bite of the ligand as measured by the intra-ligand P-P distance is 3.111(8)Å.

Each half of the cation contains two puckered, five-membered rings. Carbon atoms C(14) and C(15) are respectively 0.28(2)Å and 0.26(2)Å out of the plane of the phosphorus atoms of the same ligand and the rhodium (Rh(1)) atom. The fluorocarbon ring is also significantly puckered. This can be seen by examination of the results in Table III for the weighted mean plane through four of the carbon atoms of this ring. C(6), the carbon atom farthest from the cationic rhodium atom, is significantly out of this plane (in fact by 0.10(3)Å). Featured in figure 4 are the conformations of the five-membered rings of the cation; the cyclopentenyl ring conformation is shown to be consistent with the orientation of the C-F bonds farthest from the rhodium atom. F(5) is in the axial position, F(7) in the equatorial.

This latter consistency does not preclude the existence of another conformation of the fluorocyclopentenyl ring. Rather it underlines that if there is another conformation existing, it is a less preferred one. Indeed, one feature of these C-F bonds lends support to the proposal of another conformation in which F(5)



Table III. Equations of best planes and distances of atoms from planes.

Anion: (1) Plane containing Rh(2) and its bonded Cl atoms

$$0.2433x + 0.9699y - 8.5976 = 0$$

Atom	distance from plane (in Å)
C(41)	0.18(4)
C(41)*	-0.18(4)
O(42)	0.32(3)
O(42)*	-0.32(3)

Cation: (2) Mean plane through Rh(1) and its bonded P atoms

$$-z + 5.193 = 0$$

Atom	distance from plane (in Å)
Rh(1)	0.008(2)
P(3)	0.008(6)
P(3)*	0.008(6)
P(4)	-0.104(6)
P(4)*	-0.104(6)

(3) Plane containing Rh(1) and only the P atoms of one ligand

$$0.0355x - 0.0321y - 0.9989z + 5.6055 = 0$$

Atom	distance from plane (in Å)
C(14)	0.28(2)
C(15)	0.26(2)

Table III. (continued)

- (4) Mean plane through C(9), C(13), C(14) and C(15)  
of the fluorocarbon ring

$$-0.0999x - 0.0414y - 0.9941z + 5.8798 = 0$$

Atom	distance from plane (in Å )
C(9)	0.01(3)
C(13)	-0.01(3)
C(14)	0.01(2)
C(15)	-0.01(2)
C(6)	-0.10(3)

Note: The equations are given in Å coordinates. Planes (2) and (4) are weighted mean planes. The weight assigned to an atom is inversely proportional to the sum of the standard deviations for the positional coordinates of the atom.

becomes equatorial and F(7) becomes axial: namely their lengths. The C(6)-F(5) bond length (see Table IV) is ostensibly rather long while the C(6)-F(7) bond length is ostensibly rather short. A range of 1.32-1.36 $\text{\AA}$  for C-F bond lengths in a similar ligand (21) suggests the average value 1.33 $\text{\AA}$  is a reasonable one for a C-F bond in this situation.) Such lengthening and shortening is to be expected if there is a spreading out of the C(6) electron density due to the "C(6)" of another "flipped" conformation. If the C(6)-F(5) bond is of the order of 0.1 $\text{\AA}$  too long the actual position of the C(6) atom would be of the order of 0.2  $\text{\AA}$  out of the plane of the other four fluorocyclopentenyl carbon atoms. This would place the C(6) atoms a distance of the order of 0.4 $\text{\AA}$  apart, which is close to the value of the root-mean-square thermal displacement of the C(6) atom along the C(6)-F(5) bond (0.34(4) $\text{\AA}$ ). Thus the apparent irregularity of C(6)-F(5,7) bond lengths is actually in keeping with the presence of the other conformation.

#### D. The Thermal Motion

Thermal parameters as obtained from the refinement procedure can only be depended on to represent reality if they are chemically and physically reasonable. If they are not so, either the data or the model of the crystal structure is suspect.

Isotropic thermal motion:

Isotropic thermal parameters for the phosphorus atoms, the

Table IV. Inter-atomic distances and bond angles with standard deviations.

## Bonded Distances (in Å )

Cation:

		Average
Rh-P distances		
Rh(1)-P(3)	2.282(6)	
Rh(1)-P(4)	2.300(6)	2.291
P-C(phenyl) distances		
P(3)-phenyl(1)	1.813(6)	
P(3)-phenyl(2)	1.80(2)	
P(4)-phenyl(3)	1.79(2)	
P(4)-phenyl(4)	1.81(2)	1.80
P-C(fluorocarbon) distances		
P(3)-C(15)	1.83(2)	
P(4)-C(14)	1.82(2)	1.83
C=C(fluorocarbon double bond)		
C(14)-C(15)	1.30(3)	
C-C(fluorocarbon single bond)		
C(14)-C(13)	1.52(3)	
C(13)-C(6)	1.48(3)	
C(6)-C(9)	1.50(3)	
C(9)-C(15)	1.44(3)	1.49
C-C(phenyl)		1.39

Table IV (continued).

## Bonded Distances (in Å)

Cation:

		Average
C-F distances (uncorrected for thermal motion) <sup>a</sup>		
C(6)-F(5)	1.46(4)	1.33
C(6)-F(7)	1.26(3)	
C(9)-F(8)	1.35(3)	
C(9)-F(10)	1.36(3)	
C(13)-F(11)	1.20(3)	
C(13)-F(12)	1.37(3)	

Anion:

Rh(2)-Cl(40)	2.35(1) <sup>b</sup>
Rh(2)-C(41)	1.90(4) <sup>c</sup>
C(41)-O(42)	0.91(3)

a The correction for thermal motion described in footnote b was not considered to be strictly applicable to the C-F bond situation. However calculations of corrections based on this riding motion model (as described in footnote b) indicated that corrections are of the order of 0.1 Å.

b Corrected for thermal motion assuming that the chlorine is riding on the rhodium according to the model used by W.R. Busing, K.O. Martin and H.A. Levy in their program "Orffe, A fortran crystallographic function and error program". A version of this program was used to calculate the RMS radial thermal displacements ( $r_{Rh}^2, r_{Cl}^2$ ) of the atoms involved and also the RMS component of thermal displacement ( $\sigma_{Rh}^2, \sigma_{Cl}^2$ ) in the direction defined by the two atoms involved (in this case the rhodium and the chlorine). The equation used was the one used in the program Orffe:

$$\bar{R} = R_0 + \frac{(\overline{r_{Rh}^2} + \overline{\sigma_{Cl}^2} + \overline{r_{Cl}^2} + \overline{\sigma_{Rh}^2})}{2R_0}$$

c Though the Rh-CO situation does not exactly fit the model of a

Table IV (continued).

