THE STRUCTURE DETERMINATION OF SOME DI-(TERTIARY ARSINE) DERIVATIVES OF METAL CARBONYLS

by

PAUL J. ROBERTS

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Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

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ABSTRACT

Supervisor: Professor James Trotter

The structures of four di-(tertiary arsine) derivatives of metal carbonyls have been determined by a selection of direct, Patterson, and Fourier methods, applied to Mo-K_α diffractometer data.

1,2- bis(dimethylarsino)tetrafluorocyclobutene-tri-iron decacarbonyl, $Me_2As\overline{C{=}C(AsMe_2)CF_2CF_2}.Fe_3(CO)_{10}$, crystallizes in the monoclinic space group $P2_1/c$, with a = 11.60, b = 20.04, c = 22.11 Å, β = 93.7°, Z = 8 (two molecules per asymmetric unit). The structure was refined by least-squares procedures (a total of 74 atoms) to a final R of 0.09 for 2524 observed (of a total of 3234) reflections. The molecule is best described as a derivative of $Fe_3(CO)_{12}$, in which one terminal carbonyl group on each of the two equivalent iron atoms is replaced by an arsenic atom of the di-(tertiary arsine) ligand. The central Fe_3As_2 cluster is significantly bent in one of the molecules of the asymmetric unit, but is more nearly planar in the other molecule. The Fe-Fe bond distances in the iron triangle (2.53,2.65,2.65 Å) do not differ significantly from those in the parent compound.

Crystals of bis(1,2- bis(dimethylarsino)tetrafluorocyclobutene)triruthenium octacarbonyl, $(Me_2As\overline{C{=}C(AsMe_2)CF_2CF_2})_2.Ru_3(CO)_8$, are orthorhombic, space group $Pbcn$, a = 9.07,

$\underline{b}$ = 18.53, $\underline{c}$ = 21.81 Å, $\underline{Z}$ = 4 (one-half molecule per asymmetric unit). The structure was refined by least-squares procedures to a final $\underline{R}$ of 0.078 for 1507 observed (of a total of 1712) reflections. The molecule lies on a crystallographic two-fold axis, and is best described as a derivative of $Ru_3(CO)_{12}$ in which two carbonyls on one ruthenium and one carbonyl on each of the other ruthenium atoms are replaced by the arsenic atoms of the bidentate di-(tertiary arsine) ligands, in such a way that each ligand bridges two ruthenium atoms, and one Ru-Ru bond remains unbridged. This unbridged Ru-Ru bond (2.785 Å) is significantly shorter than the bridged ones (2.853 Å) and than those of the parent $Ru_3(CO)_{12}$ (average 2.848Å). The skeletons of the di-(tertiary arsine) ligands do not deviate significantly from exact planarity, the plane of each ligand being twisted 18° with respect to the plane of the ruthenium triangle. The mean Ru-As bond length is 2.407 Å.

1,2- bis(dimethylarsino)tetrafluorocyclobutene-triruthenium decacarbonyl, $Me_2As\overline{C{=}C(AsMe_2)CF_2CF_2}.Ru_3(CO)_{10}$, crystallizes in orthorhombic space group $\underline{P}2_12_12_1$, $\underline{a}$ = 8.594, $\underline{b}$ = 18.795, $\underline{c}$ = 16.69 Å, $\underline{Z}$ = 4. The structure was refined by least-squares procedures to a final $\underline{R}$ of 0.076 for 1828 observed (of a total of 2028) reflections. The compound is a derivative of $Ru_3(CO)_{12}$ in which one equatorial carbonyl group on each of two ruthenium atoms

is replaced by an arsenic atom of the di-(tertiary arsine) ligand in such a way that the plane of the ligand is twisted 18° with respect to the plane of the ruthenium triangle. Ru-Ru bond distances are 2.831, 2.831, and 2.858 Å, the difference between the short and long bond lengths being statistically significant and explicable in terms of the bonding characteristics of the ligand.

1,2- bis(dimethylarsino)hexafluoropropanemolybdenum tetracarbonyl, $Me_2AsCF(CF_3)CF_2AsMe_2.Mo(CO)_4$, crystallizes in the monoclinic space group $\underline{C}2/\underline{c}$, $\underline{a}$ = 25.06, $\underline{b}$ = 13.27, $\underline{c}$ = 11.56 Å, β = 102.8°, $\underline{Z}$ = 8. The structure was refined by least squares methods to a final $\underline{R}$ of 0.073 for 1510 observed (of a total of 1750) reflections. The molecule is derived from $Mo(CO)_6$ by replacing two carbonyl groups with the arsenic atoms of the chelating di-(tertiary arsine) ligand. Two of the carbon-fluorine bond distances (mean 1.50_5 Å) are significantly longer than the others (mean 1.30 Å) and the distance between the carbon atoms of the ligand skeleton is remarkably short (1.40 Å). The weighted mean Mo-As bond length is 2.572 Å.

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I. INTRODUCTION

A. THE TECHNIQUE OF X-RAY CRYSTAL ANALYSIS

As revealed by the innumerable organic and inorganic compounds, natural products, biologically important molecules, and alloys which have been examined in the sixty years since its discovery, the technique of x-ray crystal analysis has become an extremely powerful method of structure determination for chemists, biochemists, physicists and metallurgists. The application of the technique has been tremendously facilitated by the advent of electronic computers and mechanized data collection. However, there remains one obstacle in the way of completely universal applicability of the method. Although the amplitude of the wave diffracted by the crystal lattice can be measured, its phase cannot. To overcome this difficulty, several methods have been devised, of which the Patterson function, which uses the squares of the amplitudes (F's) of the diffracted waves, and direct methods, in which the phases are determined from the magnitudes of normalized structure factors (E's), are two of the most important, and ought to be discussed here in sufficient detail to clarify the ensuing descriptions of structure determination.

Since the structure amplitudes are Fourier transforms of the periodic electron density of the crystal lattice, (eq. 1.1), it follows that the electron density must therefore be the Fourier transform of the

structure amplitudes and can be written in terms of a Fourier series of which the structure amplitudes are coefficients (eq. 1.2).

$$\underline{F}_{\underline{hk\ell}} = \int_V \rho(\underline{x},\underline{y},\underline{z}) \exp\{2\pi i(\underline{hx} + \underline{ky} + \underline{\ell z})\}dv. \qquad (1.1)$$

$$\rho(\underline{x},\underline{y},\underline{z}) = \frac{1}{V} \sum_{\underline{hk\ell}}\sum\sum \underline{F}_{\underline{hk\ell}} \exp\{-2\pi i(\underline{hx} + \underline{ky} + \underline{\ell z})\} \qquad (1.2)$$

However, each structure amplitude has an associated unknown phase, and the electron density cannot be calculated directly from experimentally observed quantities. However, if part of the structure is known, structure factors based on the positions of these known atoms can be calculated and the phases of these calculated structure factors can be assumed to be approximations to the correct phases. An electron density map calculated using these approximate phases is expected to reveal additional elements of the structure and new structure factors, whose phases will be closer to the correct values, can be calculated. The iterative application of this process results in a complete structure, the approximate atomic positions of which are then refined by least-squares methods to yield final refined parameters with a final set of phases. This method is particularly successful if the atoms of the known portion of the molecule constitute a large fraction of the scattering matter in the unit cell. Apparently the sole obstacle of structure determination is the inability to locate a starting

segment in the unit cell and it is to this problem that we now turn our attention.

Early in the history of x-ray crystallography[1], it was shown that a Fourier series (eq. 1.3) of which the coefficients were the phaseless squares of the amplitudes of the diffracted waves, produced a map which contained peaks at positions corresponding to the ends of vectors between atomic positions.

$$P(\underline{x},\underline{y},\underline{z}) = \frac{1}{v} \sum_{\underline{hk\ell}}\sum\sum |\underline{F}_{\underline{hk\ell}}|^2 \cos 2\pi(\underline{hx} + \underline{ky} + \underline{\ell z}) \quad (1.3)$$

By considering the symmetry requirements of the space group of crystallization, it would then seem a straightforward matter to locate the molecule in the unit cell. There are, however, several drawbacks to the method. Peaks in the vector distribution tend to be very much broader than in the electron distribution and the vector map can become diffuse and complicated if the molecule contains more than a few atoms. Since the intensity of the vector peak is proportional to the product of the atomic numbers of the atoms to which it corresponds, it is obvious that vectors between relatively heavy atoms will appear much more intense than vectors between the lighter atoms. Provided that the structure is dominated by a relatively small number of heavy atoms, the vector map can usually be unravelled and atomic positions assigned to these atoms.

We have seen that the presence of a large number

of atoms of similar atomic number is detrimental to the ease with which a solution can be extracted from the Patterson map, but that a small number of relatively heavy atoms makes this a powerful method. The reverse is true for direct methods, by which process phases are assigned from a statistical analysis of the structure amplitudes. The theory is formulated[2,3] on a random arrangement of similar atoms but has been successfully applied to many crystal structures which contain atoms of extremely different atomic numbers.

The cornerstone of direct methods in centrosymmetric space groups is the relation

$$\underline{F}_{\underline{hk\ell}} = \Phi_{\underline{hk\ell}} \sum_{\underline{h}'} \sum_{\underline{k}'} \sum_{\underline{\ell}'} \underline{F}_{\underline{h}'\underline{k}'\underline{\ell}'} \cdot \underline{F}_{\underline{h}-\underline{h}'\,\underline{k}-\underline{k}'\,\underline{\ell}-\underline{\ell}'} \qquad (1.4)$$

where $\Phi_{\underline{hk\ell}}$ is a simple scaling term. Although it appears that one $\underline{F}$ can be determined only if the magnitudes and phases of all others are known, the series must tend strongly in one direction (+ or -) if $\underline{F}_{\underline{hk\ell}}$ is sufficiently large, and this direction is determined by the agreement in signs among products of large $\underline{F}$'s[3]. We can therefore write the following relation.

$$S(\underline{F}_{\underline{hk\ell}}) \sim S(\underline{F}_{\underline{h}'\underline{k}'\underline{\ell}'}) \cdot S(\underline{F}_{\underline{h}-\underline{h}'\,\underline{k}-\underline{k}'\,\underline{\ell}-\underline{\ell}'}) \qquad (1.5)$$

where S means "the sign of" and ~ means "is probably equal to".[4] The probability with which this equation holds depends

on the magnitudes of the three reflections and is given by

$$P = \tfrac{1}{2} + \tfrac{1}{2}\tanh\{\sigma_3/\sigma_2^{3/2}\ |\underline{E}_{\underline{hk\ell}} \cdot \underline{E}_{\underline{h}'\ \underline{k}'\ \underline{\ell}'} \cdot \underline{E}_{\underline{h}-\underline{h}'\ \underline{k}-\underline{k}'\ \underline{\ell}-\underline{\ell}'}|\} \tag{1.6}$$

where $\sigma_3/\sigma_2^{3/2}$ is a parameter dependent on the contents of the unit cell and independent of their location and where $\underline{E}$'s are defined by

$$\underline{E}_{\underline{hk\ell}} = |\underline{F}_{\underline{hk\ell}}|^2/\varepsilon\sum_i^N f_i^2 \tag{1.7}$$

where ε is an integer which takes on different values for different classes of reflections.

A slightly more rigourous treatment of eq. 1.4 results in the most commonly used form of Sayre's equation.

$$S(\underline{F}_{\underline{hk\ell}}) \sim \sum_{\underline{h}'}\sum_{\underline{k}'}\sum_{\underline{\ell}'} S(\underline{F}_{\underline{h}'\underline{k}'\underline{\ell}'}) \cdot S(\underline{F}_{\underline{h}-\underline{h}'\ \underline{k}-\underline{k}'\ \underline{\ell}-\underline{\ell}'}) \tag{1.8}$$

with corresponding probability

$$P_+(\underline{E}_{\underline{hk\ell}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh(\sigma_3/\sigma_2^{3/2}|\underline{E}_{\underline{hk\ell}}|\sum_{\underline{h}'}\sum_{\underline{k}'}\sum_{\underline{\ell}'}\underline{E}_{\underline{h}'\underline{k}'\underline{\ell}'} \cdot \underline{E}_{\underline{h}-\underline{h}'\underline{k}-\underline{k}'\underline{\ell}-\underline{\ell}'}) \tag{1.9}$$

where P_+ is the probability that the sign of $\underline{E}_{\underline{hk\ell}}$ is positive. If the value of the summation in eq. 1.9 is negative, P_+ will be less than $\tfrac{1}{2}$ and will imply that the sign of $\underline{E}_{\underline{hk\ell}}$ is negative with a probability

$$P_- = 1 - P_+$$

In practice, phases are assigned to a small number of reflections and Sayre's equations are applied

to determine others. This can be achieved in several ways.

An initial set of ten very large reflections can be allowed to take on all possible combinations of plus and minus signs. This would result in 2^{10} possibilities, of which several will be more consistent (i.e. have higher probabilities) than the others. Each of these highly probable combinations is then taken as a starting set and phases are generated for the remaining reflections by applying Sayre's equations.

An alternative approach arises as a consequence of the fact that the origin of a centrosymmetric unit cell can be arbitrarily located at any centre of symmetry. Three or sometimes fewer reflections, depending on the space group, can be assigned arbitrary phases, corresponding to the choice of origin. Three or four other reflections are allowed to take all possible combinations of plus and minus signs, resulting in 8 or 16 possible solutions.

Either method is completed by calculating an electron density map using the phases of those solutions of highest probability.

B. CHARACTERISTICS OF METAL CARBONYLS AND THEIR DERIVATIVES

Numerous reviews have appeared recently describing metal-carbon bonding,[5-7] preparation, properties, and structure of metal carbonyls,[8,9] metal atom clusters[10] and Lewis base substituted carbonyl complexes.[11-14] The principal conclusions of these studies ought to be reviewed briefly as background to the material to be presented in following parts of this thesis.

The most regular feature of the metal carbonyls and their derivatives is the adherence of most of these compounds to the "effective atomic number" or "inert gas" law[15] which requires that the central atom accept from the ligands sufficient electrons that the total number of electrons around the metal atom results in a closed shell configuration. For example, the compound $Fe(CO)_2(NO)_2$ can be considered to consist of Fe(0) (26 electrons), two carbonyl groups (2×2 electrons) and two nitrosyl groups (2×3 electrons), for a total of 36 electrons, the krypton configuration. Since various ligands donate from one to a dozen electrons, the co-ordination number for a given metal atom will vary from one compound to another depending on the combination of ligands used to complete the inert gas configuration. For instance, inert gas configuration species exist for iron with co-ordination numbers of four (dicarbonyldinitrosyliron), five (pentacarbonyliron) and six (di-iodotetracarbonyliron).

It is obvious that an integral number of pair-donating ligands can complete the valence shell of a metal of even atomic number, whereas metal atoms of odd atomic number must receive an additional single electron. This requirement can be accommodated in several ways. A ligand which donates an odd number of electrons can be employed, resulting in compounds exemplified by $Co(NO)(CO)_3$ and $HCo(CO)_4$, or the odd electron on each atom can be shared with another such atom, resulting in a metal-metal bond, as in $Co_2(CO)_8$.

Besides this regularity in stoichiometry, metal carbonyls and their derivatives are characterized by the actual nature of the metal-ligand bond. The carbon atom of carbon monoxide possesses an sp hybridized lone pair of electrons which forms a σ-bond by overlap with a vacant transition metal orbital of the proper symmetry. The carbon monoxide group also has vacant π-antibonding orbitals which form a π-bond by overlap with filled non-bonding d orbitals on the metal atom. The metal-carbon bond order in these complexes must thereby be greater than unity, requiring a concurrent decrease in carbon-oxygen bond order. The presence of multiple bonding between metal and carbon atoms is reflected by the fact that x-ray studies show that the metal-carbon bond length is distinctly shorter than the sum of the single bond radii.[16]

Other ligands found in stable substitution complexes of metal carbonyls also possess both σ-donor and

π-acceptor properties. On ligands such as substituted phosphines and arsines, the acceptor properties arise from empty d orbitals on the phosphorus or arsenic atoms.

It has been found that most complexes of π-bonding ligands contain metals in low oxidation states. This can be explained in terms of the description of bonding presented above, since a positive charge on a metal atom enhances its acceptor properties but decreases its back-bonding capability whereas the presence of a negative charge produces the opposite effects. Since both σ- and π-bonding appear to be required for stable complexes, the presence of an electronic charge, either positive or negative, will inhibit this type of complex formation.

The four structures included in this thesis have been chosen since, as di-(tertiary arsine) derivatives of metal carbonyls, they represent a unified topic for study and discussion in terms of the principles established in this introduction. Because of the complexity of their systematic names, the ligands $Me_2AsC{=}C(AsMe_2)CF_2CF_2$ and $Me_2AsCF(CF_3)CF_2AsMe_2$ will often be denoted by the symbols L and L' respectively.

C. RESULTS OF PRELIMINARY EXPERIMENTS

Before an x-ray analysis is undertaken, several other experiments are often carried out, and the results of these experiments can lead to some idea of the structure of the compound under investigation. This is the case for three of the compounds in this thesis and these structural indications will now be discussed.

The infra-red, n.m.r. and Mössbauer spectra[17] of $LFe_3(CO)_{10}$ suggest a structure in which two terminal carbonyl groups of the two equivalent iron atoms of $Fe_3(CO)_{12}$[18] are replaced by the arsenics of the di-(tertiary arsine) ligand (Figure I.1). The presence of only one ^{19}F resonance in the n.m.r. spectrum indicates that all the fluorine atoms are equivalent, so that the di-(tertiary arsine) ligand would be expected to be planar, in contrast to the previously determined structure of $LFe_2(CO)_6$, in which the ligand is bent as a result of the formation of a π-bond from the cyclobutene system to one of the iron atoms.[19]

The ^1H n.m.r. spectrum of $L_2Ru_3(CO)_8$ contains two singlets, indicating a moderately symmetrical structure for the ligand. The ^{19}F n.m.r. spectrum[20] is a complex arrangement of fourteen peaks with some similarity to the spectrum of $LFe(CO)_4$, where only one arsenic atom of the ligand is bonded to the iron atom.[21] These two pieces of evidence, and the observation that the ligand is normally reluctant to chelate, favour the structure shown in Figure

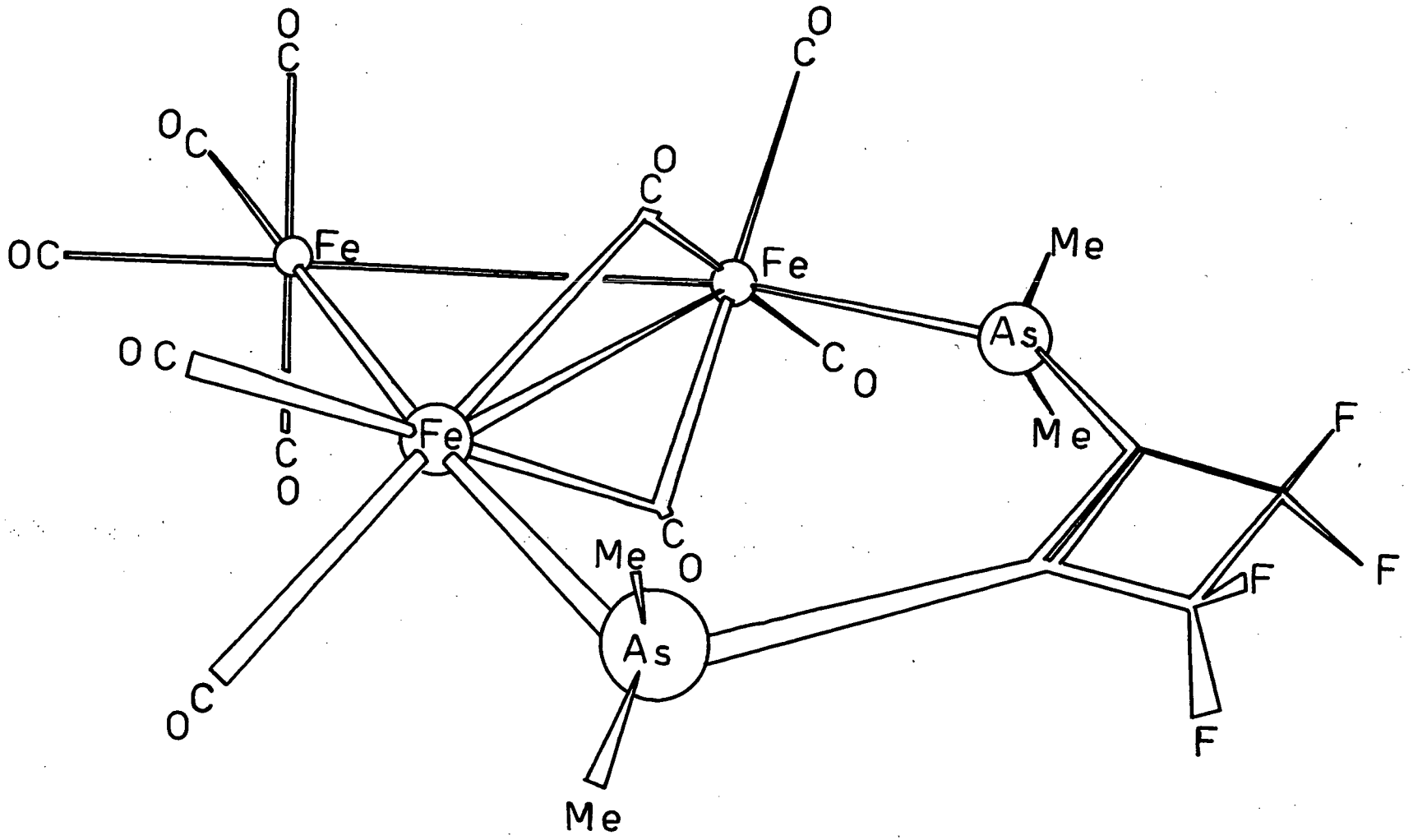
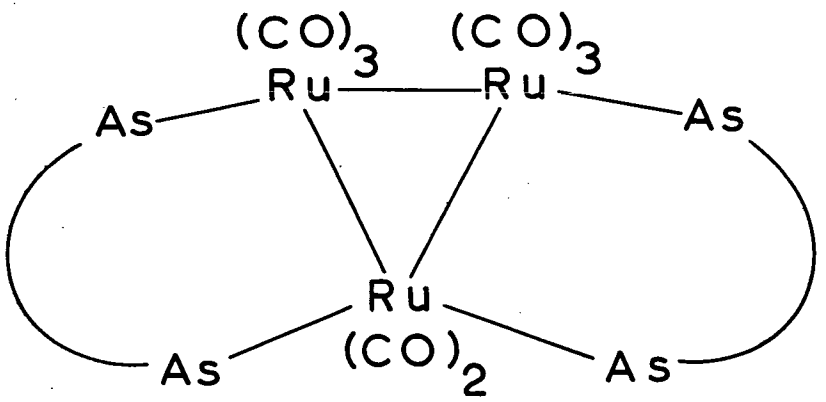


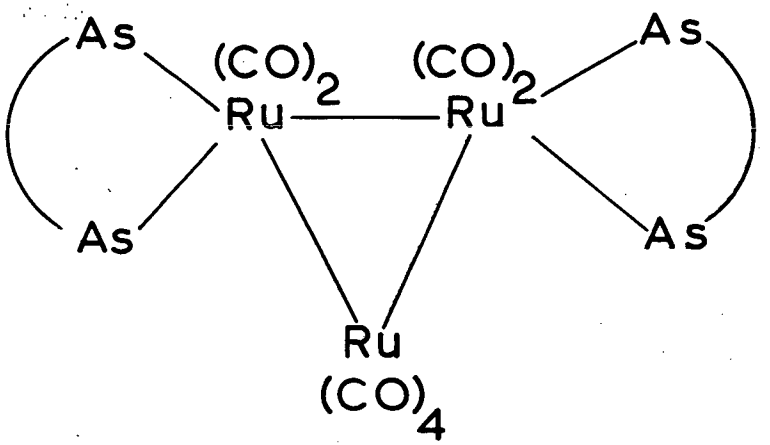
Figure I.1 Structure of $Me_2AsC{=}C(AsMe_2)CF_2CF_2 \cdot Fe_3(CO)_{10}$ expected on the basis of preliminary experiments.

I.2a rather than that of Figure I.2b.

The ^{19}F and ^{1}H n.m.r. spectra[20] of $LRu_3(CO)_{10}$ both consist of singlets, indicating a highly symmetrical structure for this complex. This could be accomplished by having the ligand either chelating (Figure I.3a) or bridging (Figure I.3b) in an equatorial position. The latter is favoured because of the similarity of the infra-red spectra of $LFe_3(CO)_{10}$ and $LRu_3(CO)_{10}$ in the terminal carbonyl region and because of the known reluctance of the ligand to chelate without also involving the double bond of the cyclobutene ring.