Non-bonded Distances (in Å)		
Anion:	Cl(40)-Cl(40)'	3.24(3)
Cation:	P(4)-P(4)'	4.59(1)
Anion-Cation:	Cl(40)-Rh(1)	5.23(1)
Shortest Anion-Cation distance:	Cl(40)-C(39)(Phenyl(4))	3.40(3)
Inter-Anion:	O(42)-Rh(2)	4.77(3)
	C(41)-C(41)	4.10(7)
	O(42)-O(42)	3.66(6)

## Bond Angles (in degrees)

Cation:		
	P(3)-Rh(1)-P(4) (for one ligand)	85.5(2)
	P(3)-Rh(1)-P(4) (inter-ligand)	94.5(2)
	Phenyl(1)-P(3)-Phenyl(2)	109.4(7)
	Phenyl(3)-P(4)-Phenyl(4)	106 (1)
	Rh(1)-P(4)-C(14)	106.4(6)
	Rh(1)-P(3)-C(15)	107.6(7)
	C(15)-C(14)-P(4)	121 (2)
	C(14)-C(15)-P(3)	119 (2)
	C(15)-C(14)-C(13)	110 (2)

c (continued) light atom alone riding on a heavy atom, it was felt that this model still might provide a close approximation to the Rh-CO bond distance correction. A negligible correction was obtained, however.

Table IV (continued).

## Bond Angles (in degrees)

## Cation:

C(14)-C(15)-C(9)	113 (2)
C(15)-C(9)-C(6)	104 (2)
C(14)-C(13)-C(6)	104 (2)
C(13)-C(6)-C(9)	108 (2)
F(11)-C(13)-F(12)	109 (3)
F(8)-C(9)-F(10)	104 (2)
F(5)-C(6)-F(7)	94 (3)

## Anion:

Cl(40)-Rh(2)-Cl(40)'	89.2(7)
Cl(40)-Rh(2)-C(41)	91 (1)
C(41)-Rh(2)-C(41)'	90 (2)
Cl(40)-Rh(2)-C(41)'	175 (1)
Rh(2)-C(41)-O(42)	177 (6)

carbon atoms of the fluorocyclopentenyl ring (except for C(6), the carbon farthest from the cationic rhodium) and the phenyl carbon atoms were allowed to vary in the least-squares procedure. When refinement was terminated, physically reasonable values were obtained. Parameters for the phosphorus atoms and for the adjoining carbon atoms of the fluorocyclopentenyl ring are small. They would appear to be rigidly fixed by bonds to other atoms; hence little thermal motion would be expected. On the other hand more motion would be expected for carbon atoms farthest from the phosphorus atoms. The root-mean-square radial thermal displacements of the phenyl carbon atoms are arranged in arbitrary classes in Table V. These class divisions are based on the distances of the carbon atoms from the phosphorus. Thus class 1 contains the phenyl carbon atoms bonded to the phosphorus, class 2 contains the phenyl carbon atoms two bonds away from the phosphorus, class 3 contains the phenyl carbon atoms three bonds away from the phosphorus, and class 4 contains the carbon atoms farthest from the phosphorus atoms. The generally increasing amplitude of vibration of the phenyl carbon atoms with increasing distance from the phosphorus is evidence that their thermal parameters are physically reasonable.

#### Anisotropic thermal motion:

Anisotropic thermal parameters as obtained from least-squares refinement can sometimes be simply accommodating disorder in the crystal, or even perhaps inaccurate data, rather than any genuine anisotropic motion of the atoms. Therefore the direction of maximum amplitude of the vibration of an atom must be considered, as well as the amplitude of the vibration of an atom, in assessing the legitimacy of any anisotropic thermal parameters.

The anion: The direction of maximum amplitude of vibration of the chlorine



Table V. Root-mean-square radial thermal displacements of atoms with isotropic thermal parameters.

Phosphorus atoms:

Atoms	displacement (in Å)
P(3)	0.20(1)
P(4)	0.21(1)

Fluorocyclopentenyl carbon atoms bonded to the phosphorus atoms:

Atoms	displacement (in Å)
C(14)	0.19(2)
C(15)	0.20(2)

Fluorocyclopentenyl carbon atoms two bonds from the phosphorus atoms:

Atoms	displacement (in Å)
C(9)	0.25(2)
C(13)	0.26(2)

Phenyl carbon atoms:

Atom class	displacements (in Å) for atoms listed according to the phenyl ring to which they belong			
	phenyl 1 C(16)-C(21)	phenyl 2 C(22)-C(27)	phenyl 3 C(28)-C(33)	phenyl 4 C(34)-C(39)
class 1	0.24(1)	0.22(1)	0.20(2)	0.21(2)
class 2	0.26(1) 0.26(2)	0.25(1) 0.23(1)	0.23(1) 0.23(2)	0.24(1) 0.27(2)
class 3	0.32(1) 0.29(1)	0.30(2) 0.28(2)	0.28(2) 0.27(2)	0.28(2) 0.30(2)
class 4	0.31(2)	0.28(2)	0.26(2)	0.31(2)

atom is at right-angles to the Rh-Cl bond (Table VI); and the amplitude of this vibration is greater than that of the rhodium atom. This picture of the chlorine atom riding on the rhodium is physically reasonable, though the relation of this motion to the vibration of the anion as a whole is obscured by uncertainty as to the behaviour of the carbonyl group.

It might be expected that at least the oxygen of the carbonyl group would be vibrating as much as or more than the chlorine atom; but O(42) appears to be vibrating with considerably less amplitude than the chlorine atom (Table VI). That this inconsistency is the fault of the carbonyl atom parameters is suggested by the unreliability of the positional parameters for these atoms (see page 21), and the high correlation coefficients between the thermal parameters of one atom of the carbonyl group and the positional and thermal parameters of the other (Table VII). In fact, the highest correlation coefficient in the correlation matrix is the one (value: 0.60) between the z-coordinate of the carbon atom and the z-component of the thermal motion of the oxygen atom. So there is uncertainty as to how the carbonyl group is vibrating; perhaps this is the fault of the vibration itself-- of the carbonyl group or even of the anion as a whole.

The cation: As for the rhodium atom, its anisotropic parameters are reasonable. Its amplitude of vibration is comparable to those of the phosphorus atoms bonded to it which appear to be just as rigidly fixed (Tables V and VI). Also, the direction of maximum displacement of the rhodium atom is in a direction normal to the "square plane" of the cation. That this is so is easily deduced from the thermal ellipsoid plot (figure 3) given that the direction of maximum displacement of the cationic rhodium is at right-angles to the

Table VI. Anisotropic motion analysis

Atom	Root-mean-square of atomic displacement along the three principal axes of the thermal ellipsoid (Å)	Angle between principal axis and a given bond (degree)	Atoms defining bond
<b>Cation:</b>			
Rh(1)	0.187(4) 0.195(4) 0.206(4)	33(27) 123(27) 90.0(2)	Rh(1)-P(3)
F(5)	0.27(3) 0.39(3) 0.60(3)	53(8) 124(9) 55(5)	F(5)-C(6)
F(7)	0.21(3) 0.29(2) 0.56(3)	1(8) 89(11) 91(3)	F(7)-C(6)
F(8)	0.20(2) 0.30(2) 0.40(2)	116(10) 27(10) 98(9)	F(8)-C(9)
F(10)	0.16(3) 0.30(2) 0.42(2)	127(7) 142(7) 81(7)	F(10)-C(9)
F(11)	0.20(3) 0.27(2) 0.69(4)	137(16) 129(16) 104(3)	F(11)-C(13)
F(12)	0.21(3) 0.33(3) 0.71(4)	119(9) 141(8) 66(4)	F(12)-C(13)
C(6)	0.21(4) 0.27(4) 0.38(4)	125(23) 135(23) 67(15)	C(6)-C(9)
<b>Anion:</b>			
Rh(2)	0.284(5) 0.303(5) 0.305(4)	63(7) 57(7) 135.4(4)	Rh(2)-Cl(40)

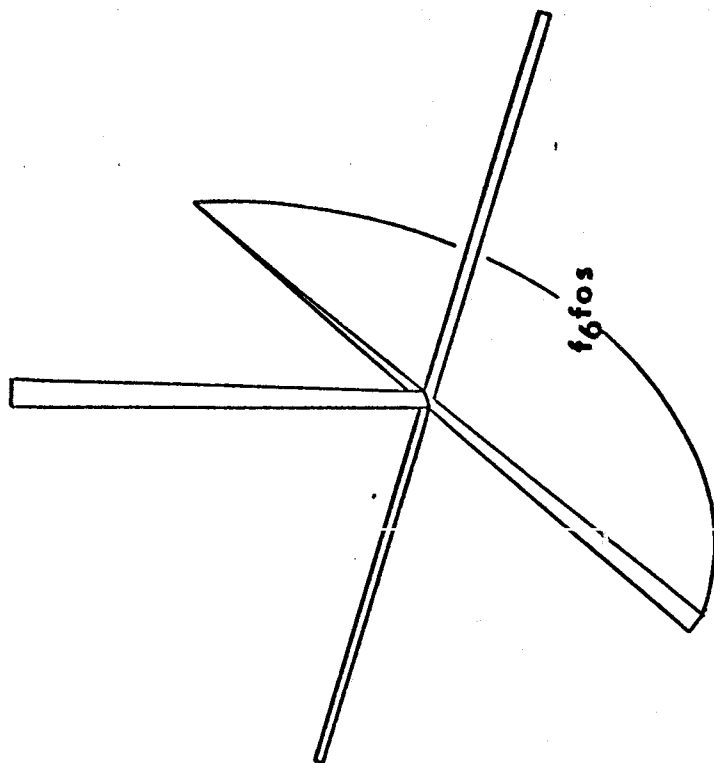
Table VI (continued).

Atom	Root-mean-square of atomic displacement along the three principal axes of the thermal ellipsoid (Å)	Angle between principal axis and a given bond (degree)	Atoms defining bond
Anion:			
Cl(40)	0.33(1)	108(18)	Cl(40)-Rh(2)
	0.36(1)	162(18)	
	0.60(2)	93(3)	
C(41)	0.25(5)	107(84)	C(41)-Rh(2)
	0.28(5)	32(61)	
	0.34(5)	64(33)	
O(42)	0.28(4)	149(10)	O(42)-C(41)
	0.34(3)	87(21)	
	0.41(4)	120(10)	

Table VII. Correlation coefficients( $\delta$ ) greater than 0.45 between parameters of the carbonyl atoms.

carbon atom parameter	oxygen atom parameter	$\delta$
x	z	0.54
x	B <sub>11</sub>	0.48
y	B <sub>12</sub>	0.56
y	B <sub>23</sub>	0.59
z	x	0.52
z	B <sub>33</sub>	0.60
B <sub>11</sub>	B <sub>11</sub>	0.56
B <sub>12</sub>	B <sub>23</sub>	0.58
B <sub>33</sub>	B <sub>33</sub>	0.50
B <sub>23</sub>	B <sub>12</sub>	0.48

structure "a"



structure "b"