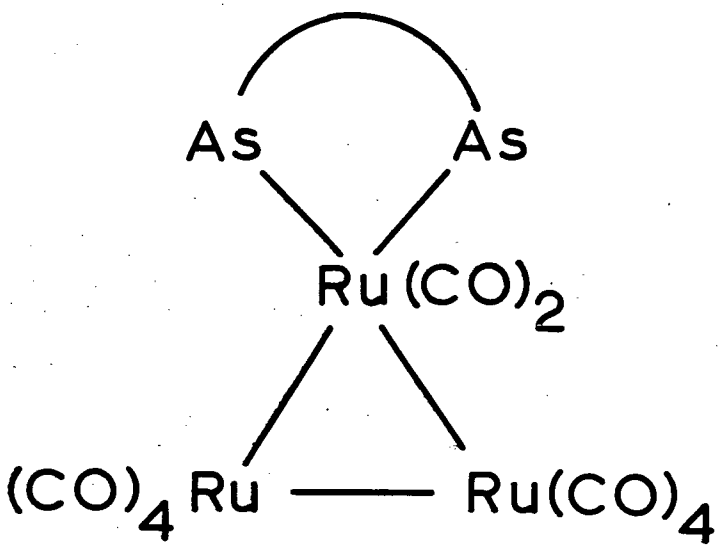


(a)

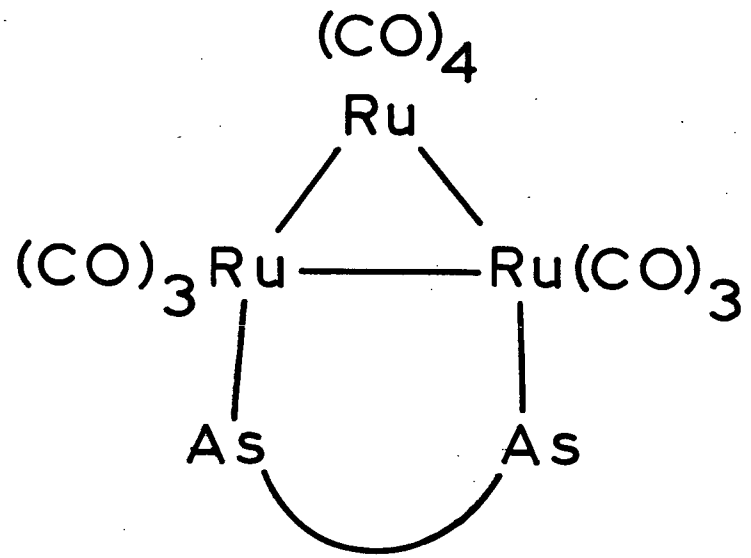


(b)

Figure I.2 Two possible structures for $(Me_2AsC{=}C(AsMe_2)CF_2CF_2)_2 \cdot Ru_3(CO)_8$.



(a)



(b)

Figure I.3 Two possible structures for $Me_2AsC{=}C(AsMe_2)CF_2CF_2 \cdot Ru_3(CO)_{10}$.

II. EXPERIMENTAL SECTION

$LFe_3(CO)_{10}$ is obtained by chromatography of the mixture of products formed by ultraviolet irradiation of $Fe_3(CO)_{12}$ and the di-(tertiary arsine).[17] The crystals are black needles elongated along a. The intensity data were collected using a sample of dimensions 0.3 ×0.03 × 0.04 mm.

$L_2Ru_3(CO)_8$ is prepared by chromatography of the products of the reaction of $Ru_3(CO)_{12}$ with the ligand refluxed in hexane.[20] The crystal used to record the data was an irregular plate with {001} developed. Its dimensions were 0.05 mm. parallel to c and about 0.2 mm. across.

Ultraviolet irradiation of equimolar quantities of $Ru_3(CO)_{12}$ with the di-(tertiary arsine) results in the formation of $LRu_3(CO)_{10}$.[20] A single flake of the compound of dimensions 0.07 ×0.44 ×0.25 mm. was recrystallized from diethyl ether for use in intensity measurements.

$L'Mo(CO)_4$ is prepared by recrystallization from petroleum ether-benzene of the products formed by refluxing $Mo(CO)_6$ with the ligand in toluene.[22] The crystals are colourless needles elongated along c. Intensity data were recorded using a specimen of dimensions 0.16 ×0.07 ×0.57 mm.

Unit cell and space group data for each compound were obtained by photographic methods and accurate lattice parameters for each were determined by least-squares treatment of $\sin^2\theta/\lambda^2$ values for thirty reflections measured on a diffractometer with Mo-K_α radiation.[23]

Reflection intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Mo-K_α radiation (Zr filter and pulse-height analyser), and a θ-2θ scan. The scan range in 2θ was $(1.80 + 0.86 \tan\theta)$ degrees and backgrounds were measured at both ends of each scan.

The standard deviation of an intensity was calculated from the counting statistics using

$$\sigma^2(I) = S + B + (dS)^2$$

where S = scan count

B = background, corrected to time of scan

$I = S - B$

d = an empirical constant which allows for unknown experimental errors; values used for each structure are given in Table II.I

Reflections whose intensities were less than 1σ were classified as unobserved. Lorentz and polarization factors were applied and the structure amplitudes were derived. Absorption corrections were not applied.

Crystal data and parameters of data collection are given in Table II.I.

Table II.I

Crystal and experimental data.

	$LFe_3(CO)_{10}$	$L_2Ru_3(CO)_8$	$LRu_3(CO)_{10}$	$L'Mo(CO)_4$†
formula	$C_{18}H_{12}As_2F_4Fe_3O_{10}$	$C_{24}H_{24}As_4F_8Ru_3O_8$	$C_{18}H_{12}As_2F_4Ru_3O_{10}$	$C_{11}H_{12}As_2F_6MoO_4$
molecular weight (gm.)	781.2	1195.3	917.3	567.7
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
cell dimensions (Å,deg.)	$\underline{a}$ = 11.60(2)	$\underline{a}$ = 9.07(1)	$\underline{a}$ = 8.594(3)	$\underline{a}$ = 25.06(2)
	$\underline{b}$ = 20.04(2)	$\underline{b}$ = 18.53(1)	$\underline{b}$ = 18.795(5)	$\underline{b}$ = 13.27(2)
	$\underline{c}$ = 22.11(2)	$\underline{c}$ = 21.81(1)	$\underline{c}$ = 16.69(5)	$\underline{c}$ = 11.56(2)
	β = 93.7(2)			β = 102.8(2)
volume (Å^3)	5129	3666	2696	3749
measured density (gm./cm^3)	2.01±0.02	2.14±0.02	2.22±0.02	2.04±0.02
flotation in	$CC\ell_4/CH_3I$	$CC\ell_4/CHBr_3$	$CC\ell_4/CHBr_3$	$CC\ell_4/CHBr_3$
$\underline{Z}$	8	4	4	8
calculated density (gm./cm^3)	2.02	2.17	2.26	2.01
$\underline{F}$(000)	3040	2272	1736	2096
absorption coefficient μ (cm.$^{-1}$) (Mo-$\underline{K}_\alpha$)	45	51	43	45
space group	$\underline{P}2_1/\underline{c}$ ($\underline{C}_{2h}^5$)	$\underline{Pbcn}$ ($\underline{D}_{2h}^{14}$)	$\underline{P}2_12_12_1$ ($\underline{D}_2^4$)	$\underline{C}2/\underline{c}$ ($\underline{C}_{2h}^6$)

Table II.I (continued)

absent spectra	$h0\ell$ $\ell = 2n+1$ $0k0$ $k = 2n+1$	$0k\ell$ $k = 2n+1$ $h0\ell$ $\ell = 2n+1$ $hk0$ $h+k = 2n+1$	$h00$ $h = 2n+1$ $0k0$ $k = 2n+1$ 00ℓ $\ell = 2n+1$	$hk\ell$ $h+k = 2n+1$ $h0\ell$ $\ell = 2n+1$
2θ (Mo-K_α) max. (deg.)	35	40	45	40
minimum interplanar spacing (Å)	1.18	1.04	0.93	1.04
number of reflections with $2\theta < 2\theta$ max.	3234	1712	2028	1750
number of unobserveds	710	205	200	240
d in σ^2 expression	0.04	0.02	0.02	0.02
axis mounted parallel to ϕ axis of diffractometer	a*	a	c	c
scan speed (deg./min.)	4	2	2	2
time for background (sec.)	10	20	20	20

† L and L' represent the ligands $Me_2AsC{=}C(AsMe_2)CF_2CF_2$ and $Me_2AsCF(CF_3)CF_2AsMe_2$ respectively

III. THE STRUCTURE DETERMINATION OF $Me_2As\overline{C{=}C(AsMe_2)CF_2CF_2}\cdot Fe_3(CO)_{10}$

STRUCTURE ANALYSIS

The asymmetric unit contains two molecules, so that, with ten heavy atoms, the Patterson function was complicated. Two possible orientations appeared in the origin region, but as a result of the large number of peaks, it was not immediately possible to derive any further information.

An attempt was then made to solve the structure by direct methods using Hoge's series of four programs[24] which apply Sayre relationships in two dimensions in the Vand and Pepinsky[25a] version of the Cochran and Douglas procedure.[25b] The initial program first calculates a Wilson plot[2] for the data and outputs an overall scale and an overall temperature factor and then calculates and outputs normalized structure factors ($\underline{E}$'s). Average values of $|\underline{E}|$ and $|\underline{E}^2|$ are then calculated to indicate the presence or absence of a centrosymmetric electron distribution. The second program reads the tape output of the first and sorts the data into parity groups, including only those reflections for which $|\underline{E}|$ exceeds a specified value. The next stage of this program involves the determination of all Sayre relationships and the calculation of the probability with which each holds. The third program of the series uses these Sayre relationships to determine possible solutions, rejecting those for which, for any $\vec{h}$

$$\text{SMAX} = \sum_{\vec{h}} |\underline{E}_{\vec{h}}| \cdot |\underline{E}_{\vec{k}}| \cdot |\underline{E}_{\vec{h}-\vec{k}}| \qquad (3.1)$$

(where $\vec{h}$ is a reflection contained in a Sayre relationship which fails) exceeds a preset value.

Since the probability that the sign of $\underline{E}_{\vec{h}}$ is correctly given by the Sayre relationships in which it is involved is calculated from the expression

$$P(\vec{h}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh(\sigma_3/\sigma_2^{3/2} \sum_{\vec{k}} |\underline{E}_{\vec{h}}| \cdot |\underline{E}_{\vec{k}}| \cdot |\underline{E}_{\vec{h}-\vec{k}}|) \qquad (3.2)$$

then if only Sayre relationships which fail are included in the summation, eq. 3.2 becomes the probability that the sign of $\vec{h}$ is opposite to that given in the solution. Hence by setting a value of SMAX corresponding to a probability of 0.985, all solutions for which any sign is incorrect to the extent of this probability can be rejected.

Those solutions which are within the limits of SMAX are printed out with the maximum value of this quantity attained for any reflection in each solution, as well as the number of plus signs in the solution and the value of the following expression

$$\text{SEEE**2} = \sum_{\vec{h}} (\sum_{\vec{k}} |\underline{E}_{\vec{h}}| \cdot |\underline{E}_{\vec{k}}| \cdot |\underline{E}_{\vec{h}-\vec{k}}|)^2 \qquad (3.3)$$

where $\vec{h}$ is a reflection contained in a Sayre relationship which fails.

The most probable solution would then be expected to be that which has approximately equal numbers of plus and minus signs and the minimum values for SMAX and SEEE**2.

The fourth program uses the E's from the first program and the signs from the third to produce a tape suitable for input to a Fourier calculation program containing up to six solutions at once, specified only by the number of the solution as it is generated.

In the present work, the a-axis projection was examined and the signs of 34 $0k\ell$ reflections with normalized structure factor $|E| > 1.4$ were determined. Table III.I contains a comparison of the 51 solutions which meet the acceptance criteria mentioned above. Sets 17,18,24,26, 29, and 33 were used as input to a Fourier calculation. Set 29 was outstanding in having the lowest probability in the opposite-indication-of-sign test, and the E-map (Figure III.1) computed with this set of signs revealed the positions, in projection, of the ten heavy atoms in the asymmetric unit.

With this information on the y- and z-parameters of the heavy atoms, attention was refocussed on the Patterson function, and the three-dimensional structure of the two heavy atom units was derived. Sixty-one of the sixty-four carbon, oxygen, and fluorine atoms were located from a Fourier summation with phases based on the iron and arsenic atoms, and the three remaining atoms were found on a subsequent electron density map.

Preliminary least-squares refinement of the parameters utilized the block-diagonal approximation, and re-

Table III.I

Comparison of 51 solutions from

Hoge's sign determination program

Set	Number of pluses	SMAX	SEEE**2	Set	Number of pluses	SMAX	SEEE**2
1	21	12.4	1026	22	18	12.4	1525
2	22	12.8	985	23	20	12.8	1449
3	20	12.4	992	24	16	12.3	710
4	21	12.8	951	25	17	12.3	1192
5	23	12.9	1450	26	16	12.0	587
6	20	12.4	1355	27	17	12.0	1005
7	21	12.8	1275	28	25	11.9	1269
8	20	12.4	1072	29	17	10.2	686
9	22	12.4	1200	30	21	12.8	1409
10	17	12.4	1196	31	22	12.9	1612
11	21	12.8	1159	32	20	12.8	1690
12	21	12.4	1213	33	20	12.8	878
13	16	12.4	1578	34	21	12.8	1380
14	20	12.8	1173	35	24	12.8	1437
15	19	12.3	1204	36	23	12.3	1239
16	22	12.3	1069	37	24	12.8	1342
17	21	11.8	541	38	19	11.3	1091
18	20	11.3	969	39	18	12.8	1194
19	23	12.8	1147	40	18	12.9	1254
20	22	12.9	1671	41	17	12.3	1080
21	21	12.4	1529	42	17	12.8	924

Table III.I (continued)

Set	Number of pluses	SMAX	SEEE**2	Set	Number of pluses	SMAX	SEEE**2
43	16	12.8	1416	48	19	12.8	1415
44	24	12.8	1606	49	16	12.0	1241
45	16	11.2	940	50	15	12.8	1275
46	22	12.8	1773	51	18	12.7	1084
47	18	12.3	1381				

duced $\underline{R}$ to 0.11. At this stage, a three-dimensional difference map showed electron density fluctuations around the iron and arsenic atoms which indicated anisotropic thermal motion. Refinement was continued using a modified full-matrix procedure. The function minimized was $\Sigma \underline{w}(\underline{F}_o - \underline{k}\underline{F}_c)^2$ with $\underline{w} = \{\underline{A} + \underline{B}|\underline{F}_o| + \underline{C}|\underline{F}_o|^2 + \underline{D}|\underline{F}_o|^3\}^{-1}$ for the observed reflections. Unobserved reflections were excluded from the refinement but included in the final structure factor calculation. The coefficients $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$ were adjusted by a short least-squares program written by the author (see Section VII) to achieve best constancy of local averages of $\Sigma \underline{w}(\underline{F}_o - \underline{k}\underline{F}_c)^2$ over the full range of $|\underline{F}_o|$, the final values being 600, 0.3, -0.06, and 0.00027 respectively. Scattering factors were from ref. 26 and included the real part of the dispersion correction. The variables refined were the positional parameters, anisotropic thermal parameters for the ten heavy atoms, isotropic thermal parameters for the other atoms, and a single overall scale factor, a total of

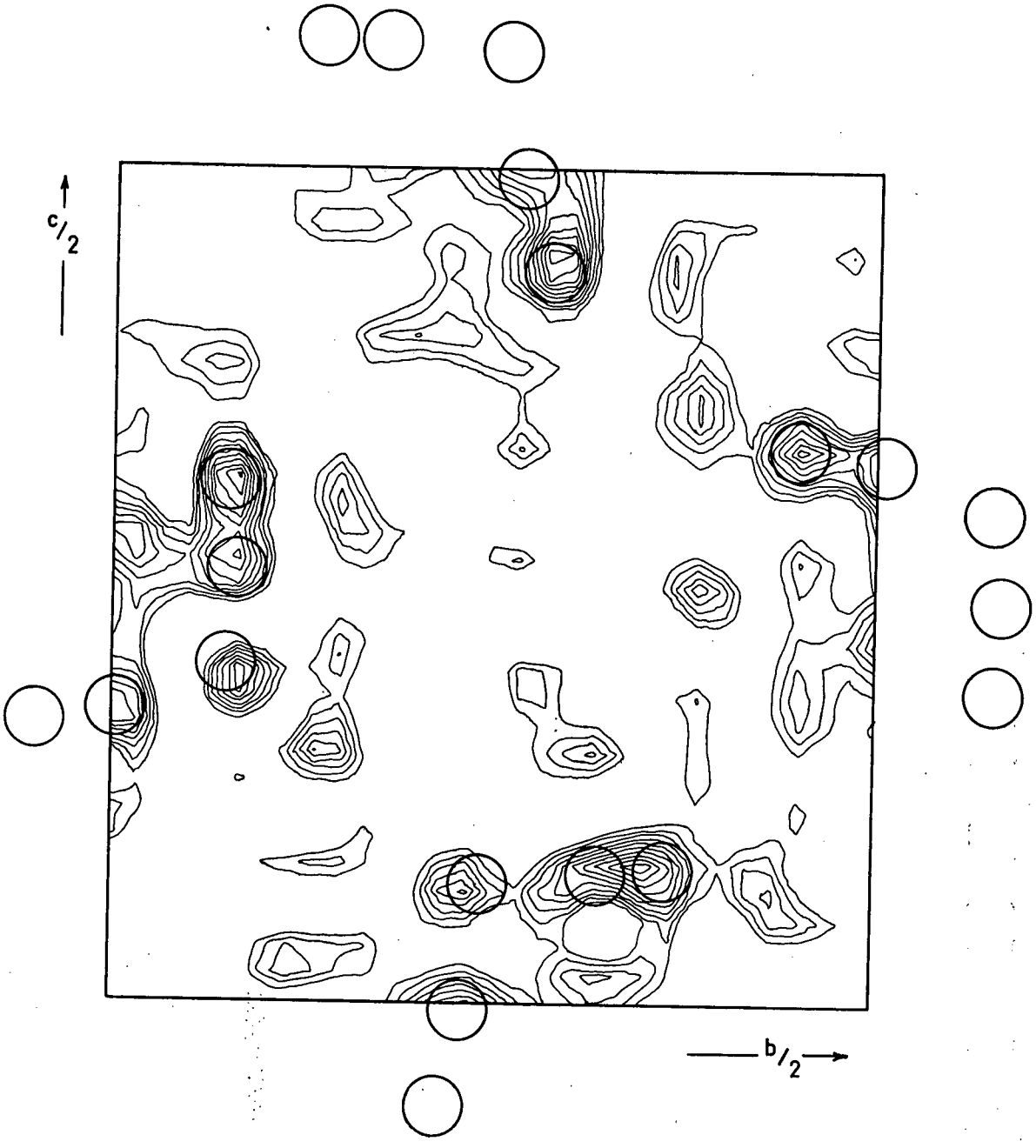


Figure III.1 E-map with final refined positions of heavy atoms superimposed.

347 variables. Since the dimensions of the computer program used were limited to 249 variables, it was necessary to vary different combinations of parameters in successive cycles. No parameter correlation coefficients greater than 0.35 were observed, and full convergence was reached after six cycles. Final values of $\underline{R}$ and $\underline{R}_{\underline{w}}$ † were 0.090 and 0.096 respectively for the 2524 observed reflections and 0.131 and 0.117 respectively for all data. A final difference synthesis showed maximum fluctuations of ±0.8 e/Å^3. Final observed and calculated structure factors are given in Table III.II.

Final positional and thermal parameters are given in Table III.III, together with their standard deviations calculated from the inverse matrix of the last refinement cycle. The weighted mean planes of the iron triangle and di-(tertiary arsine) ligand of each molecule are given in Table III.IV, and the bond distances and valency angles are in Table III.V.

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† $\underline{R} = \Sigma|\underline{F}_{\underline{o}}-\underline{F}_{\underline{c}}|/\Sigma|\underline{F}_{\underline{o}}|$; $\underline{R}_{\underline{w}} = \{\Sigma\underline{w}(\underline{F}_{\underline{o}}-\underline{F}_{\underline{c}})^2/\Sigma\underline{w}\underline{F}_{\underline{o}}^2\}^{1/2}$

Table III.II

Final measured and calculated structure factors. Unobserved reflections have an asterisk after the $|F_o|$ value.