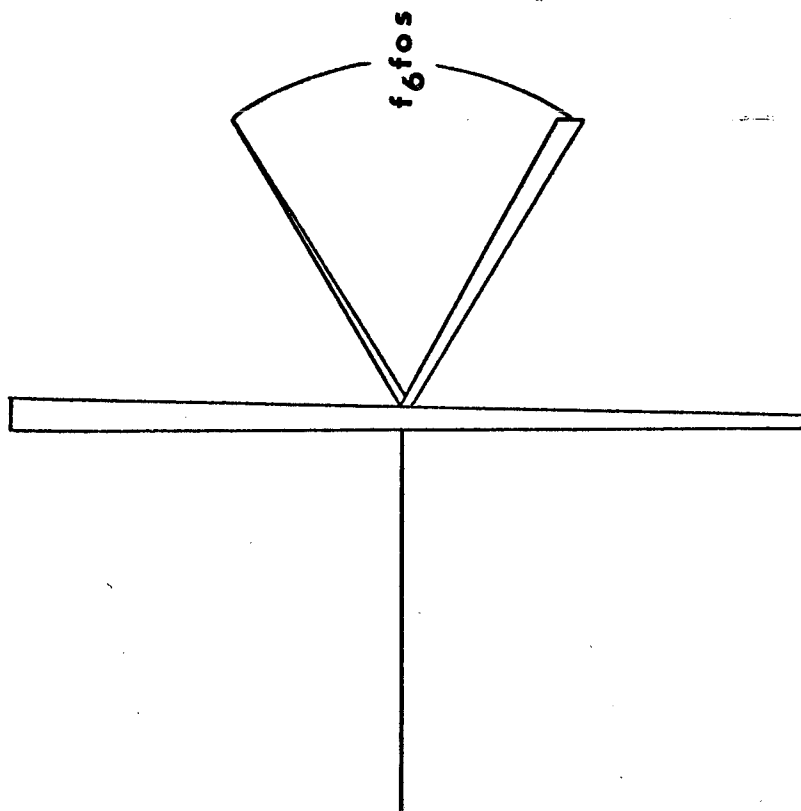


figure 5. Alternative structural proposals for  $f_6fosFe(CO)_3$ . Structure "a" is based on a square pyramidal arrangement; structure "b" is based on a trigonal bipyramidal arrangement. These alternatives were proposed by W.R. Cullen (13).

Rh(1)-P(3) vector (Table VI).

Anisotropic thermal parameters for the fluorine atoms may well be accommodating disorder due to the presence of the other conformation of the fluorocyclopentenyl ring. The root-mean-square displacements of F(8), F(10), F(11) and F(12) are greatest in the directions of fluorine atom positions of a "flipped" conformation. In addition, the magnitudes of these displacements (Table VI) are not less than the shifts in position (about  $0.4\text{\AA}$ ) these atoms would undergo were the ring flipped.

#### E. Implications of Two Structural Features of the Cation

Two structural features of the  $[\text{Rh}(\text{f}_6\text{fos})_2]^+$  cation have implications concerning other compounds containing the  $\text{f}_6\text{fos}$  ligand.

Firstly, the bite of the ligand (intra-ligand P-P distance:  $3.111(8)\text{\AA}$ ) has a bearing on the structural proposal for  $\text{f}_6\text{fosFe}(\text{CO})_3$  (13). The nmr spectrum showed that the original symmetry of the  $\text{f}_6\text{fos}$  ligand was preserved in the latter complex. Cullen et al. have suggested that this leaves two regular arrangements (figure 5) as possible structures for this compound, and that the true structure is one that is intermediate between these two possibilities.

Assuming that the Fe-P distance in  $\text{f}_6\text{fosFe}(\text{CO})_3$  is close to  $2.2\text{\AA}$  (it is  $2.18\text{\AA}$  in the compound  $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{f}_6\text{fos})\text{Sn}(\text{CH}_3)_3$  where  $\text{f}_6\text{fos}$  is monodentate(12)) and assuming that the P-P distance is no greater than  $3.1\text{\AA}$  in  $\text{f}_6\text{fosFe}(\text{CO})_3$ , the angle subtended at the Fe atom by the Fe-P vectors would be  $90^\circ$ . This suggests that

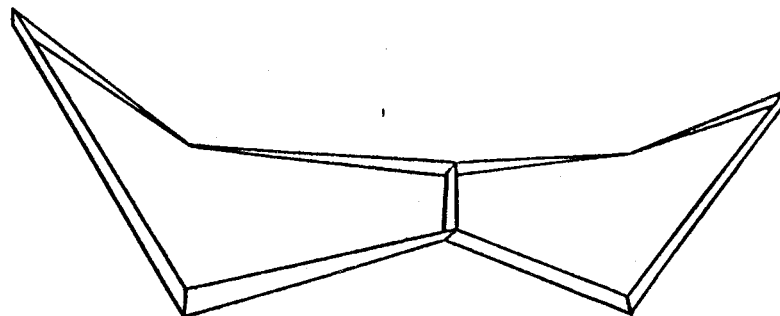
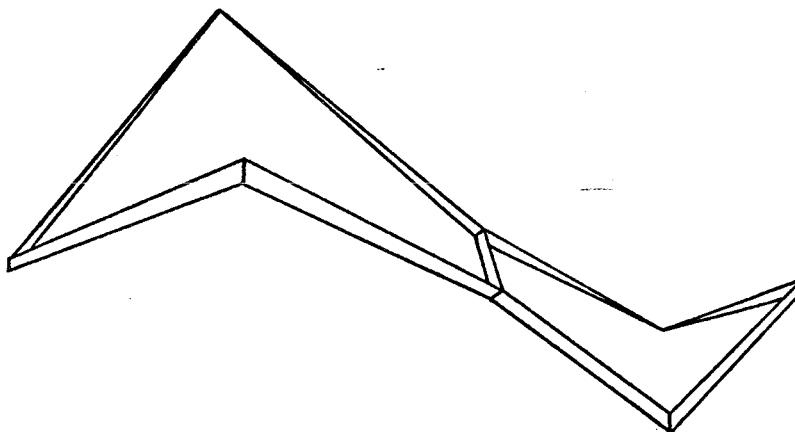
$(\text{CO})_3\text{Fe}$ **"boat"** $(\text{CO})_3\text{Fe}$ **"chair"**

figure 6. Two possible isomers of  $f_6\text{fosFe}(\text{CO})_3$ . The pucker of the five-membered rings has been much exaggerated to emphasize the difference between the two conformations.

structure (b) is much closer to the true structure.