K	L	OBS	CALC
**** H = 0 ****			
0	2	17*	4
0	4	177	193
0	6	45	49
0	8	390	380
0	10	0*	54
0	12	268	271
0	14	24*	55
0	16	107	109
0	18	46	56
1	1	100	51
1	3	198	203
1	5	203	195
1	7	157	159
1	9	71	76
1	11	109	105
1	13	282	280
1	15	167	165
1	17	0*	5
1	19	0*	15
2	0	51	52
2	2	161	165
2	4	844	829
2	6	337	357
2	8	57	54
2	10	76	76
2	12	251	249
2	14	43	31
2	16	157	156
2	18	101	103
3	1	78	77
3	3	0*	47
3	5	0*	10
3	7	207	204
3	9	100	99
3	11	0*	93
3	13	237	233
3	15	47	51
3	17	15*	32
3	19	77	83
4	0	186	192
4	2	135	135
4	4	0*	15
4	6	376	357
4	8	80	76
4	10	136	135
4	12	80	76
4	14	184	196
4	16	44	44
4	18	99	99
5	1	76	80
5	3	57	51
5	5	61	49
5	7	44	44
5	9	37	34
5	11	110	115
5	13	0*	6
5	15	137	135
5	17	0*	4
5	19	47	29
6	0	111	111
6	2	54	54
6	4	115	130
6	6	114	125
6	8	112	112
6	10	25	25
6	12	71	83
6	14	96	96
6	16	45	41
6	18	0*	1
7	1	94	92
7	3	56	41
7	5	0*	1
7	7	44	44
7	9	55	55
7	11	0*	4
7	13	0*	6
7	15	0*	1
7	17	0*	1
7	19	0*	1
8	0	62	63
8	2	474	396
8	4	320	293
8	6	199	193
8	8	261	246
8	10	449	459
8	12	184	178
8	14	199	171
8	16	0*	10
8	18	0*	77
9	1	207	207
9	3	97	89
9	5	184	185
9	7	127	127
9	9	41	41
9	11	0*	5
9	13	0*	1
9	15	0*	23
9	17	0*	4
9	19	0*	1
10	0	0*	0
10	2	0*	34
10	4	87	95
10	6	71	81
10	8	38	26
10	10	53	75
10	12	78	61
10	14	143	151
10	16	0*	0
10	18	0*	0
11	1	16*	18
11	3	85	87
11	5	205	207
11	7	44	55
11	9	44	50
11	11	24*	47
11	13	0*	0
11	15	41	34
11	17	0*	5
11	19	0*	15
12	0	71*	24
12	2	169	174
12	4	80	87
12	6	60	57
12	8	0*	60
12	10	41	17
12	12	25*	22
12	14	37	9
12	16	112	116
12	18	24*	30
13	1	51	12
13	3	50	51
13	5	0*	60
13	7	41	47
13	9	24*	1
13	11	57	44
13	13	183	183
13	15	44	43
13	17	51	49
13	19	0*	1
14	0	47	29
14	2	71	53
14	4	84	81
14	6	107	107
14	8	47	15
14	10	85	55
14	12	0*	33
14	14	41	15
14	16	0*	0
14	18	121	119
15	1	57	47
15	3	0*	33
15	5	0*	0
15	7	37	15
15	9	44	57
15	11	87	86
15	13	0*	70
15	15	0*	0
15	17	0*	1
15	19	0*	1
16	0	0*	0
16	2	121	119
16	4	57	47
16	6	0*	93
16	8	0*	0
16	10	0*	0
16	12	91	49
16	14	41	22
16	16	0*	1
16	18	0*	1
17	1	0*	0
17	3	0*	0
17	5	0*	0
17	7	0*	0
17	9	0*	0
17	11	0*	0
17	13	0*	0
17	15	0*	0
17	17	0*	0
17	19	0*	0
18	0	0*	0
18	2	0*	0
18	4	0*	0
18	6	0*	0
18	8	0*	0
18	10	0*	0
18	12	0*	0
18	14	0*	0
18	16	0*	0
18	18	0*	0
19	1	0*	0
19	3	0*	0
19	5	0*	0
19	7	0*	0
19	9	0*	0
19	11	0*	0
19	13	0*	0
19	15	0*	0
19	17	0*	0
19	19	0*	0
**** H = 1 ****			
0	0	62	63
0	2	474	396
0	4	320	293
0	6	199	193
0	8	261	246
0	10	449	459
0	12	184	178
0	14	199	171
0	16	0*	10
0	18	0*	77
1	1	207	207
1	3	97	89
1	5	184	185
1	7	127	127
1	9	41	41
1	11	0*	5
1	13	0*	1
1	15	0*	23
1	17	0*	4
1	19	0*	1
2	0	0*	0
2	2	34*	34
2	4	87	95
2	6	71	81
2	8	38	26
2	10	53	75
2	12	78	61
2	14	143	151
2	16	0*	0
2	18	0*	0
3	1	16*	18
3	3	85	87
3	5	205	207
3	7	44	55
3	9	44	50
3	11	24*	47
3	13	0*	0
3	15	41	34
3	17	0*	5
3	19	0*	15
4	0	71*	24
4	2	169	174
4	4	80	87
4	6	60	57
4	8	0*	60
4	10	41	17
4	12	25*	22
4	14	37	9
4	16	112	116
4	18	24*	30
5	1	51	12
5	3	50	51
5	5	0*	60
5	7	41	47
5	9	24*	1
5	11	57	44
5	13	183	183
5	15	44	43
5	17	51	49
5	19	0*	1
6	0	47	29
6	2	71	53
6	4	84	81
6	6	107	107
6	8	47	15
6	10	85	55
6	12	0*	33
6	14	41	15
6	16	0*	0
6	18	121	119
7	1	57	47
7	3	0*	33
7	5	0*	0
7	7	37	15
7	9	44	57
7	11	87	86
7	13	0*	70
7	15	0*	0
7	17	0*	1
7	19	0*	1
8	0	0*	0
8	2	0*	0
8	4	0*	0
8	6	0*	0
8	8	0*	0
8	10	0*	0
8	12	0*	0
8	14	0*	0
8	16	0*	0
8	18	0*	0
9	1	0*	0
9	3	0*	0
9	5	0*	0
9	7	0*	0
9	9	0*	0
9	11	0*	0
9	13	0*	0
9	15	0*	0
9	17	0*	0
9	19	0*	0
10	0	5*	71
10	2	0*	1
10	4	54	64
10	6	215	199
10	8	221	220
10	10	72	78
10	12	129	129
10	14	86	85
10	16	350	365
10	18	121	130
11	1	91	105
11	3	38	28
11	5	79	71
11	7	44	44
11	9	41	41
11	11	0*	1
11	13	0*	1
11	15	0*	1
11	17	0*	1
11	19	0*	1
12	0	143	144
12	2	189	189
12	4	0*	11
12	6	48	50
12	8	101	105
12	10	133	131
12	12	133	127
12	14	196	201
12	16	429	417
12	18	0*	39
13	1	0*	11
13	3	0*	1
13	5	0*	1
13	7	0*	1
13	9	0*	1
13	11	0*	1
13	13	0*	1
13	15	0*	1
13	17	0*	1
13	19	0*	1
14	0	106	110
14	2	0*	0
14	4	0*	0
14	6	0*	0
14	8	0*	0
14	10	0*	0
14	12	0*	0
14	14	0*	0
14	16	0*	0
14	18	0*	0
15	1	0*	0
15	3	0*	0
15	5	0*	0
15	7	0*	0
15	9	0*	0
15	11	0*	0
15	13	0*	0
15	15	0*	0
15	17	0*	0
15	19	0*	0
16	0	0*	0
16	2	0*	0
16	4	0*	0
16	6	0*	0
16	8	0*	0
16	10	0*	0
16	12	0*	0
16	14	0*	0
16	16	0*	0
16	18	0*	0
17	1	0*	0
17	3	0*	0
17	5	0*	0
17	7	0*	0
17	9	0*	0
17	11	0*	0
17	13	0*	0
17	15	0*	0
17	17	0*	0
17	19	0*	0
18	0	0*	0
18	2	0*	0
18	4	0*	0
18	6	0*	0
18	8	0*	0
18	10	0*	0
18	12	0*	0
18	14	0*	0
18	16	0*	0
18	18	0*	0
19	1	0*	0
19	3	0*	0
19	5	0*	0
19	7	0*	0
19	9	0*	0
19	11	0*	0
19	13	0*	0
19	15	0*	0
19	17	0*	0
19	19	0*	0
**** H = 2 ****			
0	0	5*	71
0	2	0*	1
0	4	54	64
0	6	215	199
0	8	221	220
0	10	72	78
0	12	129	129
0	14	86	85
0	16	350	365
0	18	121	130
1	1	91	105
1	3	38	28
1	5	79	71
1	7	44	44
1	9	41	41
1	11	0*	1
1	13	0*	1
1	15	0*	1
1	17	0*	1
1	19	0*	1
2	0	143	144
2	2	189	189
2	4	0*	11
2	6	48	50
2	8	101	105
2	10	133	131
2	12	133	127
2	14	196	201
2	16	429	417
2	18	0*	39
3	1	0*	11
3	3	0*	1
3	5	0*	1
3	7	0*	1
3	9	0*	1
3	11	0*	1
3	13	0*	1
3	15	0*	1
3	17	0*	1
3	19	0*	1
4	0	106	110
4	2	0*	0
4	4	0*	0
4	6	0*	0
4	8	0*	0
4	10	0*	0
4	12	0*	0
4	14	0*	0
4	16	0*	0
4	18	0*	0
5	1	0*	0
5	3	0*	0
5	5	0*	0
5	7	0*	0
5	9	0*	0
5	11	0*	0
5	13	0*	0
5	15	0*	0
5	17	0*	0
5	19	0*	0
6	0	0*	0
6	2	0*	0
6	4	0*	0
6	6	0*	0
6	8	0*	0
6	10	0*	0
6	12	0*	0
6	14	0*	0
6	16	0*	0
6	18	0*	0
7	1	0*	0
7	3	0*	0
7	5	0*	0
7	7	0*	0
7	9	0*	0
7	11	0*	0
7	13	0*	0
7	15	0*	0
7	17	0*	0
7	19	0*	0
8	0	0*	0
8	2	0*	0
8	4	0*	0
8	6	0*	0
8	8	0*	0
8	10	0*	0
8	12	0*	0
8	14	0*	0
8	16	0*	0
8	18	0*	0
9	1	0*	0
9	3	0*	0
9	5	0*	0
9	7	0*	0
9	9	0*	0
9	11	0*	0
9	13	0*	0
9	15	0*	0
9	17	0*	0
9	19	0*	0
10	0	0*	0
10	2	0*	0
10	4	0*	0
10	6	0*	0
10	8	0*	0
10	10	0*	0
10	12	0*	0
10	14	0*	0
10	16	0*	0
10	18	0*	0
11	1	0*	0
11	3	0*	0
11	5	0*	0
11	7	0*	0
11	9	0*	0
11	11	0*	0
11	13	0*	0
11	15	0*	0
11	17	0*	0
11	19	0*	0
12	0	0*	0
12	2	0*	0
12	4	0*	0
12	6	0*	0
12	8	0*	0
12	10	0*	0
12	12	0*	0
12	14	0*	0
12	16	0*	0
12	18	0*	0
13	1	0*	0
13	3	0*	0
13	5	0*	0
13	7	0*	0
13	9	0*	0
13	11	0*	0
13	13	0*	0
13	15	0*	0
13	17	0*	0
13	19	0*	0
14	0	180	185
14	2	18*	31
14	4	73*	42
14	6	29*	9
14	8	30*	25
14	10	52	52
14	12	110	112
14	14	0*	20
14	16	0*	41
14	18	0*	95
15	1	77	74
15	3	77	77
15	5	0*	11
15	7	0*	34
15	9	0*	90
15	11	20*	33
15	13	0*	0
15	15	0*	0
15	17	0*	0
15	19	0*	0
16	0	0*	0
16	2	0*	0
16	4	0*	0
16	6	0*	0
16	8	0*	0
16	10	0*	0
16	12	0*	0
16	14	0*	0
16	16	0*	0
16	18	0*	0
17	1	0*	0
17	3	0*	0
17	5	0*	0
17	7	0*	0
17	9	0*	0
17	11	0*	0
17	13	0*	0
17	15	0*	0
17	17	0*	0
17	19	0*	0
18	0	0*	0
18	2	0*	0
18	4	0*	0
18	6	0*	0
18	8	0*	0
18	10	0*	0
18	12	0*	0
18	14	0*	0
18	16	0*	0
18	18	0*	0
19	1	0*	0
19	3	0*	0
19	5	0*	0
19	7	0*	0
19	9	0*	0
19	11	0*	0
19	13	0*	0
19	15	0*	0
19	17	0*	0
19	19	0*	0
**** H = 3 ****			
0	0	47	32
0	2	68	68
0	2	79	71
0	4	227	212
0	6	50	53
0	8	701	639
0	10	488	446
0	12	83	85
0	14	34	39
0	16	144	141
0	18	0*	0
1	1	57	49
1	3	159	157
1	5	137	139
1	7	49	59
1	9	180	164
1	11	209	200
1	13	148	137
1	15	171	171
1	17	0*	21
1	19	183	183
2	0	49	49
2	2	139	131
2	4	137	139
2	6	11*	22
2	8	125	124
2	10	66	71
2	12	37	8
2	14	148	137
2	16	171	171
2	18	0*	21
3	1	109	104
3	3	78	79
3	5	25	34
3	7	131	131
3	9	127	127
3	11	79	79
3	13	127	127
3	15	92	92
3	17	51	55
3	19	102	6
4	0	147	152
4	2	20*	31
4	4	125	124
4	6	71	71
4	8	137	137
4	10	121	121
4	12	78	79
4	14	117	116
4	16	34	31
4	18	0*	21
5	1	25*	17
5	3	25	25
5	5	164	157
5	7	46	70
5	9	171	111
5	11	77	86
5	13	135	145
5	15	89	101
5	17	0*	1
5	19	0*	1
6	0	0*	0
6	2	0*	0
6	4	0*	0
6	6	0*	0
6	8	0*	0
6	10	0*	0
6	12	0*	0
6	14	0*	0
6	16	0*	0
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19	3	0*	0
19	5	0*	0
19	7	0*	0
19	9	0*	0
19	11	0*	0
19	13	0*	0
19	15	0*	0
19	17	0*	0
19	19	0*	0

Table III.II (continued)

K	L	OBS	CALC
14	5	28*	36
14	-6	81	77
14	6	64	74
14	-7	59	50
14	7	0*	21
14	-8	20*	19
14	8	81	89
14	-9	84	75
15	0	50	60
15	-1	0*	9
15	1	0*	31
15	-2	55	13
15	2	15*	14
15	-3	34	10
15	3	59	52
15	-4	0*	4
15	4	0*	25
15	-5	59	64
15	5	0*	39
15	-6	43	39
15	6	0*	0
16	0	51	43
16	-1	77	76
16	1	93	93
16	-2	0*	14
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0	0	226	218
0	-2	345	320
0	2	215	198
0	-4	235	178
0	4	226	223
0	-6	65	68
0	6	78	68
0	-8	53	66
0	8	29*	49
0	-10	71	67
0	10	265	267
0	-12	79	85
0	12	164	170
0	-14	83	72
0	14	128	127
0	-16	115	114
0	16	17*	39
1	0	358	341
1	-1	26	25
1	1	108	103
1	-2	27	16
1	2	240	238
1	-3	264	258
1	3	180	175
1	-4	152	155
1	4	150	148
1	-5	219	206
1	5	19*	28
1	-6	193	192
1	6	110	113
1	-7	234	237
1	7	114	106
1	-8	55	57
1	8	9*	8
1	-9	159	158
1	9	0*	2
1	-10	57	67
1	10	140	150
1	-11	105	107
1	11	25*	21
1	-12	124	120
1	12	0*	8
1	-13	46	31
1	13	131	136
1	-14	124	128
1	14	54	53
1	-15	79	83
1	15	112	107
1	-16	0*	32
1	16	34	21
1	-17	24*	59
2	0	225	230
2	-1	76	74
2	1	43	29
2	-2	149	142
2	2	251	239
2	-3	30	22
2	3	48	45
2	-4	52	59
2	4	137	128
2	-5	109	110
2	5	149	147
2	-6	63	67
2	6	186	186
2	-7	70	72
2	7	170	170
2	-8	137	128
2	8	56	67
2	-9	0*	4
2	9	53	63
2	-10	134	146
2	10	68	75
2	-11	36	36
2	11	54	53
2	-12	90	85
2	12	176	178
2	-13	95	106
2	13	121	122
2	-14	90	100
2	14	0*	29
2	-15	27*	19
2	15	38	20
2	-16	16*	21
2	16	18*	32
2	-17	11*	23
3	0	34	46
3	-1	389	359
3	1	136	135
3	-2	25	22
3	2	26	9
3	-3	151	161
3	3	116	121
3	-4	443	430
3	4	339	336
3	-5	92	81
3	5	82	78
3	-6	193	189
3	6	46	58
3	-7	41	28
3	7	123	116
3	-8	27	33
3	8	73	72
3	-9	96	88
3	9	76	65
3	-10	70	70
3	10	58	61
3	-11	173	174
3	11	36	45
3	-12	29*	55
3	12	250	251
3	-13	49	59
3	13	65	30
3	-14	17*	31
3	14	31	40
3	-15	0*	29
3	15	0*	29
3	-16	54	31
3	16	31*	18
3	-17	41	27
4	0	41	44
4	-1	0*	13
4	1	227	220
4	-2	0*	18
4	2	68	59
4	-3	185	182
4	3	180	181
4	-4	180	184
4	4	120	328
4	-5	0*	4
4	5	179	131
4	-6	116	108
4	6	24	44
4	-7	29	27
4	7	16*	7
4	-8	132	134
4	8	6*	49
4	-9	73	66
4	9	39	20
4	-10	76	74
4	10	34	23
4	-11	158	145
4	11	63	60
4	-12	162	169
4	12	26*	15
4	-13	37	39
4	13	38	33
4	-14	84	76
4	14	32	15
4	-15	60	21
4	15	76	77
4	-16	64	55
5	0	31	32
5	-1	78	86
5	1	189	189
5	-2	312	319
5	2	158	160
5	-3	20*	3
5	3	143	149
5	-4	121	132
5	4	55	52
5	-5	160	160
5	5	143	163
5	-6	40	9
5	6	187	184
5	-7	224	228
5	7	95	92
5	-8	107	110
5	8	158	150
5	-9	0*	0
5	9	137	134
5	-10	0*	6
5	10	211	206
5	-11	18*	14
5	11	37	28
5	-12	0*	43
5	12	32	20
5	-13	169	173
5	13	36	11
5	-14	43	44
5	14	62	55
5	-15	70	73
5	15	52	40
5	-16	0*	35
6	0	0*	16
6	-1	60	59
6	1	153	166
6	-2	111	122
6	2	185	181
6	-3	94	90
6	3	30	4
6	-4	84	77
6	4	49	47
6	-5	150	153
6	5	40	42
6	-6	119	130
6	6	85	86
6	-7	97	91
6	7	165	169
6	-8	91	81
6	8	0*	20
6	-9	123	128
6	9	22*	15
6	-10	150	149
6	10	55	43
6	-11	97	101
6	11	74	65
6	-12	93	87
6	12	92	91
6	-13	45	37
6	13	15*	15
6	-14	56	47
6	14	114	120
6	-15	54	30
6	15	35	13
6	-16	30*	10
7	0	97	90
7	-1	58	69
7	1	76	83
7	-2	55	40
7	2	74	75
7	-3	107	109
7	3	27	27
7	-4	85	84
7	4	90	90
7	-5	290	283
7	5	139	146
7	-6	0*	26
7	6	23*	11
7	-7	167	163
7	7	211	195
7	-8	251	250
7	8	14*	34
7	-9	111	106
7	9	73	59
7	-10	0*	2
7	10	83	84
7	-11	56	61
7	11	67	74
7	12	33	15
7	-12	55	56
7	-13	73	78
7	13	49	59
7	-14	30*	24
7	14	83	79
7	-15	132	149
8	0	71	69
8	-1	143	133
8	1	72	76
8	-2	0*	30
8	2	11*	39
8	-3	29	23
8	3	81	78
8	-4	70	88
8	4	66	52
8	-5	46	50
8	5	67	66
8	-6	77	77
8	6	74	81
8	-7	54	63
8	7	53	69
8	-8	49	39
8	8	21*	3
8	-9	51	57
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8	-10	34	18
8	10	64	55
8	-11	30*	31
8	11	65	61
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8	12	0*	5
8	-13	60	69
8	13	92	93
8	-14	0*	4
8	14	94	89
8	-15	103	119
9	0	0*	35
9	-1	173	116
9	1	0*	16
9	-2	112	120
9	2	125	121
9	-3	19*	25
9	3	0*	33
9	-4	71	72
9	4	65	69
9	-5	49	39
9	5	113	108
9	-6	257	266
9	6	104	93
9	-7	102	105
9	7	120	129
9	-8	59	63
9	8	46	49
9	-9	54	55
9	9	16*	33
9	-10	42	33
9	10	117	114
9	-11	0*	12
9	11	77	71
9	-12	45	54
9	12	44	16
9	-13	158	160
9	13	28*	20
9	-14	40	54
10	0	95	104
10	-1	39	25
10	1	106	109
10	-2	35	29
10	2	53	50
10	-3	0*	19
10	3	119	120
10	-4	192	190
10	4	53	60
10	-5	44	47
10	5	67	53
10	-6	52	58
10	6	35	40
10	-7	0*	13
10	7	18*	6
10	-8	37	21
10	8	44	49
10	-9	74	64
10	9	25*	10
10	-10	22*	30
10	10	31*	40
10	-11	50	17
10	11	124	119
10	-12	111	103
10	12	68	67
10	-13	71	64
11	0	62	77
11	-1	52	24
11	1	113	107
11	-2	97	101
11	2	32	20
11	-3	125	137
11	3	182	182
11	-4	160	169
11	4	143	143
11	-5	146	145
11	5	67	75
11	-6	58	59
11	6	0*	10
11	-7	54	47
11	7	33	9
11	-8	89	87
11	8	36	39
11	-9	27*	50
11	9	79	83
11	-10	60	58
11	10	15*	9
11	-11	103	93
11	11	78	61
11	-12	24*	15
12	0	93	101
12	-1	30*	25
12	1	72	75
12	-2	64	63
12	2	67	49
12	-3	115	116
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12	-4	70	71
12	4	0*	12
12	-5	46	31
12	5	96	94
12	-6	47	29
12	6	33	23
12	-7	56	65
12	7	32	37
12	-8	0*	14
12	8	122	111
12	-9	91	75
12	9	22*	45
12	-10	119	119
12	10	47	23
12	-11	68	64
13	0	66	82
13	-1	140	142
13	1	70	87
13	-2	37	44
13	2	73	82
13	-3	145	143
13	3	0*	0
13	-4	50	43
13	4	38	51
13	-5	49	61
13	5	77	75
13	-6	0*	37
13	6	25*	25
13	-7	63	79
13	7	56	48
13	-8	47	89
13	8	10*	3
13	-9	19*	38
14	0	42	53
14	-1	21*	14
14	1	37	19
14	-2	30*	2
14	2	64	71
14	-3	30*	16
14	3	29*	37
14	-4	40	40
14	4	59	47
14	-5	0*	28
14	5	59	45
14	-6	45	40
14	6	73	72
14	-7	86	83
15	0	62	73
15	-1	37	24
15	1	0*	8
15	-2	50	54
15	2	32*	11
15	-3	57	65
15	3	0*	46
15	-4	89	83
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0	-2	158	163
0	2	263	287
0	-4	190	185
0	4	109	101
0	-6	20*	10
0	6	220	229
0	-8	166	167
0	8	39	29
0	-10	111	114
0	10	74	66
0	-12	34	33
0	12	169	178
0	-14	64	51
0	14	182	178
0	-16	81	80
1	0	237	250
1	-1	51	70
1	1	79	85
1	-2	216	224
1	2	147	168
1	-3	123	117
1	3	34	29
1	-4	18*	22
1	4	65	81
1	-5	96	95
1	5	74	87
1	-6	98	93
1	6	53	66
1	-7	97	99
1	7	28	23
1	-8	163	157
1	8	55	66
1	-9	80	89
1	9	162	164
1	-10	53	43
1	10	47	46
1	-11	61	65
1	11	25*	21
1	-12	127	128
1	12	57	48
1	-13	17*	30
1	13	0*	20
1	-14	169	171
1	14	55	56
1	-15	70	52
1	15	0*	17
1	-16	56	51
2	0	178	193
2	-1	178	184
2	1	8*	22
2	-2	224	221
2	2	22*	44
2	-3	93	93
2	3	50	50
2	-4	22*	6
2	4	25	12
2	-5	103	106
2	5	127	133
2	-6	68	59
2	6	159	157
2	-7	111	132
2	7	116	107
2	-8	39	25
2	8	213	229
2	-9	146	142
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2	-10	61	76
2	10	128	130
2	-11	155	149
2	11	79	90
2	-12	37	14
2	12	39	47
2	-13	30*	28
2	13	14*	31
2	-14	61	56
2	14	50	48
2	-15	41	2
2	15	58	62
2	-16	70	49
3	0	132	137
3	-1	142	154
3	1	28	23
3	-2	28	19
3	2	172	183
3	-3	75	91
3	3	170	170
3	-4	36	33
3	4	73	78
3	-5	154	158
3	5	58	67
3	-6	50	53
3	6	67	66
3	-7	23*	24
3	7	55	61
3	-8	48	45
3	8	21*	19
3	-9	158	152
3	9	22*	22
3	-10	52	48
3	10	86	86
3	11	76	72
3	-11	85	92
3	-12	88	74
3	12	44	36
3	-13	0*	8
3	13	37	21
3	-14	50	45
3	14	41	76
3	-15	26*	12
3	15	75	81
3	-16	82	70
4	0	33	40
4	-1	55	65
4	1	35	24
4	-2	0*	7
4	2	53	51
4	-3	165	143
4	3	50	61
4	-4	145	149
4	4	47	36
4	-5	171	175
4	5	147	152
4	-6	0*	38
4	6	29	35
4	-7	44	41
4	7	57	54
4	-8	0*	22
4	8	45	41
4	-9	108	105
4	9	17*	1
4	-10	0*	2
4	10	0*	29
4	-11	106	106
4	11	76	74
4	-12	96	99
4	12	64	72
4	-13	93	92
4	13	93	96
4	-14	21*	25
4	14	62	17
4	-15	45	16
4	-16	30*	5
5	0	38	42
5	-1	76	80
5	1	45	32
5	-2	44	26
5	2	36	28
5	-3	152	159
5	3	25	13
5	-4	19*	60
5	4	190	192
5	-5	81	81
5	5	147	148
5	-6	0*	15
5	6	130	129
5	-7	59	47
5	7	107	110
5	-8	97	100
5	8	41	44
5	-9	63	64
5	9	29	37
5	-10	29	26
5	10	22*	24
5	-11	84	91
5	11	25*	5
5	-12	17*	4
5	12	45	64
5	-13	0*	2
5	13	56	18
5	-14	14*	35
5	14	67	54
5	-15	33*	4
6	0	137	139
6	-1	91	88
6	1	75	75
6	-2	146	144
6	2	32	46
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5	3	42	27
5	-4	23*	10
5	4	76	67
5	-5	0*	5
5	5	84	67
5	-6	22*	12
5	6	33	28
5	-7	8*	7
5	7	57	57
5	-8	86	76
5	8	69	41
5	-9	86	95
5	-10	63	61
6	0	69	53
6	-1	40	53
6	1	115	122
6	-2	113	106
6	2	21*	16
6	-3	93	100
6	3	7*	2
6	-4	8*	13
6	4	39	26
6	-5	45	51
6	5	70	66
6	-6	46	59
6	6	117	115
6	-7	129	125
6	7	83	71
6	-8	87	93
6	-9	125	128
7	0	22*	24
7	-1	37	35
7	1	0*	3
7	-2	54	40
7	2	0*	8
7	-3	106	100
7	3	51	37
7	-4	73	73
7	4	66	54
7	-5	22*	31
7	5	113	106
7	-6	95	96
7	6	90	94
7	-7	101	102
7	-8	45	12
8	0	111	112
8	-1	73	71
8	1	0*	0
8	-2	51	58
8	2	110	106
8	-3	47	37
8	3	42	11
8	-4	54	52
8	4	135	137
8	-5	127	130
8	5	33	33
8	-6	76	85
8	-7	20*	15
9	0	104	37
9	-1	25*	45
9	1	0*	21
9	-2	55	52
9	2	92	75
9	-3	72	90
9	3	93	79
9	-4	53	52
9	-5	47	21
**** H = 9****			
0	0	74	74
0	-2	38	21
0	2	32	14
0	-4	8*	27
0	4	38	42
0	-6	39	12
0	6	70	91
0	-8	35	7
1	0	0*	8
1	-1	26*	0
1	1	46	47
1	-2	41	35
1	2	48	34
1	-3	39	6
1	3	0*	26
1	-4	39	45
1	4	47	19
1	-5	7*	78
1	5	52	53
1	-6	0*	8
1	6	36	37
1	-7	118	130
1	-8	76	85
2	0	30*	10
2	-1	17*	30
2	1	64	65
2	-2	0*	18
2	2	49	33
2	-3	75	75
2	3	8*	20
2	-4	22*	13
2	4	92	83
2	-5	27*	14
2	5	0*	17
2	-6	28*	1
2	-7	20*	7
2	-8	26*	17
3	0	27*	27
3	-1	38	46
3	1	43	15
3	-2	17*	13
3	2	8*	20
3	-3	22*	35
3	3	40	23
3	-4	106	108
3	4	94	103
3	-5	31*	9
3	5	59	77
3	-6	58	44
3	-7	0*	32
4	0	38	23
4	-1	41	34
4	1	85	70
4	-2	74	76
4	2	54	39
4	-3	0*	1
4	3	86	88
4	-4	0*	6
4	4	75	68
4	-5	47	35
4	-6	0*	11
4	-7	21*	37
5	0	41	45
5	-1	37	56
5	1	57	42
5	-2	94	80
5	2	112	122
5	-3	0*	10
5	3	1*	6
5	-4	56	17
5	-5	64	63
5	-6	59	72
6	0	34	34
6	-1	59	64
6	1	21*	10
6	-2	30*	4
6	2	40	34
6	-3	56	56
6	-4	41	46

Table III.III

Final positional (fractional, × 10^4) and thermal parameters. Standard deviations are given in parentheses.