Secondly, the conformations found for the five-membered rings of the cation suggest that other complexes shown to contain  $f_6\text{fos}$  (eg.,  $f_6\text{fosFe}(\text{CO})_3$  and  $f_6\text{fosM}(\text{CO})_4$ ,  $M=\text{Cr, Mo, W}$ ) also may contain two puckered, five-membered rings. It is conceivable that two short-lived isomers might appear in solution. They might be loosely described as "boat" and "chair" forms. (See figure 6.) The carbonyl stretching (ir) spectrum of  $f_6\text{fosFe}(\text{CO})_3$  shows four bands, one more than the number expected for a compound with  $C_{2v}$  symmetry(14). Similarly in  $f_6\text{fos M}(\text{CO})_4$  complexes four bands are predicted yet five are observed. The evidence here adds credibility to the suggestion of Cullen and coworkers that this extra band could arise from the presence of two distinct isomers in solution which have a long enough lifetime to be detected by ir spectroscopy.



REFERENCES

1. George H. Stout and Lyle H. Jensen, "X-ray Structure Determination", The Macmillan Company, New York, 1968.
2. W.R. Cullen and J.A.J. Thompson, Canadian Journal of Chemistry, 48, 1730 (1970).
3. D.H. Templeton in "International Tables for X-ray Crystallography", vol. 3, The Kynoch Press, Birmingham, England, 1962, p.216. Both real ( $\Delta F'$ ) and imaginary ( $\Delta F''$ ) corrections were applied.
4. "International Tables for X-ray Crystallography", vol.3, The Kynoch Press, Birmingham, England, 1962, p.201.
5. J.T. Mague and J.P. Mitchener, Inorganic Chemistry, 8, 119 (1969).
6. L.M. Vallarino, Inorganic Chemistry, 4, 161 (1965).
7. O.S. Mills and J.P. Nice, Journal of Organometallic Chemistry, 10, 337 (1967).
8. S.J. LaPlaca and J.A. Ibers, Journal of the American Chemical Society, 85, 3501 (1963).
9. F.R. Corey, L.F. Dahl and W. Beck, Journal of the American Chemical Society, 85, 1202 (1963).
10. Linda R. Bateman, P.M. Maitlis and L.F. Dahl, Journal of the American Chemical Society, 91, 7292 (1969).
11. L.F. Dahl, C. Martell and D.L. Wampler, Journal of the American Chemical Society, 83, 1761 (1961).
12. Private Communication, Dr. R. Restivo.
13. W.R. Cullen, D.A. Harbourne, B.V. Liengme and J.R. Sams, Inorganic Chemistry, 8, 1464 (1969).
14. W.R. Cullen, D.F. Dong, J.A.J. Thompson, Canadian Journal of Chemistry, 47, 4673 (1969).
15. F.W.B. Einstein, B.R. Penfold and Q.T. Tapsell, Inorganic Chemistry, 4, 186 (1965).
16. A. Stock and B. Herscovici, Berichte der Deutschen Chemischen Gesellschaft, 43, 414 (1910).

17. J.M. Andrews, J.E. Ferguson and C.J. Wilkins, *Journal of Inorganic and Nuclear Chemistry*, 25, 829 (1963).
18. D.M. Adams and J.B. Raynor, "Advanced Practical Inorganic Chemistry", Wiley, London, 1965, p. 94.
19. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry; a comprehensive text", Interscience Publishers, New York, 1968, p. 113.
20. J.T. Mague, *Inorganic Chemistry*, 8, 1975 (1969).
21. F.W.B. Einstein and A.M. Svensson, *Journal of the American Chemical Society*, 91, 3663 (1969).
22. W.R. Cullen, D.A. Harbourne, B.V. Liengme and J.R. Sams, *Inorganic Chemistry*, 9, 702 (1970).
23. W.R. Cullen. "Fluorine Chemistry Reviews", vol. 3, Paul Tarrant, ed., Marcel Dekker, Inc., New York (1969).
24. W.R. Cullen and D.A. Harbourne, *Canadian Journal of Chemistry*, 47, 3371 (1969).
25. W.R. Cullen, D.A. Harbourne, B.V. Liengme and J.R. Sams, *Inorganic Chemistry*, 8, 95 (1969).
26. M.N. Hughes, *Quarterly Reviews*, 22, 1 (1968).
27. L. Kuhn and E.R. Lippincott, *Journal of the American Chemical Society*, 78, 1820 (1956).
28. D.J. Millen, C.N. Polydoropoulos and D. Watson, *Journal of the Chemical Society*, 687 (1960).
29. J.E. Rauch and J.C. Decius, *Spectrochimica Acta*, 22, 1963 (1966).
30. R.D. Dragsdorf, J.L. Lambert, R.L. Hollis, G.P. Reese and G.L. Stucky, United States Clearinghouse for Federal Scientific and Technical Information, AD 651647 (reported in U.S.Govt.Res. Develop.Rep., 67 (13), 127 (1967)).

APPENDIX

- A. A computer program for calculating preliminary cell dimensions from precession photo measurements.

This is a program to calculate preliminary values of cell dimensions from one real angle, two reciprocal angles, and the reciprocal cell elements  $a^*$ ,  $b^*$  and  $c^*$ . This information can be easily obtained from precession photos.

Only one input card is required. Crystal system need not be specified.

Input Card (9F8.4):

1 - 8	$\alpha^*$	)	specify any two
9 - 16	$\beta^*$		
17 - 24	$\gamma^*$		
25 - 32	$\alpha$	)	specify any one
33 - 40	$\beta$		
41 - 48	$\gamma$		
49 - 56	$a^*$	)	specify all three
57 - 64	$b^*$		
65 - 72	$c^*$		

Program will print out  $a$ ,  $b$ ,  $c$ ,  $a^*$ ,  $b^*$ ,  $c^*$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\alpha^*$ ,  $\beta^*$ ,  $\gamma^*$ ,  $V$  and  $V^*$ .

```

C A PROGRAM TO CALCULATE CELL ELEMENTS FROM PRECESSION MEASUREMENTS
DOUBLE PRECISION ASTA, BSTA, CSTA, AA, BB, CC, GAM, ALPH, BET, ALPHST, BETST
1, GAMST
READ(5, 1) AFASTD, BTASTD, GMASTD, ALFADG, BTADG, GMADEG, ASTAR, BSTAR,
ICSTAR
1 FORMAT(9F8.4)
C RENAMING CELL ELEMENTS TO CONFORM TO A CALCULATION OF CELL ELEMENTS
C STARTING WITH ALPHASTAR, BETASTAR, GAMMA, AND ASTAR, BSTAR AND CSTAR (AXES
C MUST ALSO BE RENAMED)
N=1
IF (AFASTD.EQ.0) GO TO 2
IF (BTASTD.EQ.0) GO TO 3
ASTA=ASTAR
BSTA=BSTAR
CSTA=CSTAR
GO TO 4
2 AFASTD=GMASTD
GMADEG=ALFADG
CSTA=ASTAR
ASTA=CSTAR
BSTA=BSTAR
N=0
GO TO 4
3 BTASTD=GMASTD
GMADEG=BTADG
CSTA=BSTAR
BSTA=CSTAR
ASTA=ASTAR
N=-1
C CONVERT TO RADIAN FROM DEGREES
4 GAM=0.01745329*GMADEG
ALPHST=0.01745329*AFASTD
BETST=0.01745329*BTASTD
C CALCULATE CELL PARAMETERS

```

```

VSTAR=ASTA*BSTA*CSTA*(DSIN(ALPHST)*(DSIN(BETST))*(DSIN(GAM)))
V=1/VSTAR
AA=(BSTA*CSTA*(DSIN(ALPHST)))/VSTAR
BB=(CSTA*ASTA*(DSIN(BETST)))/VSTAR
GAMST=DARCOS((DCOS(ALPHST))*(DCOS(BETST))-(DCOS(GAM)))*(DSIN(ALPHST
1))*(DSIN(BETST)))
ALPH=DARCOS(((DCOS(BETST))*(DCOS(GAMST))-(DCOS(ALPHST)))/((DSIN(BE
1TST))*(DSIN(GAMST))))
BET=DARCOS(((DCOS(ALPHST))*(DCOS(GAMST))-(DCOS(BETST)))/((DSIN(ALP
1HST))*(DSIN(GAMST))))
CC=1/(CSTA*(DSIN(ALPH))*(DSIN(BETST)))
C CONVERT RADIAN TO DEGREES AGAIN
GAM=57.295779*GAM
GAMST=57.295779*GAMST
BET=57.295779*BET
BETST=57.295779*BETST
ALPH=57.295779*ALPH
ALPHST=57.295779*ALPHST
C CELL ELEMENTS REGAIN INPUT NAMES
A=AA
B=BB
C=CC
ASTAR=ASTA
BSTAR=BSTA
CSTAR=CSTA
ALPHA=ALPH
BETA=BET
GAMMA=GAM
ALFAST=ALPHST
BETAST=BETST
GMAST=GAMST
IF(N)5,6,7
5 BETAST=GAMST

```



```

GAMMA=BET
GMAST=BETST
BETA=GAM
ALPHA=ALPH
ALFAST=ALPHST
A=AA
B=CC
C=BB
ASTAR=ASTA
BSTAR=CSTA
CSTAR=BSTA
GO TO 7
6 A=CC
C=AA
B=BB
ASTAR=CSTA
CSTAR=ASTA
BSTAR=BSTA
BETAST=BETST
GMAST=ALPHST
ALFAST=GAMST
GAMMA=ALPH
BETA=BET
ALPHA=ALPH

```

C PRINT PARAMETERS

```

7 WRITE(6,8) A,B,C,ASTAR,BSTAR,CSTAR,ALPHA,BETA,GAMMA,ALFAST,BETAST,
1GMAST,V,VSTAR
8 FORMAT(1H0,'A = ',F7.2,' ANGSTROMS',10X,'B = ',F7.2,' ANGSTRO
1MS',10X,'C = ',F7.2,' ANGSTROMS'///1X,'ASTAR = ',F7.4,' ANGSTRO
2OMS**(-1)',8X,'BSTAR = ',F7.4,' ANGSTROMS**(-1)',8X,'CSTAR = ',F
37.4,' ANGSTROMS**(-1)'///1X,'ALPHA = ',F7.2,' DEGREES'///1X,'BET
4A = ',F7.2,' DEGREES',8X,'GAMMA = ',F7.2,' DEGREES'///1X,'ALPH
5ASTAR = ',F7.2,' DEGREES',8X,'BETASTAR = ',F7.2,' DEGREES',8X,
6'GAMMASTAR = ',F7.2,' DEGREES'///1X,'V = ',F10.2,' ANGSTROMS C
7UBED',16X,'VSTAR = ',F10.7,' ANGSTROMS**(-3)')
STOP
END