	Molecule 1				Molecule 2			
ATOM	x	y	z	B(Å^2)	x	y	z	B(Å^2)
Fe(1)	3759(3)	0773(2)	1986(2)		8370(4)	2441(3)	0695(2)	
Fe(2)	1932(3)	0822(2)	2646(2)		6462(4)	3155(2)	0738(2)	
Fe(3)	1871(4)	0053(2)	1738(2)		6492(4)	2248(2)	-0048(2)	
As(4)	0196(3)	0762(2)	3092(1)		4616(3)	3527(2)	0792(1)	
As(5)	0123(3)	-0490(2)	1633(1)		4683(3)	2109(2)	-0529(1)	
C(6)	4694(31)	1330(18)	2313(16)	5.7(8)	9362(36)	2764(20)	1247(19)	7.5(10)
C(7)	4249(33)	0122(20)	2501(18)	6.7(10)	7881(31)	1830(19)	1184(17)	6.3(9)
C(8)	3046(30)	1380(19)	1537(17)	6.2(9)	8602(28)	3035(18)	0172(16)	5.4(8)
C(9)	4546(25)	0498(15)	1421(14)	4.0(7)	9233(33)	1892(20)	0354(17)	6.7(10)
C(10)	1994(27)	1685(17)	2609(14)	4.5(8)	7087(25)	3905(16)	0714(13)	3.9(7)
C(11)	2881(25)	0779(15)	3292(14)	4.1(7)	6759(29)	3031(18)	1546(18)	6.3(9)
C(12)	2732(26)	-0627(15)	1691(13)	3.6(7)	6756(29)	1425(20)	0014(15)	5.6(9)
C(13)	1908(27)	0271(16)	0975(16)	4.9(8)	7265(34)	2323(20)	-0694(19)	7.4(10)
C(14)	1945(29)	-0133(18)	2620(16)	5.2(8)	5772(27)	2228(16)	0699(15)	4.7(8)
C(15)	0999(27)	0868(16)	1849(14)	4.6(7)	6281(27)	3266(17)	-0138(15)	4.6(8)
C(16)	0063(31)	-1445(19)	1706(17)	7.1(10)	3993(31)	1239(18)	-0461(16)	6.6(9)
C(17)	-0819(30)	-0300(18)	0884(16)	6.4(9)	4406(33)	2319(19)	-1404(17)	7.2(10)
C(18)	0165(29)	0405(17)	3903(16)	5.8(9)	3900(27)	3356(16)	1546(14)	5.1(8)
C(19)	-0710(32)	1564(19)	3118(17)	7.3(10)	4256(29)	4471(17)	0625(15)	5.7(9)
C(20)	-0903(21)	0172(12)	2681(12)	2.3(6)	3474(29)	3127(18)	0239(16)	5.9(9)
C(21)	-0919(25)	-0222(14)	2224(13)	3.9(7)	3508(24)	2691(15)	-0202(13)	3.7(7)
C(22)	-2184(29)	-0009(18)	2810(16)	5.3(8)	2143(31)	3240(19)	0099(17)	6.1(9)
C(23)	-2172(35)	-0456(21)	2266(18)	7.2(10)	2195(28)	2755(18)	-0377(16)	5.1(8)
F(24)	-2237(19)	-0284(11)	3355(11)	8.5(6)	1544(17)	3078(10)	0555(9)	7.6(5)
F(25)	-2908(19)	0507(11)	2770(10)	8.6(6)	1874(18)	3854(11)	-0066(10)	8.1(6)
F(26)	-2951(19)	-0304(11)	1840(10)	8.5(6)	1897(17)	2950(10)	-0961(10)	7.6(5)
F(27)	-2341(17)	-1098(11)	2398(9)	7.7(5)	1612(18)	2176(11)	-0322(10)	8.2(6)

Table III.III (continued)

	Molecule 1				Molecule 2			
ATOM	x	y	z	B(Å^2)	x	y	z	B(Å^2)
O(28)	5359(21)	1724(12)	2543(11)	6.9(6)	9953(25)	3063(15)	1584(13)	9.3(8)
O(29)	4592(21)	-0263(13)	2820(12)	7.1(6)	7668(22)	1444(14)	1560(12)	8.2(7)
O(30)	2664(19)	1789(12)	1218(10)	5.8(5)	8924(22)	3447(14)	-0155(12)	8.0(7)
O(31)	5040(20)	0279(11)	1018(11)	6.2(6)	9753(21)	1455(14)	0158(11)	7.5(6)
O(32)	3328(21)	-1087(13)	1590(11)	7.1(6)	6905(21)	0838(14)	0083(11)	7.4(6)
O(33)	1875(20)	0403(12)	0464(12)	6.8(6)	7665(25)	2401(14)	-1167(14)	9.2(8)
O(34)	3426(20)	0789(12)	3745(11)	6.6(6)	6826(20)	2973(12)	2062(12)	7.2(6)
O(35)	1945(20)	2253(13)	2615(10)	6.6(6)	7446(21)	4475(13)	0667(11)	7.1(6)
O(36)	1916(19)	-0608(12)	2926(10)	6.1(6)	5238(18)	1911(11)	1023(10)	5.3(5)
O(37)	0301(18)	1215(9)	1602(9)	4.8(5)	6110(19)	3625(12)	-0531(11)	6.3(6)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}*
Molecule 1						
Fe(1)	53	26	22	-4	4	0
Fe(2)	44	27	21	-6	4	-10
Fe(3)	56	30	17	-6	4	- 5
As(4)	48	21	20	-4	5	- 6
As(5)	59	24	21	-10	0	- 7
Molecule 2						
Fe(1)	48	41	26	0	-1	3
Fe(2)	66	27	31	-1	-6	-8
Fe(3)	54	30	26	3	2	-6
As(4)	65	21	23	1	5	-3
As(5)	71	26	19	-2	-4	-3
Mean σ	4	1	1	2	2	1

* COEFFICIENTS IN THE TEMPERATURE EXPRESSION: $\exp -10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + 2b_{12}hk + 2b_{13}h\ell + 2b_{23}k\ell)$

Table III.IV

Equations of weighted mean planes

Equations of planes in the form $\ell X' + mY + nZ' = p$, where X', Y, Z' are coordinates in Å, referred to orthogonal axes a, b, c^*

	ℓ	m	n	p	Maximum displacement (Å)
Iron triangle (3 Fe atoms)					
Molecule 1	0.3477	-0.7384	0.5778	2.8059	0
Molecule 2	0.3921	0.6513	-0.6497	5.9574	0
Di-(tertiary arsine) (2 As and 4 C atoms)					
Molecule 1	0.2872	-0.7502	0.5956	2.8559	0.009
Molecule 2	0.2296	0.7076	-0.6683	5.0354	0.037

Table III.V

Bond distances (Å) and valency angles (degrees). Unless otherwise specified, standard deviations of bond lengths are 0.03-0.04 Å; of angles at Fe and As, 0.7-1.8°; and of angles at C, 2.2-3.4°.

	Molecule 1	Molecule 2
Fe(1)-Fe(2)	2.652(8)	2.643(7)
Fe(1)-Fe(3)	2.651(7)	2.671(9)
Fe(2)-Fe(3)	2.527(6)	2.517(7)
Fe(2)-As(4)	2.301(7)	2.278(6)
Fe(3)-As(5)	2.300(6)	2.307(7)
Fe(1)-C(6)	1.69	1.75
Fe(1)-C(7)	1.80	1.75
Fe(1)-C(8)	1.74	1.69
Fe(1)-C(9)	1.69	1.70
Fe(2)-C(10)	1.73	1.67
Fe(2)-C(11)	1.75	1.81
Fe(3)-C(12)	1.70	1.68
Fe(3)-C(13)	1.75	1.74
AVERAGE Fe-C_{term}	1.73	
Fe(2)-C(14)	1.91	2.02
Fe(2)-C(15)	2.01	1.95
Fe(3)-C(14)	1.98	1.90
Fe(3)-C(15)	1.94	2.06
As(4)-C(18)	1.93	1.94
As(4)-C(19)	1.92	1.97
As(5)-C(16)	1.92	1.93
As(5)-C(17)	1.96	1.98
AVERAGE As-Me	1.94	

	Molecule 1	Molecule 2
As(4)-C(20)	1.92	1.92
As(5)-C(21)	1.91	1.97
C(20)-C(21)	1.28	1.31
C(20)-C(22)	1.58	1.57
C(21)-C(23)	1.54	1.55
C(22)-C(23)	1.50	1.44
C(22)-F(24)	1.33	1.30
C(22)-F(25)	1.33	1.32
C(23)-F(26)	1.30	1.37
C(23)-F(27)	1.34	1.35
AVERAGE C-F	1.33	
C(6)-O(28)	1.19	1.15
C(7)-O(29)	1.10	1.17
C(8)-O(30)	1.15	1.17
C(9)-O(31)	1.18	1.16
C(10)-O(35)	1.14	1.22
C(11)-O(34)	1.15	1.14
C(12)-O(32)	1.18	1.20
C(13)-O(33)	1.16	1.18
C(14)-O(36)	1.17	1.17
C(15)-O(37)	1.18	1.13
AVERAGE C-O	1.16	

Table III.V (continued)

	Molecule 1	Molecule 2
C(6)-Fe(1)-C(7)	92	93
C(6)-Fe(1)-C(8)	93	95
C(6)-Fe(1)-C(9)	100	100
C(6)-Fe(1)-Fe(2)	105	107
C(7)-Fe(1)-C(9)	94	93
C(7)-Fe(1)-Fe(2)	85	93
C(7)-Fe(1)-Fe(3)	88	90
C(8)-Fe(1)-C(9)	94	92
C(8)-Fe(1)-Fe(2)	86	79
C(8)-Fe(1)-Fe(3)	85	81
C(9)-Fe(1)-Fe(3)	96	97
Fe(2)-Fe(1)-Fe(3)	56.9(2)	56.5(2)
C(10)-Fe(2)-C(11)	94	96
C(10)-Fe(2)-C(15)	86	83
C(10)-Fe(2)-As(4)	97	97
C(11)-Fe(2)-C(14)	88	88
C(11)-Fe(2)-As(4)	100	96
C(14)-Fe(2)-Fe(3)	51	48
C(14)-Fe(2)-As(4)	88	86
C(15)-Fe(2)-Fe(3)	49	53
C(15)-Fe(2)-As(4)	87	89
Fe(1)-Fe(2)-C(10)	89	97
Fe(1)-Fe(2)-C(11)	88	82
Fe(1)-Fe(2)-C(14)	87	80
Fe(1)-Fe(2)-C(15)	86	94
Fe(1)-Fe(2)-Fe(3)	61.5(2)	62.3(2)
Fe(3)-Fe(2)-As(4)	109.1(2)	109.1(2)
C(12)-Fe(3)-C(13)	95	93
C(12)-Fe(3)-C(14)	86	90
C(12)-Fe(3)-As(5)	97	94
C(13)-Fe(3)-C(15)	88	84
C(13)-Fe(3)-As(5)	96	98
C(14)-Fe(3)-Fe(2)	48	52
C(14)-Fe(3)-As(5)	90	88
C(15)-Fe(3)-Fe(2)	51	49
C(15)-Fe(3)-As(5)	87	89
Fe(1)-Fe(3)-C(12)	88	87
Fe(1)-Fe(3)-C(13)	90	93
Fe(1)-Fe(3)-C(14)	85	82
Fe(1)-Fe(3)-C(15)	87	90
Fe(1)-Fe(3)-Fe(2)	61.6(2)	61.2(2)
Fe(2)-Fe(3)-As(5)	110.4(3)	110.7(2)

	Molecule 1	Molecule 2
Fe(2)-As(4)-C(18)	119	116
Fe(2)-As(4)-C(19)	118	120
Fe(2)-As(4)-C(20)	114	116
C(18)-As(4)-C(19)	104	104
C(18)-As(4)-C(20)	99	99
C(19)-As(4)-C(20)	100	99
Fe(3)-As(5)-C(16)	120	116
Fe(3)-As(5)-C(17)	116	121
Fe(3)-As(5)-C(21)	113	113
C(16)-As(5)-C(17)	104	103
C(16)-As(5)-C(21)	101	99
C(17)-As(5)-C(21)	100	102
As(4)-C(20)-C(21)	137	134
As(4)-C(20)-C(22)	131	134
C(21)-C(20)-C(22)	92	92
As(5)-C(21)-C(20)	137	136
As(5)-C(21)-C(23)	127	130
C(20)-C(21)-C(23)	96	93
C(20)-C(22)-F(24)	111	112
C(20)-C(22)-F(25)	114	114
C(20)-C(22)-C(23)	86	88
F(24)-C(22)-C(23)	119	117
F(24)-C(22)-F(25)	109	109
F(25)-C(22)-C(23)	117	117
C(21)-C(23)-F(26)	120	116
C(21)-C(23)-F(27)	118	113
C(21)-C(23)-C(22)	86	88
F(26)-C(23)-C(22)	114	119
F(26)-C(23)-F(27)	106	103
F(27)-C(23)-C(22)	113	118
Fe(1)-C(6)-O(28)	180	170
Fe(1)-C(7)-O(29)	177	172
Fe(1)-C(8)-O(30)	174	170
Fe(1)-C(9)-O(31)	176	171
Fe(2)-C(10)-O(35)	174	174
Fe(2)-C(11)-O(34)	173	173
Fe(3)-C(12)-O(32)	173	177
Fe(3)-C(13)-O(33)	176	172
Fe(2)-C(14)-O(36)	143	134
Fe(3)-C(14)-O(36)	136	146
Fe(2)-C(15)-O(37)	139	147
Fe(3)-C(15)-O(37)	142	136

DISCUSSION

The molecule (Figure III.2) is best described as a derivative of $Fe_3(CO)_{12}$[18], with one equatorial carbonyl group on each of the two equivalent iron atoms replaced by the arsenic atoms of the di-(tertiary arsine) ligand. In each of the two molecules in the asymmetric unit, the arsenic and carbon atoms of the ligand are coplanar (Table III.IV) in contrast to the non-planarity in $LFe_2(CO)_6$.[19] Presumably the deviation from planarity in the latter compound is associated with the involvement of the cyclobutene π-electrons in bonding to one of the iron atoms; this bonding is not present in $LFe_3(CO)_{10}$, so that planarity of the ligand is not unexpected. The difference in bonding in the two compounds is further indicated by the C=C bond lengths; the distance (Table III.V) in $LFe_3(CO)_{10}$ is 1.30(3) Å (standard deviation in parentheses), indicating retention of double-bond character, while the corresponding length in $LFe_2(CO)_6$ is 1.51(4) Å, consistent with the involvement of the π-electrons in bonding to an iron atom.

In each of the two $LFe_3(CO)_{10}$ molecules in the asymmetric unit, the ligand is not quite coplanar with the iron triangle, and the amount of bending is slightly different in the two molecules. In molecule 1 the angle between the triangle and ligand planes is only 3.7°, but molecule 2 is more significantly bent, the angle being 9.9°. Since the angle is different in the two molecules, the

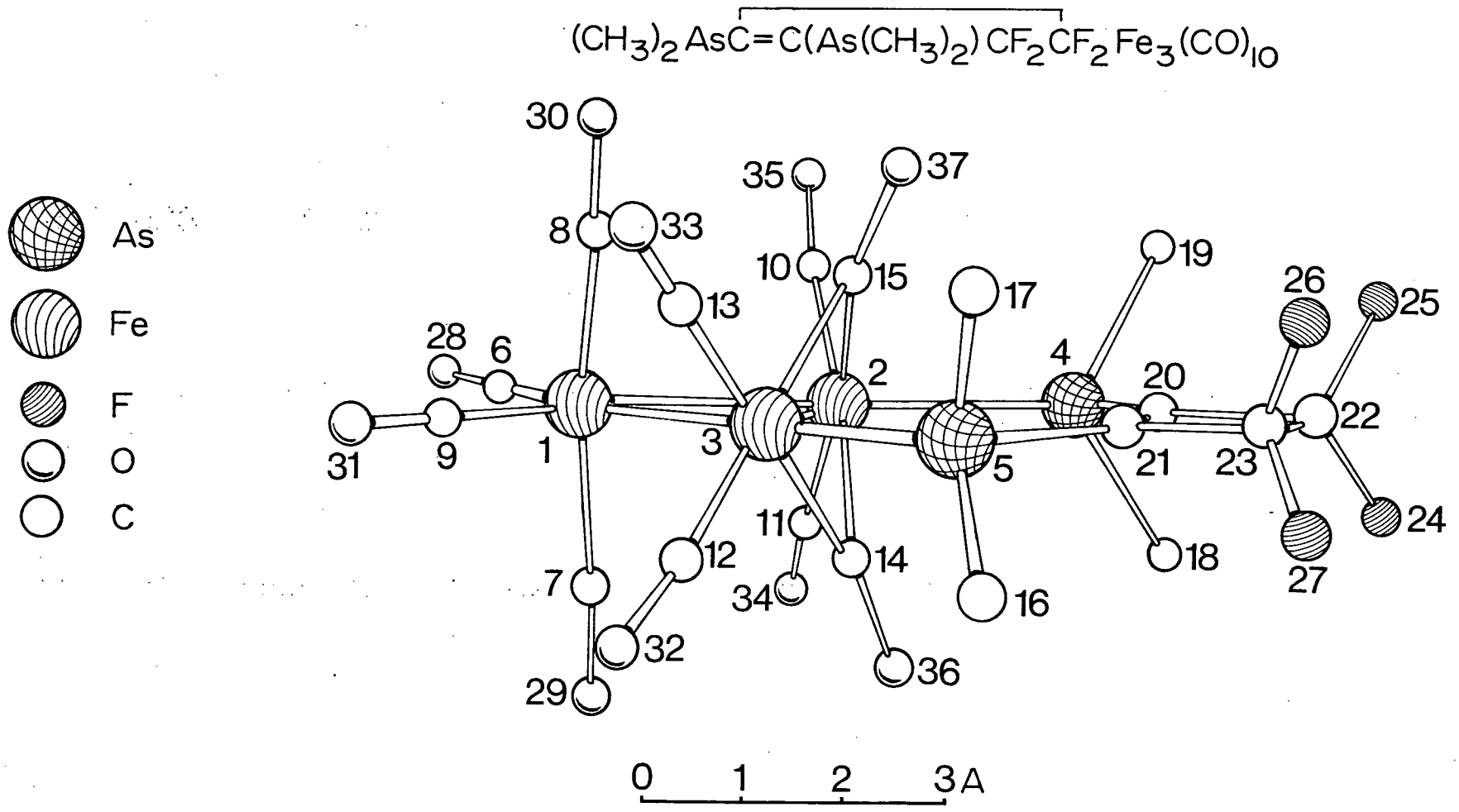

Figure III.2 Molecular structure of $LFe_3(CO)_{10}$.

small deviations from planarity are probably a result of crystal packing forces.

The bond lengths and valency angles in the two $LFe_3(CO)_{10}$ molecules in the asymmetric unit are not significantly different (Table III.V). The Fe-Fe distances in the isosceles iron triangle are 2.65(1) Å for the equivalent bonds, and 2.53(1) Å for the carbonyl-bridged bond. These lengths are close to the distances of 2.67(1) Å and 2.56(1) Å for the parent $Fe_3(CO)_{12}$ molecule,[18] so that replacement of two terminal carbonyl groups by the di-(tertiary arsine) ligand has apparently proceeded with little disturbance of the bonding in the iron triangle.

The mean Fe-C(terminal) distance is 1.73 Å, close to the distance found in related compounds,[27-30] and all the Fe-C-O are close to linear, as expected.[31] The Fe-C (bridging) distances are considerably longer, and the bridges appear to be slightly asymmetric (Figure III.3). The mean of the four longer Fe-C(bridging) bonds (with standard deviation of the mean) is 2.02(2) Å, while the average of the shorter bonds is 1.93(2) Å, the difference being greater than 3σ and probably significant. This asymmetry is similar to, although not as pronounced as that found in $Ph_3PFe_3(CO)_{11}$ (average Fe-C(bridging), 2.04 and 1.87 Å).[27] As Dahm and Jacobson point out,[27] this asymmetry need not be the result of crystal packing forces, but could be inherent in the bonding of the parent $Fe_3(CO)_{12}$,

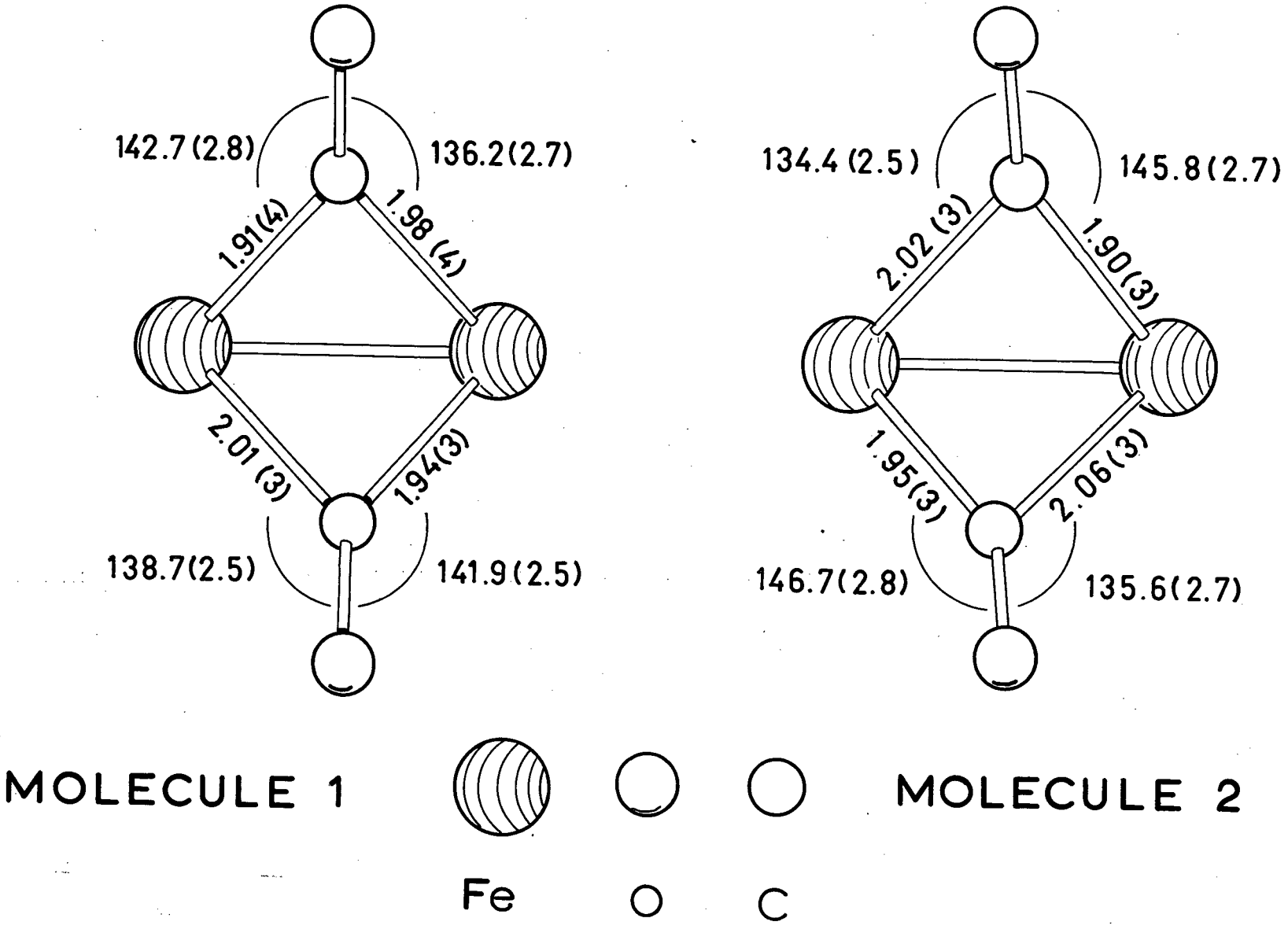

Figure III.3 View of asymmetric carbonyl bridges.

in which there is some evidence for unsymmetrical bridging carbonyl groups.[18] The C-O bond lengths average 1.17 Å, and the distances in the bridging carbonyls are not significantly longer than the average.

All the other bond lengths and valency angles (Table III.V) are quite similar to those in related compounds. The angles in the $Fe_3(CO)_{10}$ moiety are similar to those in $Ph_3PFe_3(CO)_{11}$[27] and the dimensions of the di-(tertiary arsine) ligand are close to those in $LCo_2(CO)_6$[32] and $LFe_2(CO)_6$[19] apart from the differences caused by the non-planarity of the ligand in the latter compound. The valency angles at arsenic show deviations from the exact tetrahedral value (Figure III.4), the Fe-As-C angles (113-121°) being larger than the C-As-C angles (99-104°). Fe-As bond lengths (mean 2.297 Å) correspond to those found in $LFe_2(CO)_6$[19] and $\{Fe(CO)_3\}_2(AsMe_3)_4$.[33]

The magnitudes of the principal axes of the thermal vibration ellipsoids of the iron and arsenic atoms are given in Table III.VI. The largest vibrations are approximately perpendicular to the plane of the iron triangle.

All the intermolecular distances correspond to normal van der Waals interactions, the closest approaches being about 3.1 Å. The molecules are arranged (Figure III.5) so that an oxygen atom of a bridging carbonyl group of each molecule in the asymmetric unit is approximately equidistant

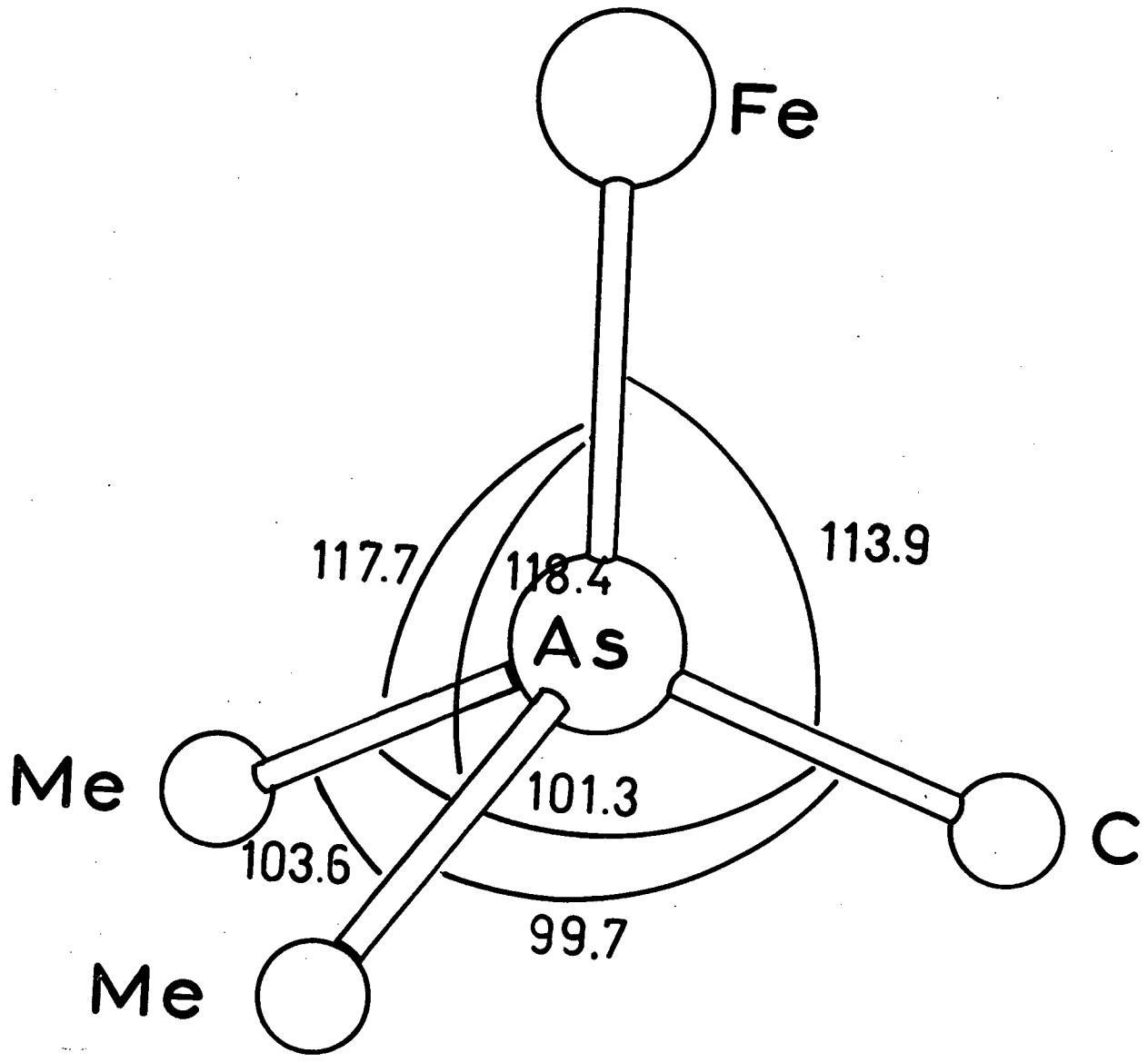

Figure III.4 Co-ordination about arsenic atoms, showing angles averaged over the four arsenic atoms in the asymmetric unit.

Table III.VI

Magnitudes (Å, σ = 0.005-0.008 Å) of the principal axes of the thermal vibration ellipsoids of the iron and arsenic atoms

	Molecule 1			Molecule 2		
	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3
Fe(1)	0.186	0.233	0.235	0.179	0.249	0.292
Fe(2)	0.165	0.175	0.277	0.195	0.223	0.298
Fe(3)	0.190	0.192	0.261	0.190	0.222	0.273
As(4)	0.177	0.179	0.249	0.194	0.212	0.243
As(5)	0.166	0.218	0.260	0.193	0.232	0.240

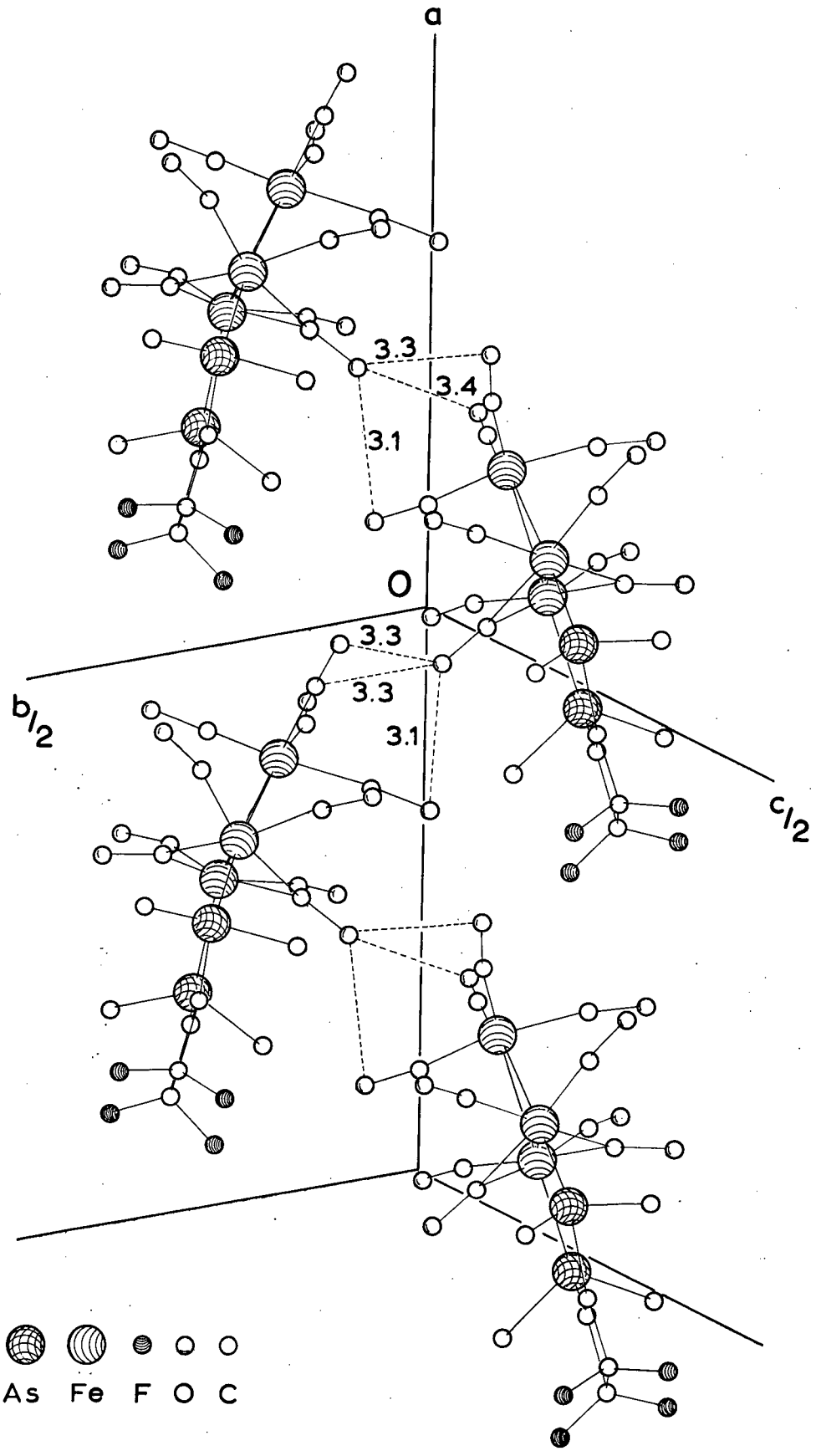

Figure III.5 Intermolecular contacts in general view.

from three of the four terminal carbonyl groups of the unique iron atom of the other molecule. Another, simplified view of the molecular packing is shown in Figure III.6.

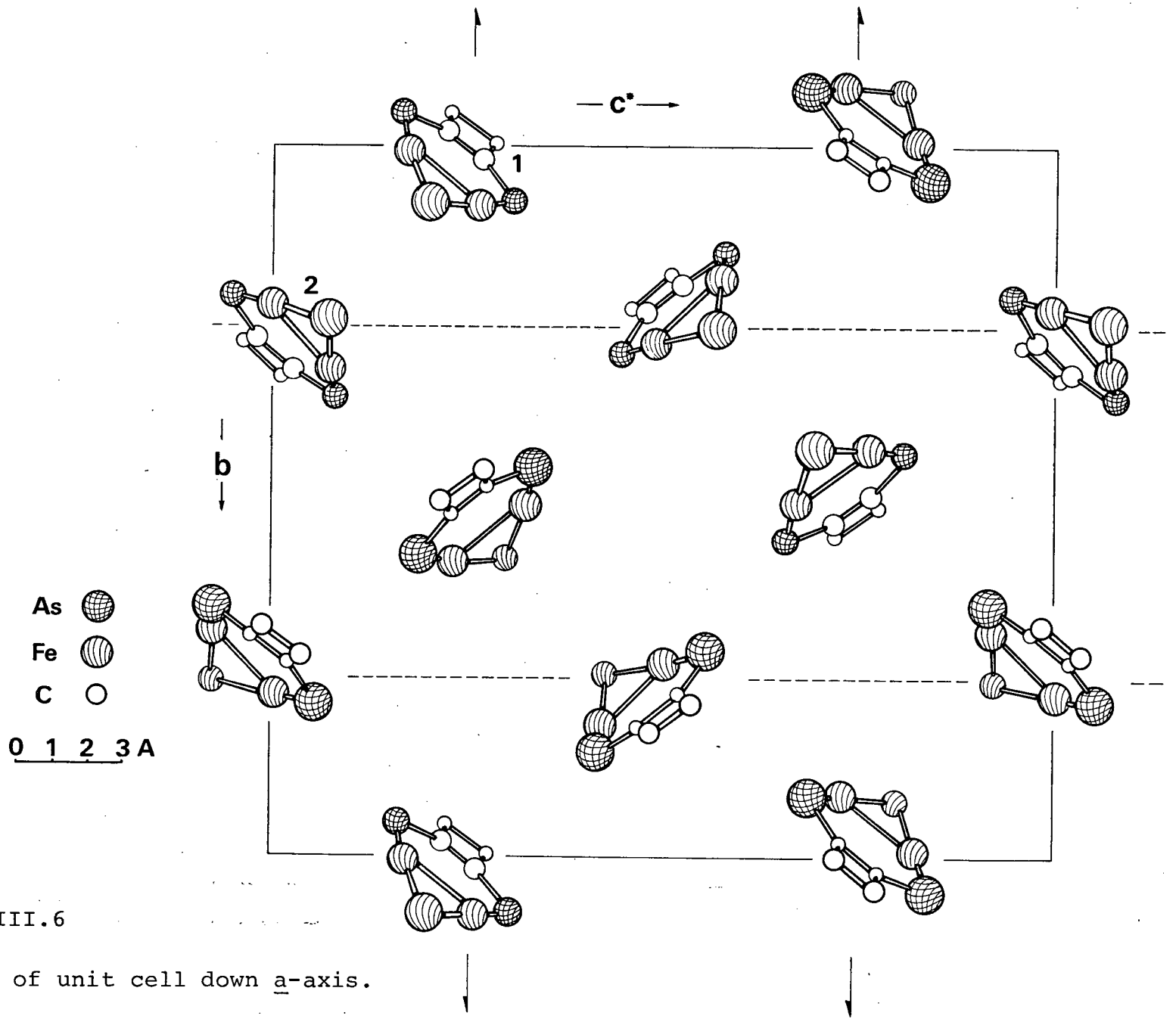

Figure III.6

Projection of unit cell down a-axis.

IV. THE STRUCTURE DETERMINATION OF

$\{Me_2AsC{=}C(AsMe_2)CF_2CF_2\}_2 \cdot Ru_3(CO)_8$

STRUCTURE ANALYSIS

The asymmetric unit contains half a molecule, requiring that the molecule be located on a crystallographic symmetry element. Since the molecule is not centrosymmetric (it contains three ruthenium atoms in a triangle), it was expected to lie on the two-fold axis at $(0,\underline{y},\frac{1}{4})$ of Pbcn. The structure was solved by the use of three dimensional direct methods. Sixteen sets of signs for 219 reflections having normalized structure factor $|\underline{E}| > 1.50$ were determined by Long's computer program, in which Sayre relationships were applied in an iterative procedure.[34] The program uses a starting set of seven signs and applies Sayre's equation in conjunction with other conditions imposed on the $\underline{E}$'s by space group symmetry. The first three $\underline{E}$'s are chosen to specify the origin and can be arbitrarily assigned positive signs. The other four are allowed to take on both positive and negative signs in turn. The $\underline{E}$'s are ordered in such a way that the starting set is at the beginning, followed by the remainder, sorted in order of decreasing $|\underline{E}|$. From each of the starting sets, the program predicts the signs for reflections below on the list. Each new prediction is used to determine signs further down the list. When the bottom of the list is reached, the iteration is repeated, starting with the eighth reflection (the signs of the starting set are not allowed to change). The number of sign changes and the number of signs newly determined

are counted for each cycle and the iteration is said to have converged when there are no additions to or changes in the list of signs.

A consistency index, $\underline{U}$, is defined as[34]

$$\underline{U} = \frac{\langle |\underline{E}_{\vec{h}_1} \Sigma \underline{E}_{\vec{h}_2} \underline{E}_{\vec{h}_3}| \rangle}{\langle |\underline{E}_{\vec{h}_1}| \Sigma |\underline{E}_{\vec{h}_2}| \, |\underline{E}_{\vec{h}_3}| \rangle} \qquad (4.1)$$

where the sums are over all pairs $\vec{h}_2$ and $\vec{h}_3$ for which $\vec{h}_2+\vec{h}_3=\vec{h}_1$ and where <> means "average over all values of $\vec{h}_1$". The true solution will usually be the most consistent one, *i.e.* it will have the highest consistency index. Usually the correct solution requires fewer iterative cycles and converges to a set of signs which are approximately equally distributed between positive and negative. Table IV.I gives a comparison of the sixteen possible solutions generated for the present structure. Solution 9 was outstanding in that the iteration procedure converged in three cycles to a set of signs having the highest consistency index (0.95) and equal numbers of positive and negative signs. An $\underline{E}$-map calculated with this set of signs indicated the positions of four independent atoms, one of which was situated on the two-fold rotation axis as expected. The positions and thermal parameters of these four atoms (assigned as two As and two Ru) were improved by two cycles of full-matrix least-squares refinement, with use of the scattering factors of ref. 26. The real part of the dispersion correction was applied. A difference synthesis

Table IV.I

Comparison of the 16 solutions from

Long's sign determination program

Set	Signs of starting set	Number of cycles	Number of pluses	Number of minuses	Consistency index U
1	+++++++	7	109	110	0.539
2	++++++-	8	103	116	0.464
3	+++++-+	12	112	107	0.641
4	+++++--	5	117	102	0.896
5	++++-++	12	116	103	0.588
6	++++-+-	6	108	111	0.638
7	++++--+	5	108	111	0.691
8	++++---	8	103	116	0.543
9	+++-+++	3	109	110	0.954
10	+++-++-	6	109	110	0.909
11	+++-+-+	5	110	109	0.684
12	+++-+--	10	108	111	0.481
13	+++--++	7	106	113	0.899
14	+++--+-	8	102	117	0.557
15	+++---+	7	110	109	0.680
16	+++----	12	105	114	0.424

phased on the refined parameters revealed the positions of all twenty carbon, oxygen, and fluorine atoms.

Two cycles of full-matrix refinement, with minimization of $\Sigma \underline{w}(\underline{F}_o-\underline{F}_c)^2$, $\underline{w} = \{\underline{A} + \underline{B}|\underline{F}_o| + \underline{C}|\underline{F}_o|^2 + \underline{D}|\underline{F}_o|^3\}^{-1}$ for observed reflections (unobserveds were excluded from refinement but included in final structure factor calculation), reduced $\underline{R}$ to 0.124. $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$ were adjusted to give constant average values of $\underline{w}(\underline{F}_o-\underline{F}_c)^2$ over the whole range of $|\underline{F}_o|$, the final values being 37.32, 1.09, -0.0159, and 0.00008 respectively. At this stage a difference map showed small peaks and troughs around the positions of the ruthenium and arsenic atoms. Two further cycles of full-matrix refinement using anisotropic thermal parameters for the heavy atoms reduced $\underline{R}$ to 0.089. A difference map computed at this stage indicated the necessity of also treating the fluorine atoms anisotropically. Two final cycles of full-matrix refinement were carried out varying the positional parameters, anisotropic thermal parameters for the ruthenium, arsenic, and fluorine atoms, isotropic thermal parameters for the other atoms, and a single overall scale factor, for a total of 133 variables. At final convergence of the refinement, $\underline{R}$ and $\underline{R}_w$ were 0.078 and 0.098 respectively, for the 1507 observed reflections, and 0.088 and 0.114 respectively, for all data. Measured and calculated structure factors are listed in Table IV.II. A final difference map showed fluctuations around the heavy

Table IV.II

Final measured and calculated structure factors. Unobserved reflections have an asterisk after the $|\underline{F_o}|$ value.

K	L	OBS	CALC
**** H = 0****			
0	4	0*	37
0	6	145	159
0	8	94	109
0	10	51	45
0	12	111	127
0	14	333	354
0	16	123	125
0	18	6*	5
0	20	112	103
2	0	456	433
2	1	216	191
2	2	303	304
2	3	27	29
2	4	84	97
2	5	86	92
2	6	290	307
2	7	224	231
2	8	93	98
2	9	162	192
2	10	266	291
2	11	215	227
2	12	189	207
2	13	159	177
2	14	159	159
2	15	9*	18
2	16	152	152
2	17	0*	9
2	18	102	93
2	19	31	31
2	20	106	95
4	0	286	252
4	1	319	311
4	2	48	49
4	3	15	2
4	4	501	476
4	5	141	147
4	6	154	136
4	7	395	392
4	8	116	121
4	9	157	169
4	10	339	350
4	11	89	92
4	12	274	257
4	13	60	54
4	14	69	73
4	15	14	18
4	16	49	49
4	17	44	42
4	18	62	61
4	19	0*	5
4	20	36	31
6	0	245	238
6	1	306	267
6	2	11	18
6	3	320	302
6	4	609	583
6	5	240	229
6	6	284	277
6	7	18	3
6	8	66	66
6	9	127	121
6	10	263	254
6	11	92	85
6	12	40	34
6	13	28	27
6	14	78	70
6	15	101	92
6	16	62	67
6	17	204	198
6	18	146	140
6	19	147	141
8	0	113	113
8	1	316	305
8	2	199	192
8	3	309	292
8	4	18*	24
8	5	117	113
8	6	269	248
8	7	0*	11
8	8	248	243
8	9	106	104
8	10	165	151
8	11	0*	2
8	12	118	115
8	13	51	56
8	14	69	74
8	15	147	139
8	16	78	68
8	17	195	184
8	18	0*	7
10	0	336	327
10	1	245	237
10	2	101	96
10	3	71	72
10	4	112	109
10	5	166	162
10	6	151	145
10	7	285	277
10	8	243	239
10	9	223	209
10	10	121	118
10	11	0*	11
10	12	125	121
10	13	73	61
10	14	160	154
10	15	60	57
10	16	5*	3
10	17	19	19
12	0	31	43
12	1	170	170
12	2	76	74
12	3	80	71
12	4	167	164
12	5	36	26
12	6	203	198
12	7	95	96
12	8	193	187
12	9	195	186
12	10	84	80
12	11	241	231
12	12	33	24
12	13	137	124
12	14	57	59
12	15	67	35
14	0	227	224
14	1	23	16
14	2	256	266
14	3	27	15
14	4	137	139
14	5	76	82
14	6	145	145
14	7	153	150
14	8	197	200
14	9	75	76
14	10	99	101
14	11	45	34
14	12	92	92
14	13	13*	7
16	0	36	25
16	1	52	53
16	2	125	132
16	3	64	67
16	4	185	195
16	5	21	26
16	6	61	59
16	7	66	67
16	8	87	84
16	9	69	50
**** H = 1****			
0	2	274	374
0	4	70	91
0	6	39	40
0	8	59	66
0	10	35	48
0	12	230	259
0	14	61	69
0	16	56	50
0	18	23	16
0	20	45	43
1	0	594	631
1	1	257	223
1	2	355	361
1	3	31	38
1	4	17	2
1	5	50	44
1	6	115	131
1	7	16	16
1	8	142	167
1	9	72	75
1	10	30	34
1	11	150	157
1	12	65	68
1	13	129	135
1	14	145	146
1	15	0*	28
1	16	112	104
1	17	30	40
1	18	111	99
1	19	32	31
1	20	92	87
2	1	154	155
2	2	222	202
2	3	170	174
2	4	19	26
2	5	10	15
2	6	151	153
2	7	30	34
2	8	179	199
2	9	4*	8
2	10	27	32
2	11	15	10
2	12	171	169
2	13	41	38
2	14	77	81
2	15	23	22
2	16	45	41
2	17	0*	16
2	18	10*	5
2	19	3*	17
2	20	41	37
3	0	120	109
3	1	121	103
3	2	17	13
3	3	78	68
3	4	132	125
3	5	272	210
3	6	58	64
3	7	329	326
3	8	107	108
3	9	174	191
3	10	244	267
3	11	127	138
3	12	200	213
3	13	18	19
3	14	24	24
3	15	8*	1
3	16	106	112
3	17	13*	13
3	18	127	121
3	19	17	17
3	20	54	52
4	1	100	91
4	2	255	245
4	3	43	56
4	4	5*	17
4	5	111	97
4	6	52	46
4	7	0*	4
4	8	113	105
4	9	16	4
4	10	95	93
4	11	56	54
4	12	147	143
4	13	45	49
4	14	62	66
4	15	15	3
4	16	115	122
4	17	0*	2
4	18	26	23
4	19	6*	11
4	20	0*	13
5	0	326	317
5	1	248	236
5	2	27	29
5	3	93	84
5	4	196	189
5	5	74	74
5	6	397	377
5	7	175	167
5	8	194	186
5	9	184	177
5	10	128	126
5	11	45	41
5	12	14	19
5	13	32	27
5	14	29	24
5	15	62	66
5	17	51	51
5	18	81	79
5	19	56	60
5	20	14*	17
6	1	191	167
6	2	221	208
6	3	50	46
6	4	17	10
6	5	85	78
6	6	109	101
6	7	28	21
6	8	158	158
6	9	26	19
6	10	107	102
6	11	50	47
6	12	138	137
6	13	86	91
6	14	6*	1
6	15	52	48
6	16	105	107
6	17	21	18
6	18	11*	14
6	19	18	22
7	0	66	73
7	1	186	170
7	2	80	64
7	3	250	240
7	4	94	84
7	5	193	188
7	6	53	54
7	7	75	72
7	8	70	67
7	9	93	90
7	10	50	47
7	11	123	120
7	12	59	62
7	13	16	20
7	14	15	0
7	15	128	121
7	16	12*	21
7	17	225	210
7	18	0*	7
7	19	153	144
8	1	87	84
8	2	165	159
8	3	43	48
8	4	105	97
8	5	90	87
8	6	131	127
8	7	52	55
8	8	138	122
8	9	16	16
8	10	85	84
8	11	23	23
8	12	114	104
8	13	76	70
8	14	24	22
8	15	40	43
8	16	73	67
8	17	0*	19
8	18	0*	6
9	0	43	29
9	1	379	368
9	2	31	25
9	3	167	159
9	4	140	128
9	5	75	74
9	6	188	179
9	7	205	200
9	8	177	166
9	9	116	111
9	10	60	60
9	11	35	27
9	12	23	23
9	13	105	100
9	14	34	28
9	15	101	98
9	16	54	49
9	17	62	62
10	1	44	37
10	2	99	97
10	3	166	154
10	4	63	59
10	5	38	35
10	6	210	200
10	7	70	69
10	8	106	102
10	9	0*	20
10	10	22	17
10	11	36	24
10	12	73	76
10	13	56	52
10	14	8*	8
10	15	16	14
10	16	76	68
10	17	18	2
11	0	153	144
11	1	55	49
11	2	44	40
11	3	11*	5
11	4	47	36
11	5	64	64
11	6	26	26
11	7	126	121
11	8	97	92
11	9	167	157
11	10	211	196
11	11	128	123
11	12	180	175
11	13	41	47
11	14	70	63
11	15	0*	2
11	16	71	60
12	1	9*	11
12	2	106	111
12	3	49	49
12	4	144	139
12	5	22	30
12	6	173	170
12	7	21	15
12	8	79	73
12	9	65	59
12	10	55	58
12	11	32	36
12	12	55	52
12	13	0*	6
12	14	4*	1
12	15	38	31
13	0	288	291
13	1	85	85
13	2	213	217
13	3	44	43
13	4	0*	8
13	5	22	21
13	6	159	155
13	7	57	61
13	8	154	147
13	9	127	127
13	10	0*	7
13	11	142	142
13	12	48	48
13	13	99	91
13	14	83	76
14	1	0*	18
14	2	63	62
14	3	13*	21
14	4	108	111
14	5	36	33
14	6	139	140
14	7	22	15
14	8	60	60
14	9	0*	6
14	10	87	88
14	11	20	17
14	12	48	46
15	0	178	194
15	1	78	89
15	2	140	148
15	3	19	12
15	4	108	115
15	5	68	80
15	6	24	14
15	7	72	77
15	8	24	29
15	9	0*	8
15	10	36	41
15	11	58	66
16	1	21	12
16	2	70	78
16	3	11*	3
16	4	89	93
16	5	22	26
16	6	86	97
16	7	14*	12
16	8	23	18
17	0	40	45
17	1	24	36
17	2	50	56
17	3	28	31
17	4	65	66
17	5	110	124
**** H = 2****			
0	0	130	124
0	2	331	497
0	4	44	61
0	6	344	443
0	8	209	245
0	10	105	114
0	12	254	275
0	14	17	26
0	16	87	80
0	18	102	97
0	20	37	34
1	1	53	61
1	2	152	161
1	3	8*	15
1	4	173	188
1	5	0*	8
1	6	175	198
1	7	14	17
1	8	118	140
1	9	48	61
1	10	67	78
1	11	27	30
1	12	122	132
1	13	26	25
1	14	64	63
1	15	49	53
1	16	0*	9
1	17	10*	1
1	18	14*	9
1	19	0*	7
1	20	44	35
2	0	227	235
2	1	129	126
2	2	98	89
2	3	110	106
2	4	245	257
2	5	89	87
2	6	19	28
2	7	28	39
2	8	204	218
2	9	163	174
2	10	9*	5
2	11	146	155
2	12	80	92
2	13	112	121
2	14	84	87
2	15	33	47
2	16	102	106
2	17	38	40
2	18	200	190
2	19	0*	9
2	20	35	31
3	1	111	100
3	2	50	46
3	3	119	121
3	4	125	123
3	5	245	226
3	6	143	139
3	7	0*	3
3	8	77	81
3	9	32	33
3	10	0*	10
3	11	80	89
3	12	118	128
3	13	45	44
3	14	97	105
3	15	32	34
3	16	31	34
3	17	16	11
3	18	13*	9
3	19	0*	17
3	20	35	31
4	0	180	167
4	1	162	158
4	2	9*	16
4	3	16	19
4	4	174	165
4	5	281	270
4	6	222	218
4	7	233	233
4	8	235	235
4	9	199	202
4	10	49	47
4	11	13	1
4	12	22	29
4	13	32	30
4	14	151	159
4	15	8*	6
4	16	10*	9
4	17	26	19
4	18	90	93
4	19	50	48
5	1	86	78
5	2	52	56
5	3	255	230
5	4	40	35
5	5	68	68
5	6	99	99
5	7	135	131
5	8	18	9
5	9	0*	12
5	10	51	49
5	11	41	40
5	12	125	123
5	13	101	106
5	14	41	42
5	15	35	33
5	16	26	19
5	17	0*	17
5	18	26	20
5	19	27	26
6	0	128	105
6	1	106	90
6	2	70	61
6	3	88	87
6	4	63	53
6	5	78	74
6	6	311	292
6	7	30	36
6	8	295	269
6	9	61	57
6	10	151	145
6	11	122	115
6	12	61	55
6	13	42	39
6	14	95	93
6	15	97	88
6	16	68	65
6	17	120	118
6	18	19	15
6	19	99	98
7	1	68	68
7	2	47	42
7	3	124	126
7	4	6*	6
7	5	142	129
7	6	44	38
7	7	101	97
7	8	52	53
7	9	32	24
7	10	31	21
7	11	60	53
7	12	66	70
7	13	131	125
7	14	27	26
7	15	91	90
7	16	7*	17
7	17	33	24
7	18	0*	11
8	0	341	307
8	1	218	207
8	2	20	31
8	3	153	146
8	4	282	263
8	5	73	68
8	6	139	125
8	7	28	24
8	8	22	29
8	9	33	32
8	10	80	76
8	11	57	66
8	12	29	23
8	13	44	41
8	14	95	95
8	15	115	111
8	16	57	58
8	17	106	99
8	18	137	131
9	1	149	143
9	2	65	59
9	3	149	136
9	4	79	74
9	5	172	166
9	6	60	57
9	7	35	34
9	8	41	38
9	9	66	69
9	10	21	22
9	11	91	91
9	12	7*	9
9	13	101	98
9	14	0*	17
9	15	56	56
9	16	26	18
9	17	16	1
10	0	9*	3
10	1	235	229
10	2	116	109
10	3	61	56
10	4	171	160
10	5	136	134
10	6	71	59
10	7	162	153
10	8	29	21
10	9	80	78
10	10	246	239
10	11	9*	4
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3	2	164	156
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9	3	118	113
9	4	67	64
9	5	63	58
9	6	83	79
9	7	25	16
9	8	66	60
9	9	64	57
9	10	25	21
10	0	109	108
10	1	60	49
10	2	123	115
10	3	54	58
10	4	140	136
10	5	34	34
10	6	20	19
10	7	13*	11
10	8	30	33
10	9	81	78
11	1	0*	7
11	2	71	69
11	3	39	42
11	4	35	35
11	5	24	25
11	6	73	79
11	7	16*	20
11	8	13*	5
12	0	41	41
12	1	148	150
12	2	84	82
12	3	84	84
12	4	83	83
12	5	9*	5
**** H = 7****			
0	2	0*	9
0	4	67	83
0	6	34	47
0	8	82	94
0	10	100	114
0	12	21	22
1	0	170	159
1	1	102	100
1	2	37	22
1	3	26	30
1	4	56	60
1	5	4*	4
1	6	25	23
1	7	24	23
1	8	65	77
1	9	20	15
1	10	146	167
1	11	33	31
1	12	77	90
2	1	14*	8
2	2	78	72
2	3	36	36
2	4	0*	1
2	5	9*	12
2	6	47	41
2	7	11*	7
2	8	24	20
2	9	47	50
2	10	0*	23
2	11	17	1
2	12	28	26
3	0	288	268
3	1	106	97
3	2	111	100
3	3	97	89
3	4	79	78
3	5	52	54
3	6	44	38
3	7	13*	5
3	8	34	13
3	9	18	2
3	10	66	71
3	11	22	21
3	12	0*	6
4	1	36	36
4	2	46	52
4	3	75	69
4	4	28	26
4	5	45	41
4	6	60	57
4	7	34	28
4	8	27	26
4	9	52	55
4	10	0*	15
4	11	35	32
5	0	122	117
5	1	88	81
5	2	58	59
5	3	70	55
5	4	23	13
5	5	0*	7
5	6	87	80
5	7	54	62
5	8	47	45
5	9	83	77
5	10	82	80
5	11	66	61
6	1	23	30
6	2	0*	11
6	3	23	15
6	4	78	68
6	5	38	42
6	6	60	61
6	7	25	22
6	8	64	63
6	9	32	26
6	10	35	36
7	0	86	78
7	1	109	102
7	2	3*	12
7	3	11*	0
7	4	69	64
7	5	95	93
7	6	25	21
7	7	146	139
7	8	35	33
7	9	132	122
8	1	18	28
8	2	84	84
8	3	21	5
8	4	11*	13
8	5	15*	2
8	6	28	20
8	7	21	8
8	8	12*	10
9	0	33	29
9	1	48	41
9	2	74	66
9	3	20	12
9	4	117	118
9	5	13*	4
9	6	0*	15
10	1	36	40
10	2	10*	12
10	3	54	47
10	4	29	19
**** H = 8****			
0	0	5*	23
0	2	18	12
0	4	13*	20
0	6	52	57
0	8	112	128
1	1	29	29
1	2	61	63
1	3	47	41
1	4	22	30
1	5	26	31
1	6	18	23
1	7	16	15
1	8	62	71
2	0	84	80
2	1	108	95
2	2	69	70
2	3	65	58
2	4	18	2
2	5	22	14
2	6	88	91
2	7	21	2
2	8	99	109
3	1	20	4
3	2	127	115
3	3	30	9
3	4	35	29
3	5	13*	5
3	6	21	15
3	7	0*	7
4	0	84	79
4	1	58	61
4	2	92	79
4	3	68	64
4	4	63	64
4	5	41	35
4	6	28	24
5	1	17	3
5	2	40	35
5	3	0*	1
5	4	46	37
5	5	0*	12
5	6	38	38
6	0	0*	12
6	1	63	58
6	2	51	47
6	3	0*	14
6	4	80	80
7	1	36	43