```

B. Description of computer programs used in  
this work.

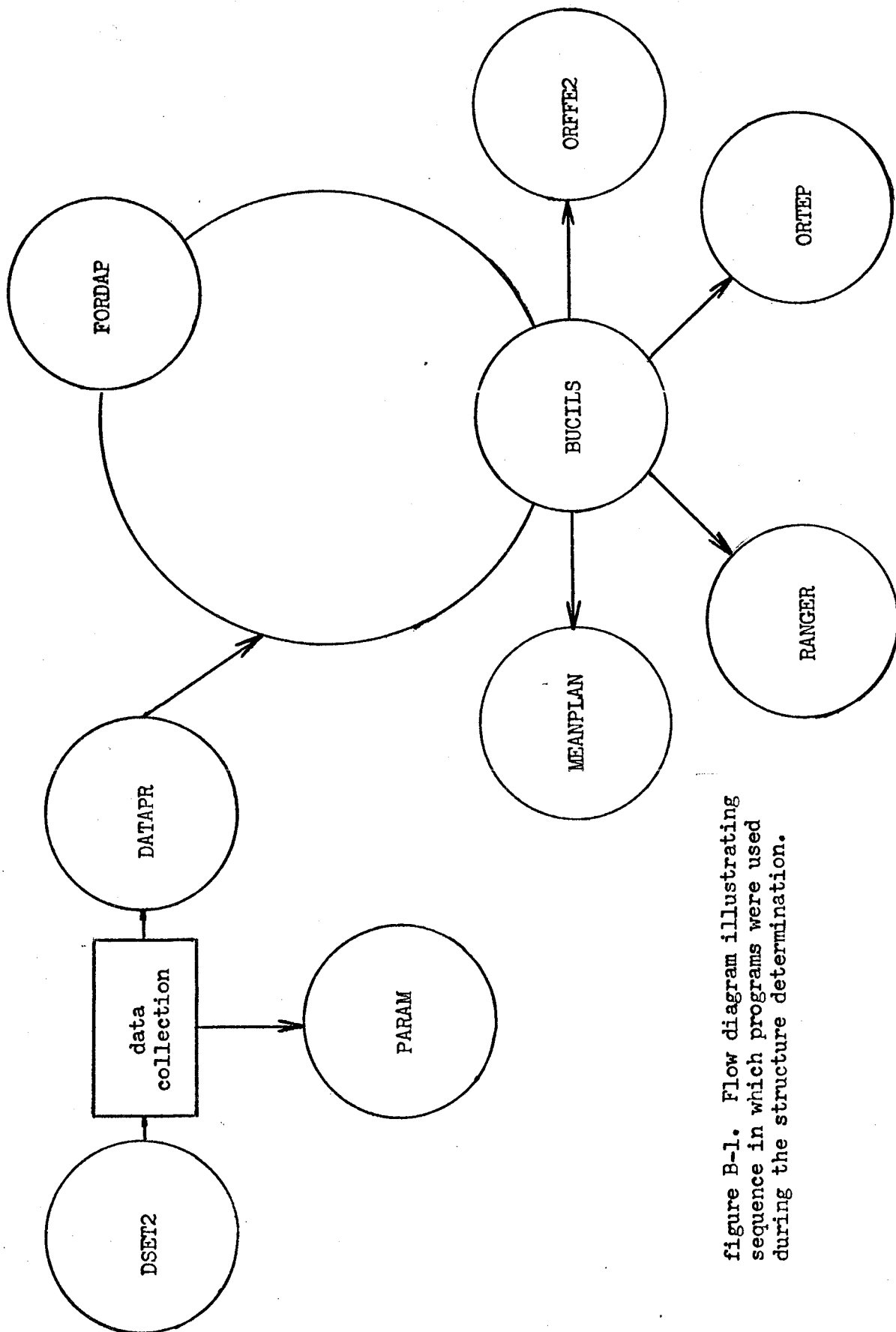


figure B-1. Flow diagram illustrating sequence in which programs were used during the structure determination.

Some of these programs have other functions which are not described here; functions not used are not described.

The output from one of these programs can be used, where necessary, as input for another without change of format.

DSET2: "A program to calculate goniostat settings for chi-ninety line-up on a real or imaginary reflection written by E.L. Enwall at Montana State University and further modified at Simon Fraser University." Input for this program includes indices of the chi-ninety reflection, the indices of a phi-zero reflection, the real cell constants, the wavelength of the radiation, and the scan width.

DATAPR: A program to convert raw intensity data into structure amplitudes, applying Lorentz and polarization corrections. The correction used is:

$$\frac{1}{L_p} = \frac{2 \sin 2\theta}{1 + \cos^2 2\theta}$$

This program was originally written by F.R. Ahmed and has been modified at Simon Fraser University. Input includes  $F(000)$ , the number of planes, the multiplicities of  $h00$ ,  $0k0$ ,  $hk0$ ,  $00c$ ,  $h0l$ ,  $0kl$  and  $hkl$ , the overall scale, and planes cards containing intensity and scale information.

BUCIIS: "Crystallographic structure factor and full-matrix least-squares." This program is a version of the original UCILS (Northwestern University and University of California, Irvine) and has

undergone various modifications at the University of British Columbia, and at Simon Fraser University. Input includes the real cell dimensions, symmetry information, scale factor and atomic parameters (both to be varied in the least-squares procedure), as well as observed structure factor information obtained from BUCFILE.

BUCILS was used to write the following files:

FORFILE: Contains calculated and observed structure factor information for use in analysis of R factors and weights (Program RANGER) and also for use in calculating electron density by Fourier synthesis (program FORDAP).

ORFFILE: Contains atomic coordinates and temperature factors, standard deviations for these atomic parameters, and the correlation matrix for the latest cycle of least-squares refinement.

FORDAP: A program to compute Fourier syntheses and Fourier difference syntheses of the structure factors, as well as to compute the Patterson function of  $F_{\text{obs}}^2$ . This program was originally written by A. Zalkin, University of California, and has undergone various modifications including that by J.A. Ibers, and also modifications at the University of Canterbury and the University of British Columbia. It is the University of British Columbia version (January 1969) which was used here. Input includes unit cell dimensions, symmetry information and the observed structure factors and the phases of the calculated structure factors from the FORFILE. In the case of the Patterson function computation, the observed structure factors were obtained from the BUCFILE.

RANGER: A program to analyze R factors and weights for different classes of reflections based on magnitudes,  $\sin \theta$  and indices.

This program was originally written by P.W.R. Corfield at Northwestern University; the University of British Columbia version (January 1969) used for this work is almost identical with a previous version of Dr. Corfield's program used at the University of Canterbury. Input includes the approximate maximum absolute value of a structure factor, the value of  $(NO-NV)$  (ie., the number of observations minus the number of variables), the wavelength of radiation used, and the information contained in the FORFILE.

ORFFE2: A program to calculate inter-atomic distances and angles with standard deviations, and to calculate root-mean-square displacements for thermal motion of atoms. The original program was written by W.R. Busing, K.O. Martin and H.A. Levy at Oak Ridge National Laboratory, Oak Ridge, Tennessee. This version has undergone modifications including that at Simon Fraser University. Input includes cell dimensions with their standard errors, and the information contained in the ORFFILE, viz., the correlation matrix, and atomic parameters from the latest cycle of refinement by BUCILS.

ORTEP: "A fortran thermal-ellipsoid plot program for crystal structure illustrations", written by Carroll K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee. This program has been modified slightly at Simon Fraser University. Input includes atomic coordinates and thermal parameters, as well as unit cell dimensions.

MEANPLAN: A program to calculate weighted mean planes through atom

groups and deviations of atoms from those planes. This program was originally written by M.E. Pippy and F.R. Ahmed of the National Research Council. The present is the University of British Columbia version (January 1969). Input includes atomic coordinates with estimated standard deviations, and unit cell dimensions.