atoms of ±1.5 e/Å^3, which could not be attributed to any elements of the structure and were assumed to be a result of random experimental error.

Table IV.III gives the final positional and thermal parameters, with standard deviations calculated from the inverse matrix of the last cycle of refinement. Bond distances and valence angles are given in Table IV.IV. Standard deviations for these quantities include a contribution from the standard deviations of the lattice parameters. Table IV.V gives the equations of the weighted mean planes of the ruthenium triangle and the arsenic and carbon atoms of the di-(tertiary arsine) ligand. The magnitudes of the principal axes of anisotropic thermal vibration ellipsoids are in Table IV.VI.

Table IV.III

Final positional (fractional, × 10^4) and thermal parameters,

with standard deviations in parentheses.

ATOM	x	y	z	B or b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23} †
Ru(1)	0	1014(1)	2500	1014(39)	101(8)	189(7)	0	- 68(12)	0
Ru(2)	0686(2)	-0329(1)	3071(1)	1013(29)	113(6)	187(5)	28(9)	- 44(9)	8(4)
As(1)	0189(3)	1847(1)	3340(1)	1386(41)	110(7)	245(7)	72(13)	-125(13)	- 35(5)
As(2)	2288(2)	0000(1)	3909(1)	1003(35)	162(8)	188(6)	66(13)	- 61(11)	- 15(5)
F(1)	2657(22)	2546(10)	4549(8)	3493(319)	267(79)	463(53)	-298(130)	-637(111)	- 7(53)
F(2)	0652(23)	2200(12)	4981(10)	3799(392)	623(94)	396(66)	617(163)	-107(136)	-158(66)
F(3)	1952(19)	1013(10)	5378(8)	4149(310)	414(72)	210(51)	181(120)	-122(100)	- 10(51)
F(4)	3968(22)	1332(11)	4931(9)	2783(363)	294(83)	571(58)	128(140)	-691(111)	- 91(56)
C(1)	2102(29)	0973(14)	2434(12)	4.5(6)					
C(2)	2281(25)	-0586(12)	2560(10)	3.6(5)					
C(3)	0225(28)	-1266(14)	3311(11)	4.3(5)					
C(4)	-0948(26)	0081(13)	3505(11)	3.8(5)					
C(5)	1275(25)	1560(12)	4054(10)	3.3(5)					
C(6)	1734(32)	1978(15)	4623(12)	5.4(6)					
C(7)	2003(23)	0956(12)	4265(10)	3.2(4)					
C(8)	2448(31)	1294(14)	4843(12)	5.2(5)					
Me(1)	1250(35)	2780(17)	3192(13)	6.2(7)					
Me(2)	-1618(39)	2147(20)	3771(16)	7.4(8)					
Me(3)	2171(29)	-0563(14)	4650(12)	4.6(6)					
Me(4)	4427(33)	0051(17)	3766(13)	6.0(7)					
O(1)	3360(22)	1028(10)	2400(8)	5.7(4)					
O(2)	3278(19)	-0782(9)	2276(8)	5.1(4)					
O(3)	-0111(22)	-1861(11)	3432(9)	6.5(5)					
O(4)	-1890(19)	0271(10)	3810(8)	5.2(4)					

†coefficients in the temperature expression: $\exp -10^{-5}(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + 2b_{12}hk + 2b_{13}h\ell + 2b_{23}k\ell)$

Table IV.IV

Bond distances (Å) and valence angles (degrees), with standard deviations in parentheses.

Ru(1)-Ru(2)	2.853(3)	C(5)-C(7)	1.39(3)
Ru(1)-As(1)	2.401(3)	C(5)-C(6)	1.52(3)
Ru(1)-C(1)	1.91(3)	C(6)-C(8)	1.46(3)
		C(7)-C(8)	1.46(3)
Ru(2)-Ru(2')	2.785(4)		
Ru(2)-C(2)	1.89(2)	C(6)-F(1)	1.35(3)
Ru(2)-C(3)	1.86(3)	C(6)-F(2)	1.32(3)
Ru(2)-C(4)	1.92(2)	C(8)-F(3)	1.36(3)
Ru(2)-As(2)	2.413(3)	C(8)-F(4)	1.39(3)
As(1)-Me(1)	2.00(3)	C(1)-O(1)	1.15(3)
As(1)-Me(2)	1.97(4)	C(2)-O(2)	1.15(2)
As(1)-C(5)	1.92(2)	C(3)-O(3)	1.17(3)
		C(4)-O(4)	1.14(3)
As(2)-Me(3)	1.93(3)		
As(2)-Me(4)	1.97(3)		
As(2)-C(7)	1.95(2)		
C(1)-Ru(1)-Ru(2)	77.3(8)	Ru(2)-As(2)-C(7)	116.8(6)
C(1)-Ru(1)-Ru(2')	98.6(8)	Me(3)-As(2)-Me(4)	102.3(12)
C(1)-Ru(1)-As(1)	90.7(8)	Me(3)-As(2)-C(7)	98.6(10)
C(1)-Ru(1)-As(1')	92.3(8)	Me(4)-As(2)-C(7)	98.7(11)
C(1)-Ru(1)-C(1')	175.4(16)		
As(1)-Ru(1)-As(1')	100.0(1)	As(1)-C(5)-C(7)	137.9(17)
As(1)-Ru(1)-Ru(2)	102.3(1)	As(1)-C(5)-C(6)	131.5(17)
Ru(2)-Ru(1)-Ru(2')	58.42(9)	C(7)-C(5)-C(6)	90.6(18)
C(2)-Ru(2)-Ru(2')	79.3(7)	As(2)-C(7)-C(5)	131.9(17)
C(2)-Ru(2)-Ru(1)	97.4(7)	As(2)-C(7)-C(8)	134.0(17)
C(2)-Ru(2)-As(2)	92.8(7)	C(5)-C(7)-C(8)	94.1(19)
C(2)-Ru(2)-C(3)	95.9(10)		
Ru(2')-Ru(2)-Ru(1)	60.79(4)	C(5)-C(6)-F(1)	117.8(23)
Ru(2')-Ru(2)-C(3)	98.7(8)	C(5)-C(6)-F(2)	116.0(24)
Ru(2')-Ru(2)-C(4)	95.5(7)	C(5)-C(6)-C(8)	87.1(19)
C(3)-Ru(2)-As(2)	99.1(8)	F(1)-C(6)-C(8)	115.3(23)
C(3)-Ru(2)-C(4)	93.3(11)	F(1)-C(6)-F(2)	106.8(23)
C(4)-Ru(2)-As(2)	89.5(7)	F(2)-C(6)-C(8)	113.3(24)
C(4)-Ru(2)-Ru(1)	72.6(7)		
Ru(1)-Ru(2)-As(2)	104.0(1)	C(7)-C(8)-F(3)	119.0(22)
		C(7)-C(8)-F(4)	114.4(22)
Ru(1)-As(1)-Me(1)	117.8(8)	C(7)-C(8)-C(6)	88.2(19)
Ru(1)-As(1)-Me(2)	119.0(10)	F(3)-C(8)-C(6)	117.1(23)
Ru(1)-As(1)-C(5)	118.5(7)	F(3)-C(8)-F(4)	103.2(21)
Me(1)-As(1)-Me(2)	103.5(14)	C(6)-C(8)-F(4)	115.4(23)
Me(1)-As(1)-C(5)	97.1(11)		
Me(2)-As(1)-C(5)	96.8(12)	O(1)-C(1)-Ru(1)	172.5(23)
		O(2)-C(2)-Ru(2)	175.1(20)
Ru(2)-As(2)-Me(3)	117.8(8)	O(3)-C(3)-Ru(2)	176.1(23)
Ru(2)-As(2)-Me(4)	119.1(9)	O(4)-C(4)-Ru(2)	172.6(21)

Table IV.V

Equations of planes in the form $\ell X + mY + nZ = p$, where X, Y, Z are coordinates in Å, referred to orthogonal axes a, b, c.

	ℓ	m	n	p	maximum displacement (Å)
Ruthenium triangle (3 Ru atoms)	0.8945	0	-0.4471	-2.4377	0
Di-(tertiary arsine) (2 As and 4C atoms)	0.8442	0.3112	-0.4364	-1.9683	0.04

Table IV.VI

Magnitudes (Å) of the principal axes of the thermal vibration ellipsoids

	Axis 1	Axis 2	Axis 3
Ru(1)	0.13	0.19	0.22
Ru(2)	0.14	0.20	0.22
As(1)	0.13	0.21	0.27
As(2)	0.16	0.19	0.23
F(1)	0.19	0.27	0.44
F(2)	0.24	0.32	0.45
F(3)	0.22	0.26	0.42
F(4)	0.22	0.24	0.45

DISCUSSION

The molecular stereochemistry is shown in Figure IV.1. The molecule is situated on a crystallographic two-fold axis, and is conveniently described as a derivative of $Ru_3(CO)_{12}$[35] in which two carbonyl groups on one ruthenium and one carbonyl on each of the other two ruthenium atoms are replaced by the two bidentate di-(tertiary arsine) ligands, in such a way that each ligand bridges two ruthenium atoms, and one Ru-Ru bond remains unbridged.

The replacement of four carbonyl groups from $Ru_3(CO)_{12}$ to form $L_2Ru_3(CO)_8$ causes several structural changes. All Ru-Ru bond lengths are no longer equal. The distance between two ruthenium atoms which are linked by the four-membered bridge of the di-(tertiary arsine) ligand is 2.853(3) Å (standard deviation in parentheses), compared with 2.785(4) Å for the unbridged Ru-Ru distance and 2.849, 2.859, and 2.837 Å (each σ = 0.006 Å) for the three Ru-Ru distances in the parent molecule.[35] This significant shortening probably arises from differences in π-acceptor character of the di-(tertiary arsine) relative to carbonyl groups. This electronic difference has been used previously to explain the increase in isomer shift of $LFe_3(CO)_{10}$ relative to $Fe_3(CO)_{12}$.[17] Several other ruthenium cluster compounds have been studied[36-40] in which Ru-Ru bond lengths ranged from 2.853 to 2.956 Å, with one short distance of 2.782 reported for the Ru(2)-

$$[(CH_3)_2AsC{=}C(As(CH_3)_2)CF_2CF_2]_2\,Ru_3(CO)_8$$

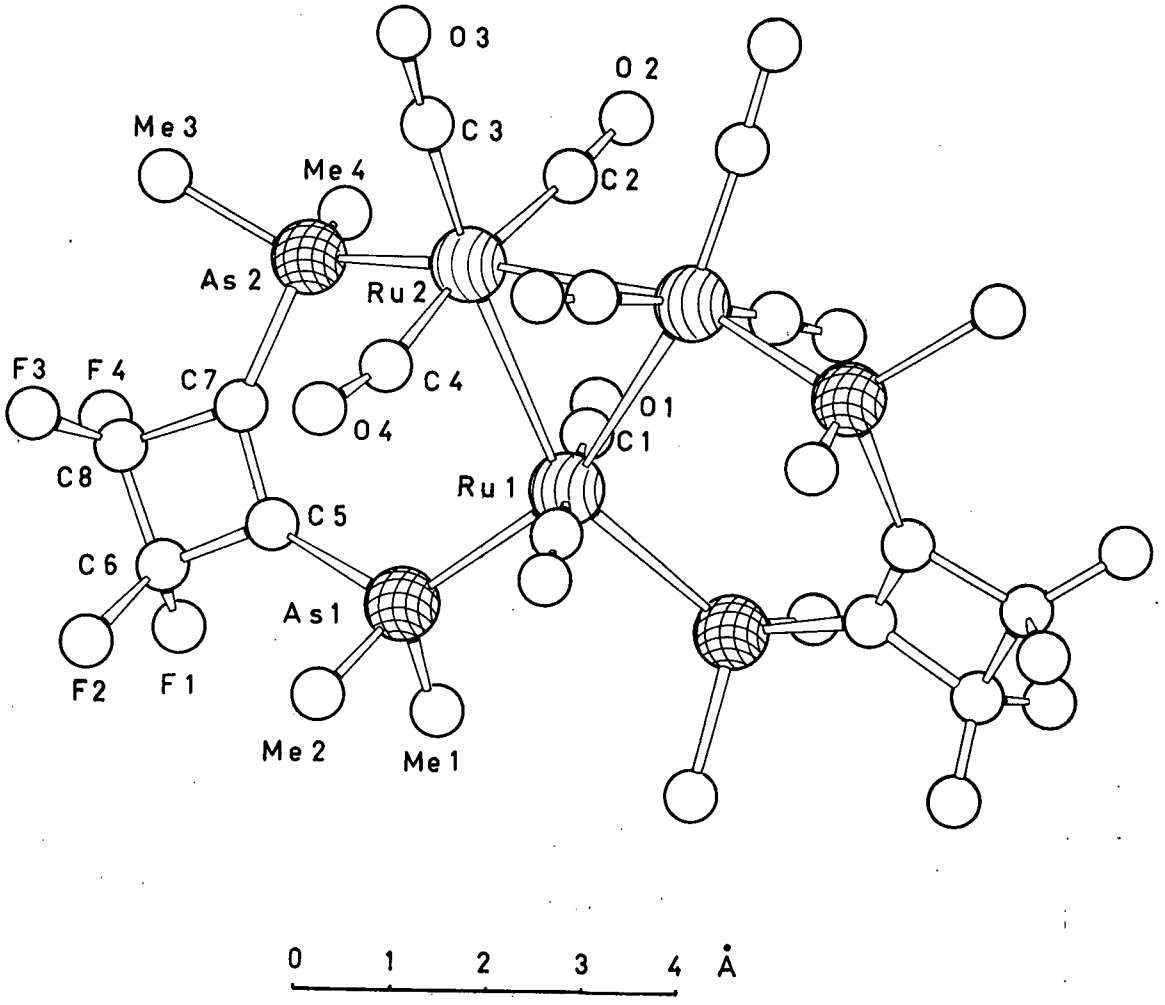

Figure IV.1 Molecular structure of $L_2Ru_3(CO)_8$.

Ru(3) bond distance in bis(cyclo-octatetraene)triruthenium tetracarbonyl (Figure IV.2a).[40] The marked similarity between Figures IV.2a and IV.2b would suggest that C_8H_8 and the di-(tertiary arsine) are exerting the same effect on the bonding properties in the cluster. In both cases, Ru-Ru bonds involving the ruthenium atoms with the greatest number of carbonyl ligands are the shortest, reflecting the superiority of the carbonyl relative to the other ligands as an extractor of electron density from non-bonding d orbitals on the metal atom. In other words, the di-(tertiary arsine) and cyclo-octatetraene ligands are weaker π-acceptors than the carbonyl group.

As expected from n.m.r. observations and from the structure of $LFe_3(CO)_{10}$, the skeleton of the ligand does not differ significantly from exact planarity. The plane of the ligand is twisted 18.2° with respect to the plane of the ruthenium triangle and this twisting causes significant displacements of the carbonyl groups from their positions in the parent carbonyl. In $Ru_3(CO)_{12}$[35] axial carbonyl groups are very nearly perpendicular to the plane of the ruthenium triangle (angles vary from 88.0 to 89.9°), whereas in $L_2Ru_3(CO)_8$ the twisting of the ligand causes the carbonyl groups to be bent from axial positions, as shown in Figure IV.3. Nevertheless, ruthenium does retain an approximately octahedral co-ordination in the complex.

The arsenic atoms also suffer minor distortions

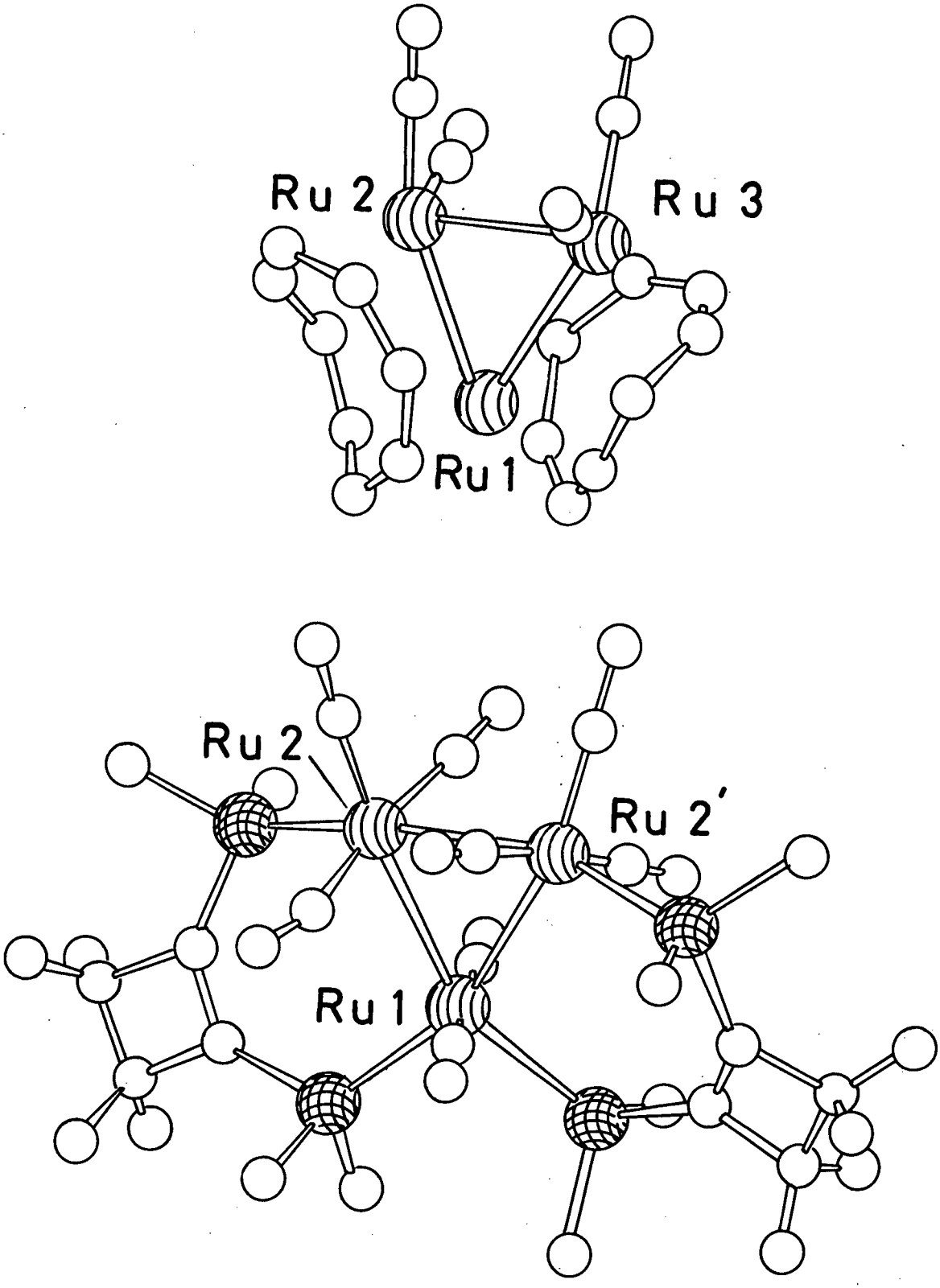

Figure IV.2 Comparison of $(C_8H_8)_2Ru_3(CO)_4$ and $L_2Ru_3(CO)_8$.

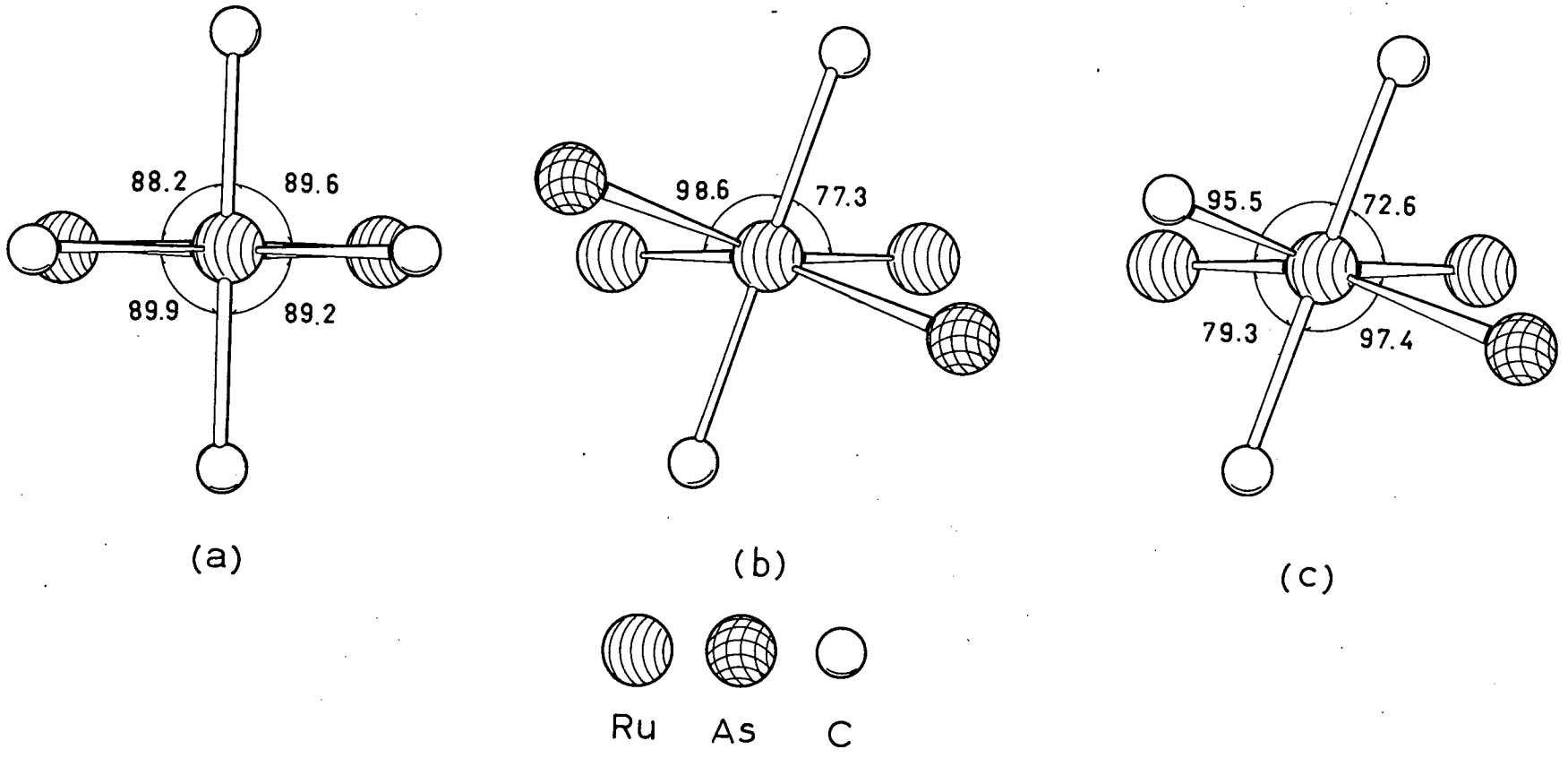

Figure IV.3 Co-ordination about ruthenium atoms (a) in parent compound and (b) Ru(1) and (c) Ru(2) of di-(tertiary arsine) complex.

of their co-ordination. As in $LFe_3(CO)_{10}$, the large size of the metal atom causes Ru-As-C angles to be larger than C-As-C angles (averages 118.1 and 99.5° respectively; *cf.* Figure III.4). Ru-As bond distances are within the range 2.308 - 2.472 Å reported for $Ru\{(Ph_2AsC_6H_4)_3As\}Br_2$.[41] Our mean value (2.407 Å) is in accord with the distance which would be predicted from the Fe-As bond length, and from the difference of atomic radii of Ru and Fe; *e.g.* the Fe-As bond distance in $LFe_3(CO)_{10}$ is 2.30 Å, the Ru-Ru distance in $Ru_3(CO)_{12}$ is 2.85 Å,[35] and the unbridged Fe-Fe distance in $Fe_3(CO)_{12}$ is 2.65 Å[18] giving a predicted Ru-As bond length of $\{2.30 + \frac{1}{2}(2.85 - 2.65)\} = 2.40$ Å.

None of the other structural parameters is particularly surprising. Average Ru-C and C-O distances are 1.89 and 1.15 Å, as in the parent compound, and the Ru-C-O angles show the same slight deviations from linearity which are found in all the metal carbonyls.[31] The retention of the double bond in the ligand between C(5) and C(7) is indicated by the short bond length of 1.39(3) Å, not significantly different from the value for the sp^2 hybridization scheme. The compound $LRu_2(CO)_6$ which forms during the preparation of the present derivative,[20] is assumed to be analogous to $LFe_2(CO)_6$[19] in which this double bond is broken to allow the involvement of the π-electrons in bonding to one of the iron atoms.

Intermolecular contacts range from 2.9 to 3.5 Å

and are normal van der Waals interactions. The most important of these are shown in a projection of the structure (Figure IV.4).

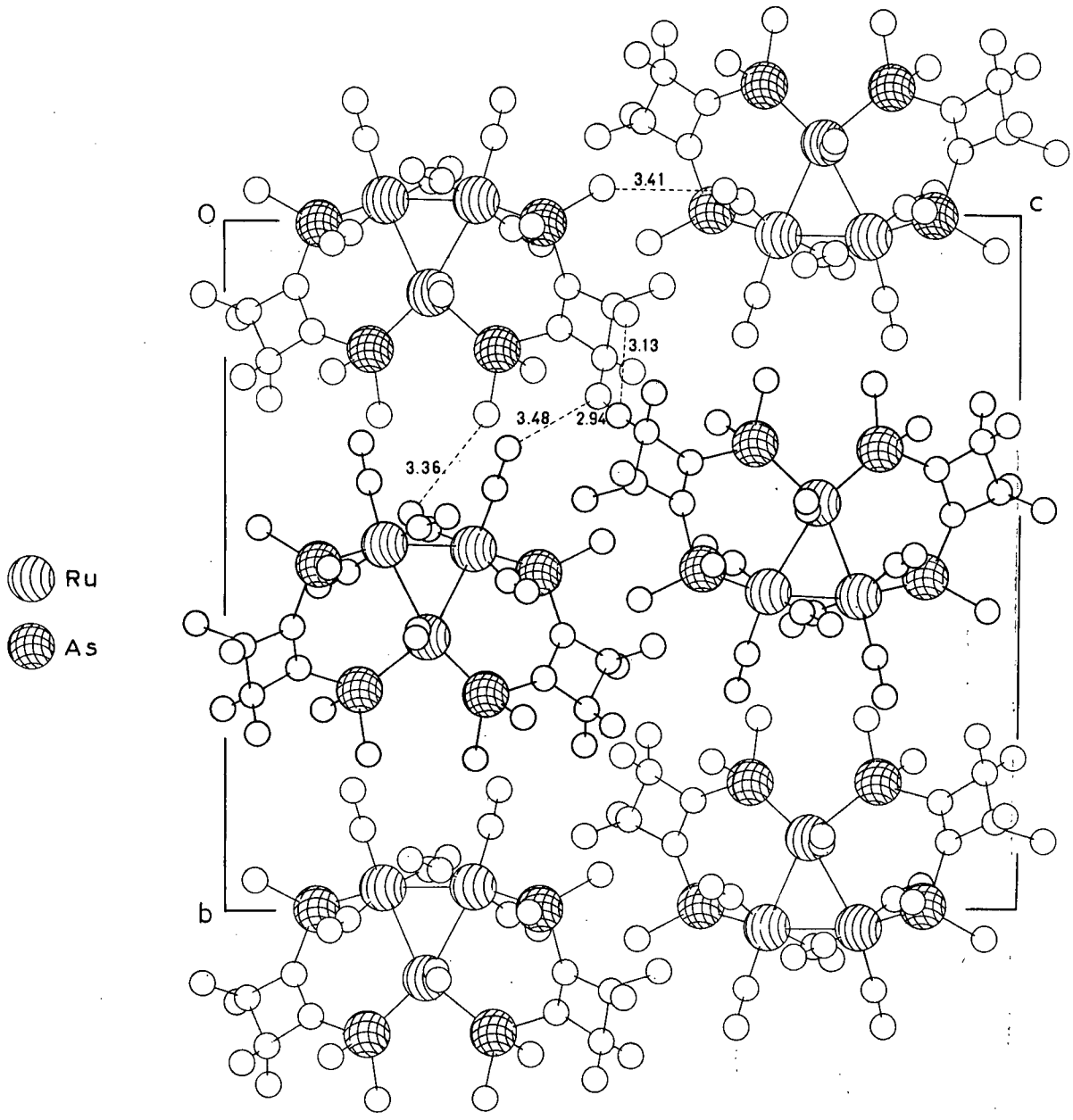

Figure IV.4 Projection of unit cell down a-axis.

V. THE STRUCTURE DETERMINATION OF

$Me_2AsC{=}C(AsMe_2)CF_2CF_2 \cdot Ru_3(CO)_{10}$

STRUCTURE ANALYSIS

The positions of the three ruthenium and two arsenic atoms in the asymmetric unit were determined from the Patterson function and improved with two cycles of full-matrix least-squares refinement using scattering factors from ref. 26. A difference synthesis phased on these refined parameters revealed the positions of all thirty-two carbon, oxygen, and fluorine atoms. One cycle of full-matrix refinement, varying an isotropic thermal parameter and three positional parameters for each of the thirty-two light atoms reduced $\underline{R}$ to 0.126. At this point, all atoms were given anisotropic temperature factors which, along with positional parameters, were improved by six cycles of block-diagonal least-squares refinement, minimizing $\Sigma \underline{w}(\underline{F}_o-\underline{F}_c)^2$. Reflections were given weights according to the following scheme.

$$\sqrt{w} = 1 \qquad \text{if } |\underline{F}_o| < F^*$$

$$\sqrt{w} = F^*/|\underline{F}_o| \qquad \text{if } |\underline{F}_o| \geq F^*$$

$$\text{and } \sqrt{w} = 0.5 \qquad \text{for unobserveds}$$

For this data, a choice of $F^* = 70$ results in approximately constant values for $\underline{w}(\underline{F}_o-\underline{F}_c)^2$ over the whole range of $|\underline{F}_o|$. At final convergence, parameter shifts were small fractions of their corresponding standard deviations and $\underline{R}$ and $\underline{R}_w$ were 0.076 and 0.096 respectively for the 1828 observed reflections and 0.088 and 0.100 for

all data. Measured and calculated structure factors are given in Table V.I. A final difference map showed fluctuations around the heavy atoms of ±1.8 e/Å^3 which have been assumed to arise from random experimental error.

Table V.II lists the final positional and thermal parameters with standard deviations calculated from the inverses of the diagonal terms of the matrix of the final refinement cycle. Bond distances and valence angles are given in Table V.III. Standard deviations of these quantities contain a contribution from the standard deviations of the unit cell parameters. Table V.IV gives the equations of the weighted mean planes of the ruthenium triangle and of the arsenic and carbon atoms of the di-(tertiary arsine) ligand. The magnitudes of the principal axes of anisotropic thermal vibration are given in Table V.V for the three ruthenium and two arsenic atoms.

Table V.I

Final measured and calculated structure factors. Unobserved reflections have an asterisk after the $|F_o|$ value.

**** L = 0****

H	K	OBS	CALC
0	2	348	326
0	4	26	42
0	6	38	29
0	8	52	54
0	10	38	39
0	12	53	50
0	14	81	83
0	16	83	83
0	18	33	29
0	20	52	48
1	1	408	327
1	2	138	77
1	3	56	54
1	4	28	24
1	5	77	74
1	6	235	236
1	7	252	266
1	8	166	167
1	9	141	141
1	10	65	61
1	11	14	10
1	12	13	7
1	13	13	19
1	14	30	26
1	15	63	62
1	16	44	43
1	17	26	28
1	18	79	71
1	19	25	22
1	20	61	54
2	0	45	42
2	1	25	25
2	2	123	104
2	3	26	24
2	4	109	91
2	5	245	220
2	6	222	201
2	7	99	92
2	8	276	280
2	9	10	12
2	10	34	42
2	11	141	139
2	12	68	71
2	13	55	53
2	14	126	133
2	15	41	37
2	16	69	72
2	17	26	19
2	18	32	30
2	19	0*	5
3	1	147	129
3	2	22	5
3	3	12	12
3	4	30	25
3	5	92	84
3	6	75	71
3	7	164	154
3	8	47	46
3	9	27	19
3	10	67	70
3	11	16	14
3	12	31	26
3	13	154	154
3	14	26	31
3	15	147	163
3	16	46	46
3	17	15	7
3	18	30	32
3	19	35	29
4	0	257	231
4	1	6*	0
4	2	115	111
4	3	163	143
4	4	135	121
4	5	134	115
4	6	142	128
4	7	153	142
4	8	64	67
4	9	21	14
4	10	66	76
4	11	82	76
4	12	31	33
4	13	64	64
4	14	68	66
4	15	10*	10
4	16	21	15
4	17	18	21
4	18	25	21
5	1	155	137
5	2	148	134
5	3	21	14
5	4	130	126
5	5	83	77
5	6	18	17
5	7	150	140
5	8	14	15
5	9	55	51
5	10	16	21
5	11	69	71
5	12	19	19
5	13	27	37
5	14	22	28
5	15	5*	5
5	16	33	36
5	17	20	17
6	0	229	207
6	1	77	73
6	2	46	41
6	3	82	74
6	4	124	119
6	5	78	81
6	6	11*	15
6	7	50	53
6	8	65	68
6	9	26	25
6	10	36	29
6	11	17	12
6	12	31	33
6	13	20	15
6	14	63	64
6	15	33	36
7	1	25	20
7	2	86	82
7	3	93	90
7	4	79	71
7	5	51	48
7	6	18	18
7	7	86	86
7	8	27	25
7	9	80	85
7	10	10*	21
7	11	34	36
7	12	19	11
7	13	33	35
8	0	5*	13
8	1	27	27
8	2	26	26
8	3	78	79
8	4	26	25
8	5	36	35
8	6	59	58
8	7	0*	13
8	8	55	54
8	9	32	29
8	10	21	9
9	1	49	49
9	2	0*	4
9	3	16	10
9	4	16	19

**** L = 1****

H	K	OBS	CALC
0	2	0*	18
0	3	112	118
0	4	0*	16
0	5	42	39
0	6	85	79
0	7	143	146
0	8	65	59
0	9	211	223
0	10	56	60
0	11	49	51
0	12	100	99
0	13	49	54
0	14	33	33
0	15	34	40
0	16	55	56
0	17	57	52
0	18	0*	9
0	19	100	90
0	20	26	32
1	0	198	151
1	1	344	295
1	2	210	176
1	3	125	119
1	4	97	94
1	5	97	93
1	6	52	47
1	7	21	20
1	8	71	73
1	9	108	110
1	10	50	55
1	11	99	102
1	12	90	89
1	13	66	68
1	14	55	51
1	15	29	29
1	16	63	56
1	17	30	28
1	18	39	29
1	19	36	31
1	20	37	36
2	0	94	79
2	1	156	140
2	2	53	48
2	3	47	42
2	4	75	65
2	5	238	219
2	6	208	186
2	7	117	115
2	8	71	65
2	9	75	73
2	10	53	49
2	11	54	55
2	12	44	44
2	13	63	61
2	14	63	66
2	15	70	66
2	16	4*	16
2	17	97	93
2	18	21	22
2	19	40	35
3	0	94	81
3	1	77	66
3	2	122	102
3	3	80	74
3	4	166	143
3	5	86	79
3	6	200	183
3	7	147	133
3	8	74	66
3	9	110	108
3	10	118	112
3	11	72	78
3	12	23	23
3	13	69	69
3	14	20	23
3	15	38	37
3	16	41	44
3	17	4*	7
3	18	30	23
3	19	8*	5
4	0	43	37
4	1	156	140
4	2	113	96
4	3	166	146
4	4	17	15
4	5	135	121
4	6	97	92
4	7	103	94
4	8	23	17
4	9	86	68
4	10	79	77
4	11	34	35
4	12	101	103
4	13	84	87
4	14	110	110
4	15	39	41
4	16	34	35
4	17	7*	4
4	18	10*	8
5	0	14	19
5	1	57	56
5	2	173	158
5	3	79	74
5	4	163	150
5	5	136	130
5	6	84	81
5	7	56	50
5	8	81	78
5	9	44	41
5	10	19	17
5	11	12	10
5	12	105	109
5	13	30	30
5	14	67	71
5	15	15	14
5	16	26	26
6	0	93	85
6	1	56	57
6	2	108	106
6	3	114	111
6	4	72	75
6	5	138	134
6	6	59	57
6	7	56	56
6	8	46	43
6	9	50	51
6	10	32	31
6	11	44	49
6	12	56	58
6	13	48	53
6	14	17	15
6	15	32	35
7	0	93	92
7	1	83	81
7	2	54	56
7	3	35	35
7	4	88	88
7	5	21	23
7	6	99	101
7	7	20	19
7	8	57	56
7	9	22	24
7	10	56	59
7	11	57	58
7	12	50	52
7	13	57	57
8	0	42	38
8	1	77	74
8	2	35	36
8	3	52	49
8	4	0*	6
8	5	10*	8
8	6	54	53
8	7	34	35
8	8	70	72
8	9	63	61
8	10	72	74
9	0	61	56
9	1	37	34
9	2	56	57
9	3	37	37
9	4	12*	20

**** L = 2****

H	K	OBS	CALC
0	0	368	332
0	1	350	322
0	2	107	81
0	3	65	66
0	4	19	24
0	5	176	165
0	6	136	122
0	7	224	218
0	8	150	146
0	9	148	140
0	10	240	235
0	11	20	19
0	12	73	75
0	13	17	22
0	14	43	38
0	15	52	47
0	16	10*	6
0	17	36	36
0	18	55	52
0	19	34	35
0	20	0*	3
1	0	311	272
1	1	84	84
1	2	197	180
1	3	47	43
1	4	108	106
1	5	79	81
1	6	146	151
1	7	108	105
1	8	181	188
1	9	27	28
1	10	129	130
1	11	107	109
1	12	89	91
1	13	22	24
1	14	108	105
1	15	15	20
1	16	130	122
1	17	50	45
1	18	80	74
1	19	22	25
2	0	22	18
2	1	220	203
2	2	226	215
2	3	124	128
2	4	120	112
2	5	139	128
2	6	43	34
2	7	138	137
2	8	164	158
2	9	97	97
2	10	54	53
2	11	26	21
2	12	37	38
2	13	102	97
2	14	31	31
2	15	121	121
2	16	6*	10
2	17	19	21
2	18	37	35
2	19	10*	8
3	0	96	79
3	1	144	125
3	2	33	27
3	3	137	125
3	4	62	62
3	5	139	124
3	6	215	201
3	7	35	26
3	8	150	144
3	9	20	24
3	10	45	47
3	11	20	22
3	12	18	20
3	13	41	40
3	14	116	120
3	15	53	50
3	16	56	58
3	17	0*	14
3	18	50	49
3	19	20	19
4	0	107	96
4	1	112	98
4	2	85	75
4	3	166	151
4	4	54	54
4	5	118	105
4	6	15	9
4	7	136	129
4	8	71	65
4	9	34	30
4	10	72	78
4	11	29	28
4	12	83	88
4	13	76	77
4	14	36	40
4	15	74	73
4	16	16	12
4	17	17	12
4	18	4*	8
5	0	160	147
5	1	35	32
5	2	77	74
5	3	43	44
5	4	74	69
5	5	56	55
5	6	116	110
5	7	78	73
5	8	88	86
5	9	20	25
5	10	21	23
5	11	104	102
5	12	64	63
5	13	66	69
5	14	54	57
5	15	30	26
5	16	33	33
6	0	17	9
6	1	86	84
6	2	25	20
6	3	66	62
6	4	39	40
6	5	110	105
6	6	18	16
6	7	147	149
6	8	25	22
6	9	62	61
6	10	26	30
6	11	16	16
6	12	30	26
6	13	24	23
6	14	68	71
6	15	22	24
7	0	84	81
7	1	79	79
7	2	38	33
7	3	61	62
7	4	78	75
7	5	21	24
7	6	54	51
7	7	31	32
7	8	57	58
7	9	19	22
7	10	41	38
7	11	36	38
7	12	33	37
7	13	60	60
8	0	20	15
8	1	49	43
8	2	44	45
8	3	23	26
8	4	37	35
8	5	50	52
8	6	35	32
8	7	60	61
8	8	25	30
8	9	35	34
9	0	14	7
9	1	84	88
9	2	31	29
9	3	27	26
9	4	19	18

**** L = 3****

H	K	OBS	CALC
0	1	15	44
0	2	243	210
0	3	108	102
0	4	76	75
0	5	26	37
0	6	88	85
0	7	41	37
0	8	23	24
0	9	113	113
0	10	36	40
0	11	125	122
0	12	61	64
0	13	10*	16
0	14	46	43
0	15	62	58
0	16	37	36
0	17	97	90
0	18	25	23
0	19	27	33
1	0	51	56
1	1	126	150
1	2	106	122
1	3	129	135
1	4	141	144
1	5	261	278
1	6	125	135
1	7	102	105
1	8	26	29
1	9	161	173
1	10	20	22
1	11	109	115
1	12	30	33
1	13	60	66
1	14	32	33
1	15	20	20
1	16	34	28
1	17	30	32
1	18	0*	2
1	19	31	32
2	0	131	116
2	1	15	15
2	2	111	110
2	3	141	145
2	4	168	163
2	5	110	114
2	6	174	174
2	7	56	59
2	8	87	86
2	9	82	79
2	10	77	77
2	11	53	53
2	12	78	80
2	13	46	40
2	14	27	28
2	15	75	70
2	16	69	67
2	17	77	68
2	18	37	32
2	19	48	43
3	0	50	44
3	1	206	198
3	2	169	152
3	3	153	140
3	4	157	142
3	5	79	84
3	6	18	19
3	7	9	11
3	8	37	37
3	9	24	25
3	10	33	38
3	11	68	64
3	12	42	43
3	13	89	90
3	14	52	52
3	15	33	32
3	16	41	35
3	17	72	67
3	18	0*	7
4	0	35	38
4	1	39	36
4	2	125	119
4	3	39	34
4	4	180	170
4	5	97	91
4	6	141	135
4	7	157	149
4	8	68	71
4	9	67	67
4	10	51	48
4	11	55	52
4	12	59	63
4	13	31	33
4	14	25	28
4	15	7*	14
4	16	31	32
4	17	7*	4
5	0	120	99
5	1	44	41
5	2	120	115
5	3	82	78
5	4	109	103
5	5	131	131
5	6	74	77
5	7	46	49
5	8	16	22
5	9	84	84
5	10	37	37
5	11	65	63
5	12	22	23
5	13	159	113
5	14	26	28
5	15	66	73
5	16	11*	13
6	0	20	22
6	1	61	57
6	2	116	112
6	3	51	48
6	4	44	45
6	5	72	67
6	6	83	82
6	7	78	78
6	8	60	62
6	9	10*	9
6	10	82	87
6	11	68	66
6	12	102	108
6	13	40	42
6	14	72	76
6	15	0*	12
7	0	30	23
7	1	75	72
7	2	17	15
7	3	58	56
7	4	55	53
7	5	77	78
7	6	103	104
7	7	91	88
7	8	53	52
7	9	70	70
7	10	26	17
7	11	32	36
7	12	25	23
8	0	167	155
8	1	11*	15
8	2	103	102
8	3	37	34
8	4	43	39
8	5	37	39
8	6	39	40
8	7	23	22
8	8	36	37
8	9	0*	11
9	0	37	41
9	1	74	72
9	2	42	48
9	3	48	47

**** L = 4****

H	K	OBS	CALC
0	0	45	45
0	1	173	143
0	2	84	75
0	3	103	102
0	4	0*	2
0	5	21	24
0	6	278	254
0	7	97	92
0	8	238	219
0	9	106	101
0	10	121	118
0	11	150	136
0	12	62	65
0	13	3*	18
0	14	98	94
0	15	0*	4
0	16	63	39
0	17	67	81
0	18	20	23
0	19	49	41
1	0	20	20
1	1	149	151
1	2	38	35
1	3	123	142
1	4	160	162
1	5	112	115
1	6	81	81
1	7	138	141
1	8	113	111
1	9	93	99
1	10	161	162
1	11	55	53
1	12	38	44
1	13	69	69
1	14	68	66
1	15	90	89
1	16	66	61
1	17	35	33
1	18	83	75
1	19	17	24
2	0	359	343
2	1	67	64
2	2	371	373
2	3	226	234
2	4	90	90
2	5	160	165
2	6	107	106
2	7	34	33
2	8	30	30
2	9	0*	13
2	10	82	80
2	11	68	69
2	12	53	53
2	13	27	28
2	14	47	48
2	15	49	50
2	16	60	54
2	17	28	26
2	18	28	31
2	19	35	27
3	0	104	95
3	1	122	129
3	2	106	105
3	3	119	118
3	4	201	200
3	5	106	101
3	6	58	55
3	7	142	132
3	8	170	168
3	9	54	56
3	10	45	49
3	11	18	20
3	12	83	83
3	13	20	23
3	14	45	43
3	15	10*	11
3	16	41	40
3	17	0*	6
3	18	43	37
4	0	54	48
4	1	86	80
4	2	44	37
4	3	155	147
4	4	30	28
4	5	161	147
4	6	83	82
4	7	80	79
4	8	89	89
4	9	8*	9
4	10	88	88
4	11	78	76
4	12	93	91
4	13	51	51
4	14	84	85
4	15	17	20
4	16	67	61
4	17	8*	10
5	0	130	115
5	1	72	65
5	2	35	35
5	3	77	71
5	4	96	89
5	5	0*	7
5	6	63	64
5	7	81	80
5	8	46	43
5	9	77	73
5	10	86	79
5	11	47	47
5	12	42	43
5	13	77	80
5	14	44	44
5	15	63	67
5	16	24	23
6	0	71	70
6	1	75	71
6	2	34	35
6	3	82	77
6	4	31	33
6	5	93	92
6	6	79	75
6	7	87	88
6	8	56	51
6	9	36	33
6	10	21	15
6	11	52	54
6	12	18	22
6	13	17	22
6	14	8*	7
7	0	31	24
7	1	78	77
7	2	66	53
7	3	52	49
7	4	49	48
7	5	29	24
7	6	45	45
7	7	31	30
7	8	16	13
7	9	32	33
7	10	37	39
7	11	52	56
7	12	17	20
8	0	34	32
8	1	54	53
8	2	25	24
8	3	32	32
8	4	19	23
8	5	35	37
8	6	50	51
8	7	23	28
8	8	27	22
8	9	25	28
9	0	46	46
9	1	49	50