PARAM: A program to calculate by a least-squares procedure cell dimensions from  $2\theta$  measurements of x-ray reflections. This program was obtained from Stewart by E.L. Enwall and revised, Montana State University, April, 1968. Input includes specification of lattice type, preliminary unit cell dimensions, and indices and  $2\theta$  measurements of x-ray reflections.

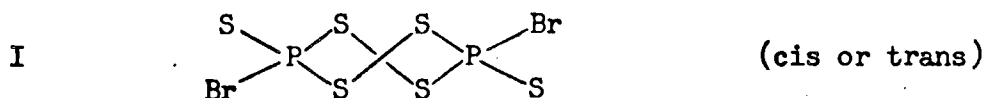
C. The preparations of  $P_2S_5Br_4$  and  $Na_2N_2O_2 \cdot 5H_2O$ .



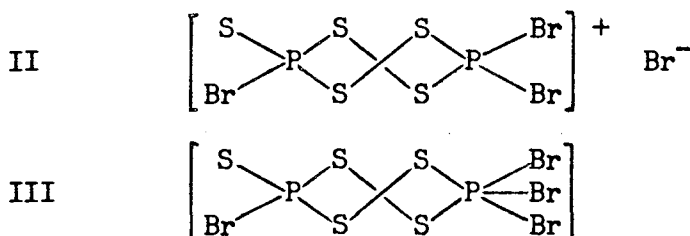
Two projects were attempted before the determination of the crystal structure of  $[\text{Rh}(\text{f}_6\text{fos})_2][\text{cis-Rh}(\text{CO})_2\text{Cl}_2]$  was undertaken. One was to prepare and determine the structure of crystals of  $\text{P}_2\text{S}_5\text{Br}_4$ . The other was to prepare and determine the structure of crystals of  $\text{Na}_2\text{N}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$ .

1. To obtain crystals and determine the structure of  $\text{P}_2\text{S}_5\text{Br}_4$ .

Discussion: The structure of  $\text{P}_2\text{S}_6\text{Br}_2$  (15), which is obtained from the same preparative reaction as  $\text{P}_2\text{S}_5\text{Br}_4$  (17), was found to involve a novel phosphorus-sulfur ring system containing S-S bonds:



This consistent with the statement previously made (17) that  $\text{P}_2\text{S}_6\text{Br}_2$  and  $\text{P}_2\text{S}_5\text{Br}_4$  must contain S-S bonds if the coordination of phosphorus with respect to sulfur is to be limited to four as expected. Because  $\text{P}_2\text{S}_5\text{Br}_4$  is prepared from the same reaction as  $\text{P}_2\text{S}_6\text{Br}_2$  and under the same conditions, and because of the limitation on the coordination of phosphorus with respect to sulfur, it is reasonable to suppose that  $\text{P}_2\text{S}_5\text{Br}_4$  also contains a  $\text{P}_2\text{S}_4$  ring with S-S bonds. Two likely structures for  $\text{P}_2\text{S}_5\text{Br}_4$  based on this ring structure are II and III:



It is noted that there is a tendency for phosphorus pentahalides to have ionic structures in the crystalline state (eg.  $[\text{PCl}_4]^+[\text{PCl}_6]^-$ ,  $[\text{PBr}_4]^+ \text{Br}^-$ ), thereby avoiding five-coordination. Because of this general tendency, and particularly because of the structure of  $\text{PBr}_5$ , structure II would seem preferable to III.

The possibility of the presence of this novel ring in the structure, and the uncertainty as to the ability of phosphorus to be five-coordinate in this situation, made this an attractive problem.

Preparation:  $P_4S_7$  first had to be prepared by the method of Stock and Herscovici (16). The preparation of  $P_2S_5Br_4$  was then attempted by the method of Andrews, Fergusson and Wilkins (17). The preparation required anhydrous and oxygen-free conditions, and any product decomposed before suitable crystals were obtained.

2. To obtain crystals and determine the structure of  $Na_2N_2O_2 \cdot 5H_2O$ .

Discussion: This was a desirable project to undertake for the following reasons: (i) there has recently been new interest in hyponitrous acid chemistry (26); (ii) we wished to confirm that the anion had the trans configuration, as indicated by ir evidence (27); (iii) the N-O bond length could be correlated with the NO stretching frequency (Raman) (27-29). It was expected to be rather long (1.2-1.3Å) as the NO stretching frequency was rather low ( $1390\text{cm}^{-1}$ ); (iv) the hydrogen bonding was of interest. At the time this project was undertaken we were not aware that the crystal structure had already been determined (30).

Preparation:  $Na_2N_2O_2 \cdot 5H_2O$  was prepared by the method given in Adams and Raynor (18). The product decomposed before acceptable crystals were obtained.

D. Description of weighting scheme used in this work.

The weighting factor for a given observed structure factor should be a measure of its reliability. Thus the weight that statistically should be used for a given observed structure factor is the reciprocal of its variance:

$$w_{F_0} = \frac{1}{\sigma_{F_0}^2}$$

where  $\sigma_{F_0}$  is the standard deviation for  $F_0$ , the observed structure factor.

However, weights are often taken as being roughly proportional to  $\frac{1}{|\overline{\Delta F}|^2}$ , where the  $|\overline{\Delta F}|$ 's are the mean  $|\Delta F|$ 's for different classes of structure factors based on magnitudes,  $\sin \theta$  or indices. ( $\Delta F = |F_0| - |F_c|$ ). If, for example, the  $|\overline{\Delta F}|$ 's were the mean  $|\Delta F|$ 's for classes based on magnitudes of the  $F_0$ 's, then a weighting function would be obtained from a plot of  $|\overline{\Delta F}|$  vs.  $|\overline{F_0}|$ , where the  $|\overline{F_0}|$ 's are mean values of  $|F_0|$  for classes of  $F_0$ 's of similar magnitudes. In this case the weighting function would be proportional to the reciprocal of a function which approximately describes the above plot:

$$w_{F_0} \propto \frac{1}{A + B|\overline{F_0}| + C|\overline{F_0}|^2}$$

In this work,  $A = 378.3599$ ,  $B = -3.4920$  and  $C = 0.0112$ .