**** L = 5****

H	K	OBS	CALC
0	1	127	113
0	2	131	115
0	3	91	85
0	4	196	177
0	5	156	155
0	6	49	48
0	7	178	179
0	8	0*	10
0	9	29	27
0	10	0*	3
0	11	0*	14
0	12	81	76
0	13	0*	0
0	14	27	23
0	15	30	31
0	16	20	21
0	17	83	70
0	18	31	23
0	19	26	23
1	0	180	172
1	1	103	110
1	2	120	129
1	3	114	111
1	4	12	14
1	5	114	114
1	6	130	137
1	7	52	53
1	8	10	9
1	9	59	61
1	10	67	65
1	11	85	84
1	12	48	46
1	13	92	92
1	14	43	41
1	15	31	33
1	16	44	43
1	17	4*	14
1	18	25	22
1	19	39	33
2	0	79	76
2	1	153	150
2	2	16	16
2	3	44	46
2	4	141	137
2	5	21	24
2	6	99	101
2	7	135	133
2	8	34	31
2	9	169	174
2	10	60	58
2	11	24	27
2	12	73	72
2	13	71	77
2	14	65	62
2	15	28	25
2	16	44	41
2	17	9*	15
2	18	28	24
3	0	113	110
3	1	81	80
3	2	100	97
3	3	81	83
3	4	77	75
3	5	42	41
3	6	63	63
3	7	43	41
3	8	123	120
3	9	44	44
3	10	15	22
3	11	78	75
3	12	90	92
3	13	57	56
3	14	50	47
3	15	50	48
3	16	46	45
3	17	66	54
3	18	24	20
4	0	92	86
4	1	146	145
4	2	71	70
4	3	145	147
4	4	33	36
4	5	110	117
4	6	12	11
4	7	43	42
4	8	65	69
4	9	41	40
4	10	33	30
4	11	39	37
4	12	45	39
4	13	51	53
4	14	56	58
4	15	67	72
4	16	32	31
4	17	58	55
5	0	16	17
5	1	30	24
5	2	56	59
5	3	47	51
5	4	135	122
5	5	65	63
5	6	155	153
5	7	26	26
5	8	84	86
5	9	91	85
5	10	26	26
5	11	60	57
5	12	44	42
5	13	6*	15
5	14	32	32
5	15	0*	10
5	16	43	44
6	0	47	31
6	1	82	76
6	2	94	95
6	3	105	103
6	4	48	49
6	5	86	82
6	6	8*	17
6	7	69	65
6	8	47	46
6	9	75	75
6	10	37	37
6	11	59	59
6	12	49	52
6	13	42	41
6	14	30	28
7	0	129	119
7	1	35	33
7	2	133	130
7	3	37	36
7	4	50	57
7	5	50	54
7	6	0*	15
7	7	40	41
7	8	38	37
7	9	30	26
7	10	57	53
7	11	18	12
8	0	43	43
8	1	67	75
8	2	46	51
8	3	46	47
8	4	58	58
8	5	64	69
8	6	30	27
8	7	50	49
8	8	44	39

**** L = 6****

H	K	OBS	CALC
0	0	196	163
0	1	23	24
0	2	134	125
0	3	149	140
0	4	199	190
0	5	25	22
0	6	72	59
0	7	26	25
0	8	44	48
0	9	35	21
0	10	81	83
0	11	97	97
0	12	22	19
0	13	128	128
0	14	67	72
0	15	77	71
0	16	0*	12
0	17	42	43
0	18	75	73
0	19	8*	2
1	0	41	39
1	1	46	42
1	2	30	33
1	3	103	116
1	4	100	113
1	5	117	131
1	6	140	152
1	7	89	97
1	8	100	112
1	9	65	67
1	10	64	69
1	11	127	135
1	12	60	59
1	13	50	48
1	14	44	43
1	15	22	23
1	16	32	33
1	17	47	45
1	18	38	36
2	0	147	149
2	1	58	69
2	2	90	98
2	3	93	108
2	4	148	171
2	5	99	108
2	6	42	47
2	7	89	95
2	8	71	74
2	9	78	81
2	10	128	145
2	11	48	47
2	12	119	124
2	13	31	28
2	14	15	19
2	15	8*	11
2	16	16	21
2	17	25	18
2	18	52	48
3	0	249	222
3	1	101	88
3	2	128	129
3	3	135	135
3	4	59	63
3	5	109	103
3	6	78	78
3	7	49	50
3	8	75	72
3	9	32	29
3	10	67	68
3	11	114	115
3	12	30	30
3	13	69	65
3	14	55	49
3	15	42	36
3	16	52	46
3	17	31	29
4	0	4*	20
4	1	39	37
4	2	110	105
4	3	47	48
4	4	177	179
4	5	75	74
4	6	24	21
4	7	117	114
4	8	83	82
4	9	79	78
4	10	55	56
4	11	65	62
4	12	21	25
4	13	35	36
4	14	24	25
4	15	22	16
4	16	14	13
5	0	87	78
5	1	27	29
5	2	62	60
5	3	121	124
5	4	68	68
5	5	64	65
5	6	60	60
5	7	42	42
5	8	68	68
5	9	27	29
5	10	48	48
5	11	52	51
5	12	36	37
5	13	37	36
5	14	31	31
5	15	52	47
6	0	15	10
6	1	44	46
6	2	22	20
6	3	68	71
6	4	33	33
6	5	50	53
6	6	22	23
6	7	30	34
6	8	0*	9
6	9	49	51
6	10	79	76
6	11	20	13
6	12	38	42
6	13	34	30
7	0	6*	11
7	1	37	40
7	2	31	28
7	3	21	16
7	4	43	42
7	5	26	24
7	6	16	13
7	7	23	28
7	8	24	23
7	9	45	42
7	10	17	21
7	11	83	86
8	0	40	38
8	1	46	43
8	2	36	31
8	3	44	50
8	4	44	48
8	5	29	28
8	6	0*	11
8	7	26	25

**** L = 7****

H	K	OBS	CALC
0	1	40	29
0	2	59	45
0	3	69	65
0	4	110	106
0	5	159	151
0	6	165	152
0	7	119	122
0	8	61	59
0	9	62	64
0	10	87	83
0	11	25	21
0	12	58	55
0	13	30	30
0	14	0*	8
0	15	60	59
0	16	0*	9
0	17	67	64
0	18	7*	10
1	0	14	11
1	1	104	109
1	2	65	76
1	3	91	98
1	4	31	31
1	5	71	74
1	6	68	73
1	7	59	62
1	8	92	96
1	9	43	40
1	10	40	44
1	11	42	41
1	12	89	88
1	13	33	33
1	14	79	72
1	15	0*	9
1	16	60	53
1	17	15	16
1	18	19	15
2	0	19	21
2	1	126	131
2	2	98	101
2	3	98	108
2	4	67	70
2	5	77	77
2	6	84	95
2	7	52	55
2	8	39	40
2	9	107	117
2	10	17	14
2	11	0*	10
2	12	58	59
2	13	46	45
2	14	31	31
2	15	5*	9
2	16	22	19
2	17	35	30
2	18	20	9
3	0	35	35
3	1	25	47
3	2	120	119
3	3	93	93
3	4	70	67
3	5	52	54
3	6	47	48
3	7	73	70
3	8	63	60
3	9	102	104
3	10	62	64
3	11	75	75
3	12	22	30
3	13	58	59
3	14	35	29
3	15	52	45
3	16	18	11
3	17	34	26
4	0	0*	2
4	1	132	122
4	2	28	28
4	3	25	26
4	4	41	41
4	5	157	151
4	6	53	53
4	7	80	79
4	8	78	78
4	9	52	48
4	10	93	94
4	11	27	23
4	12	66	66
4	13	19	11
4	14	47	48
4	15	28	31
4	16	52	49
5	0	19	22
5	1	128	116
5	2	47	48
5	3	66	78
5	4	84	82
5	5	41	42
5	6	71	73
5	7	36	35
5	8	71	66
5	9	46	42
5	10	41	37
5	11	23	26
5	12	34	34
5	13	22	14
5	14	35	26
5	15	24	20
6	0	117	108
6	1	37	33
6	2	94	100
6	3	39	38
6	4	67	66
6	5	16	18
6	6	60	58
6	7	18	17
6	8	16	17
6	9	65	63
6	10	66	64
6	11	6*	16
6	12	38	31
6	13	37	39
7	0	37	39
7	1	39	44
7	2	68	65
7	3	59	58
7	4	29	25
7	5	44	46
7	6	26	22
7	7	48	46
7	8	66	64
7	9	42	43
7	10	43	45
8	0	22	9
8	1	22	17
8	2	42	42
8	3	19	25
8	4	36	39
8	5	49	42
8	6	49	49

**** L = 8****

H	K	OBS	CALC
0	0	23	29
0	1	86	78
0	2	151	142
0	3	108	102
0	4	222	202
0	5	134	120
0	6	62	52
0	7	34	33
0	8	62	61
0	9	70	64
0	10	19	19
0	11	48	50
0	12	29	25
0	13	29	27
0	14	21	2
0	15	32	32
0	16	7*	6
0	17	20	21
0	18	28	24
1	0	26	20
1	1	48	50
1	2	151	160
1	3	110	116
1	4	132	156
1	5	134	145
1	6	43	46
1	7	59	60
1	8	5*	9
1	9	28	26
1	10	78	80
1	11	76	74
1	12	79	78
1	13	51	48
1	14	30	29
1	15	0*	9
1	16	49	50
1	17	14	18
2	0	72	72
2	1	79	76
2	2	42	40
2	3	115	126
2	4	41	44
2	5	63	64
2	6	8*	11
2	7	43	42
2	8	36	43
2	9	43	49
2	10	119	124
2	11	112	114
2	12	82	83
2	13	77	71
2	14	19	16
2	15	40	41
2	16	33	32
2	17	56	49
3	0	121	116
3	1	19	16
3	2	15	18
3	3	48	52
3	4	115	125
3	5	45	45
3	6	117	117
3	7	45	41
3	8	80	87
3	9	103	106
3	10	91	95
3	11	79	81
3	12	48	46
3	13	9*	17
3	14	24	21
3	15	17	13
3	16	18	22
4	0	95	86
4	1	73	71
4	2	102	101
4	3	141	132
4	4	43	47
4	5	61	63
4	6	0*	5
4	7	38	36
4	8	34	33
4	9	17	16
4	10	53	50
4	11	42	43
4	12	22	19
4	13	16	15
4	14	44	35
4	15	30	28
5	0	56	48
5	1	42	42
5	2	90	91
5	3	84	84
5	4	58	64
5	5	56	51
5	6	59	57
5	7	29	33
5	8	50	50
5	9	40	38
5	10	0*	12
5	11	27	28
5	12	35	33
5	13	22	13
5	14	17	11
6	0	84	78
6	1	51	51
6	2	7*	6
6	3	17	22
6	4	63	60
6	5	44	40
6	6	33	34
6	7	41	42
6	8	26	29
6	9	42	41
6	10	28	23
6	11	44	49
6	12	30	35
7	0	57	57
7	1	58	58
7	2	11	19
7	3	31	30
7	4	6*	16
7	5	42	38
7	6	9*	19
7	7	8*	11
7	8	33	36
7	9	30	28
8	0	0*	0
8	1	11*	10
8	2	29	38
8	3	24	21
8	4	47	52

**** L = 9****

H	K	OBS	CALC
0	1	16	19
0	2	67	58
0	3	116	108
0	4	159	139
0	5	86	77
0	6	104	94
0	7	59	57
0	8	54	42
0	9	0*	11
0	10	42	45
0	11	0*	11
0	12	19	26
0	13	32	32
0	14	0*	6
0	15	42	41
0	16	75	67
0	17	29	29
1	0	26	24
1	1	51	54
1	2	3*	20
1	3	31	39
1	4	80	86
1	5	49	55
1	6	78	83
1	7	0*	14
1	8	0*	6
1	9	85	85
1	10	40	39
1	11	75	68
1	12	44	41
1	13	60	59
1	14	16	12
1	15	52	44
1	16	37	31
1	17	54	45
2	0	0*	0
2	1	54	56
2	2	135	139
2	3	112	110
2	4	61	67
2	5	79	84
2	6	18	20
2	7	33	41
2	8	63	65
2	9	59	58
2	10	43	42
2	11	0*	13
2	12	43	38
2	13	47	42
2	14	28	24
2	15	55	46
2	16	22	16
3	0	0*	2
3	1	98	97
3	2	41	41
3	3	65	68
3	4	30	23
3	5	71	75
3	6	40	44
3	7	37	39
3	8	37	46
3	9	91	94
3	10	63	67
3	11	67	61
3	12	52	47
3	13	18	18
3	14	49	50
3	15	24	23
3	16	41	37
4	0	66	65
4	1	14	13
4	2	92	92
4	3	0*	9
4	4	34	42
4	5	52	56
4	6	79	81
4	7	85	86
4	8	14	19
4	9	94	95
4	10	35	35
4	11	54	56
4	12	4*	8
4	13	6*	5
4	14	13	4
4	15	14	13
5	0	139	123
5	1	52	52
5	2	92	97
5	3	20	23
5	4	0*	11
5	5	47	50
5	6	28	31
5	7	26	26
5	8	36	36
5	9	16	19
5	10	41	40
5	11	28	30
5	12	21	20
5	13	44	43
6	0	59	53
6	1	100	95
6	2	33	31
6	3	85	59
6	4	34	34
6	5	32	28
6	6	30	32
6	7	29	28
6	8	66	69
6	9	33	26
6	10	48	45
6	11	0*	8
7	0	9*	5
7	1	44	43
7	2	24	23
7	3	26	29
7	4	57	59
7	5	15	13
7	6	87	83

Table V.I (continued)

H	K	OBS	CALC
7	7	38	41
7	8	68	66
8	0	49	45
**** L =10****			
0	0	23	17
0	1	30	23
0	2	51	47
0	3	144	127
0	4	97	85
0	5	146	122
0	6	65	65
0	7	0*	4
0	8	4*	18
0	9	34	30
0	10	70	61
0	11	17	13
0	12	107	91
0	13	0*	17
0	14	80	67
0	15	52	44
0	16	49	42
1	0	32	37
1	1	47	54
1	2	42	45
1	3	123	137
1	4	110	130
1	5	84	97
1	6	64	70
1	7	48	56
1	8	63	63
1	9	31	39
1	10	27	27
1	11	52	52
1	12	69	68
1	13	42	42
1	14	14	25
1	15	47	39
1	16	2*	10
2	0	92	82
2	1	28	31
2	2	93	101
2	3	44	49
2	4	75	86
2	5	10*	14
2	6	45	46
2	7	52	53
2	8	25	28
2	9	64	69
2	10	56	60
2	11	90	87
2	12	36	33
2	13	33	32
2	14	22	20
2	15	9*	10
2	16	30	34
3	0	66	58
3	1	122	113
3	2	37	33
3	3	76	81
3	4	58	61
3	5	36	29
3	6	39	44
3	7	32	31
3	8	61	58
3	9	37	38
3	10	83	80
3	11	37	32
3	12	30	25
3	13	23	20
3	14	47	42
3	15	16	16
4	0	0*	4
4	1	34	32
4	2	37	39
4	3	72	68
4	4	34	40
4	5	18	16
4	6	29	28
4	7	51	53
4	8	69	70
4	9	25	29
4	10	71	66
4	11	30	33
4	12	51	48
4	13	27	22
5	0	0*	6
5	1	41	36
5	2	47	42
5	3	23	25
5	4	59	55
5	5	34	34
5	6	23	24
5	7	51	47
5	8	46	47
5	9	48	50
5	10	28	26
5	11	53	46
5	12	22	25
6	0	9*	14
6	1	69	69
6	2	29	29
6	3	36	34
6	4	34	34
6	5	49	42
6	6	34	31
6	7	11*	16
6	8	41	38
6	9	33	32
6	10	15	20
7	0	69	69
7	1	20	20
7	2	15	16
7	3	52	52
7	4	32	32
7	5	35	32
7	6	0*	10
**** L =11****			
0	1	43	36
0	2	3*	6
0	3	46	48
0	4	97	90
0	5	28	28
0	6	114	104
0	7	102	86
0	8	0*	16
0	9	30	31
0	10	25	28
0	11	43	39
0	12	0*	12
0	13	72	70
0	14	15	13
0	15	11*	23
0	16	33	23
1	0	34	35
1	1	47	51
1	2	20	27
1	3	21	24
1	4	20	24
1	5	26	40
1	6	6*	12
1	7	20	20
1	8	34	38
1	9	26	25
1	10	39	37
1	11	18	28
1	12	46	49
1	13	76	62
1	14	46	44
1	15	44	42
2	0	68	62
2	1	38	37
2	2	76	75
2	3	19	15
2	4	67	67
2	5	107	117
2	6	61	64
2	7	56	61
2	8	39	44
2	9	36	38
2	10	24	23
2	11	38	36
2	12	39	42
2	13	20	19
2	14	32	30
2	15	22	17
3	0	47	45
3	1	61	52
3	2	117	114
3	3	59	54
3	4	40	39
3	5	50	48
3	6	49	53
3	7	19	19
3	8	18	16
3	9	54	52
3	10	0*	12
3	11	0*	11
3	12	18	18
3	13	27	25
3	14	13	12
4	0	131	115
4	1	75	60
4	2	77	73
4	3	69	60
4	4	23	26
4	5	9*	15
4	6	47	42
4	7	19	16
4	8	0*	15
4	9	31	32
4	10	11*	12
4	11	27	28
4	12	32	26
4	13	9*	15
5	0	15	17
5	1	33	30
5	2	35	34
5	3	24	19
5	4	11*	13
5	5	30	29
5	6	0*	17
5	7	58	53
5	8	54	52
5	9	79	70
5	10	57	53
5	11	53	49
6	0	0*	0
6	1	30	24
6	2	24	25
6	3	27	16
6	4	1*	14
6	5	22	20
6	6	42	43
6	7	37	37
6	8	77	74
6	9	33	35
7	0	41	34
7	1	61	56
7	2	38	35
7	3	60	57
7	4	47	37
**** L =12****			
0	0	24	22
0	1	0*	6
0	2	9*	6
0	3	34	36
0	4	39	33
0	5	90	73
0	6	34	32
0	7	72	62
0	8	45	39
0	9	17	17
0	10	50	47
0	11	54	52
0	12	58	52
0	13	85	77
0	14	18	17
0	15	82	68
1	0	26	23
1	1	38	40
1	2	52	58
1	3	52	57
1	4	65	77
1	5	55	66
1	6	69	85
1	7	47	61
1	8	41	44
1	9	0*	16
1	10	23	32
1	11	50	51
1	12	41	41
1	13	25	19
1	14	51	43
2	0	35	35
2	1	118	113
2	2	45	42
2	3	57	64
2	4	69	73
2	5	29	32
2	6	28	26
2	7	61	63
2	8	33	35
2	9	24	24
2	10	13	15
2	11	14	18
2	12	6*	12
2	13	20	16
2	14	47	41
3	0	136	113
3	1	37	29
3	2	76	70
3	3	66	66
3	4	31	33
3	5	30	26
3	6	22	27
3	7	51	48
3	8	44	40
3	9	26	31
3	10	32	32
3	11	13	16
3	12	0*	8
3	13	16	10
4	0	65	64
4	1	32	31
4	2	21	23
4	3	8*	7
4	4	28	25
4	5	0*	3
4	6	32	26
4	7	51	47
4	8	37	33
4	9	67	64
4	10	38	38
4	11	49	42
4	12	33	28
5	0	12*	10
5	1	55	51
5	2	23	16
5	3	28	28
5	4	8*	6
5	5	23	23
5	6	44	45
5	7	10*	15
5	8	47	46
5	9	34	32
5	10	31	30
6	0	19	20
6	1	34	23
6	2	46	43
6	3	33	29
6	4	41	40
6	5	32	33
6	6	35	30
6	7	0*	15
**** L =13****			
0	1	84	90
0	2	25	26
0	3	96	92
0	4	38	41
0	5	0*	2
0	6	53	52
0	7	21	3
0	8	44	41
0	9	24	24
0	10	8*	3
0	11	0*	2
0	12	18	14
0	13	48	44
1	0	35	29
1	1	22	27
1	2	44	45
1	3	29	28
1	4	9*	20
1	5	43	61
1	6	35	42
1	7	20	25
1	8	10*	22
1	9	24	23
1	10	43	42
1	11	30	20
1	12	45	41
1	13	3*	18
2	0	38	37
2	1	20	25
2	2	40	38
2	3	41	33
2	4	52	48
2	5	68	69
2	6	32	35
2	7	9*	18
2	8	25	27
2	9	21	27
2	10	24	25
2	11	21	23
2	12	6*	10
2	13	35	24
3	0	50	40
3	1	33	26
3	2	39	42
3	3	26	21
3	4	32	33
3	5	24	22
3	6	18	22
3	7	22	23
3	8	7*	7
3	9	0*	8
3	10	26	23
3	11	31	25
3	12	62	53
4	0	1*	15
4	1	49	45
4	2	38	32
4	3	38	33
4	4	27	25
4	5	21	17
4	6	34	30
4	7	12*	18
4	8	57	49
4	9	32	31
4	10	51	46
5	0	13*	9
5	1	76	68
5	2	27	17
5	3	15	25
5	4	11*	20
5	5	26	20
5	6	33	30
5	7	22	25
5	8	53	49
6	0	74	59
6	1	45	35
6	2	40	38
6	3	46	34
6	4	29	24
**** L =14****			
0	0	42	39
0	1	28	36
0	2	19	37
0	3	26	27
0	4	53	53
0	5	21	19
0	6	85	77
0	7	0*	13
0	8	41	36
0	9	33	31
0	10	7*	0
0	11	53	43
0	12	9*	5
1	0	49	41
1	1	84	74
1	2	62	52
1	3	44	40
1	4	46	47
1	5	42	52
1	6	20	19
1	7	27	38
1	8	18	13
1	9	19	21
1	10	27	27
1	11	18	15
1	12	19	14
2	0	90	75
2	1	15	12
2	2	44	36
2	3	40	40
2	4	20	15
2	5	22	21
2	6	33	33
2	7	30	33
2	8	46	43
2	9	32	30
2	10	31	26
2	11	38	34
3	0	34	26
3	1	24	23
3	2	0*	7
3	3	21	24
3	4	41	33
3	5	28	26
3	6	15	13
3	7	80	66
3	8	37	35
3	9	72	67
3	10	8*	14
4	0	96	80
4	1	54	44
4	2	48	40
4	3	0*	3
4	4	28	26
4	5	21	12
4	6	30	24
4	7	25	20
4	8	34	31
4	9	6*	15
5	0	42	30
5	1	58	50
5	2	35	30
5	3	20	16
5	4	19	10
5	5	20	20
5	6	24	24
**** L =15****			
0	0	12*	3
0	1	114	74
0	2	17	11
0	3	22	34
0	4	0*	4
0	5	0*	20
0	6	0*	4
0	7	17	22
0	8	17	9
0	9	0*	1
1	0	63	57
1	1	0*	16
1	2	20	18
1	3	0*	12
1	4	20	21
1	5	4*	21
1	6	41	47
1	7	11*	24
1	8	24	42
2	0	5*	13
2	1	17	14
2	2	16	15
2	3	32	30
2	4	3*	16
2	5	1*	12
2	6	19	19
2	7	52	60
2	8	18	17
3	0	37	32
3	1	50	35
3	2	24	15
3	3	9*	17
3	4	6*	12
3	5	28	27
3	6	17	15
4	0	0*	1
4	1	64	54
4	2	0*	17
**** L =17****			
0	1	0*	9
0	2	0*	5
0	3	12*	4
0	4	7*	8
0	5	42	34
0	6	0*	5
1	0	35	38
1	1	6*	5
1	2	23	33
1	3	0*	10
1	4	0*	6
1	5	11*	5
1	6	0*	18
2	0	27	15
2	1	0*	18
2	2	10*	10
2	3	20	18
2	4	21	19
3	0	9*	15

Table V.II

Final positional (fractional × 10^4) and thermal parameters

with standard deviations in parentheses

ATOM	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}†
Ru(1)	2495(3)	1378(1)	0800(2)	120(3)	23(1)	52(1)	-13(1)	- 4(2)	0(1)
Ru(2)	2190(2)	-0011(1)	1438(1)	72(2)	25(1)	43(1)	- 7(1)	- 1(2)	1(1)
Ru(3)	0295(2)	0432(1)	0121(1)	72(2)	21(1)	44(1)	- 3(1)	- 1(2)	0(1)
As(1)	-0713(3)	-0690(1)	-0359(2)	72(3)	22(1)	45(1)	- 1(1)	- 6(2)	- 1(1)
As(2)	0934(3)	-1098(2)	1860(2)	92(3)	29(1)	46(1)	-13(1)	- 6(2)	- 6(1)
F(1)	-3672(20)	-1923(11)	0440(15)	104(24)	53(7)	100(12)	-38(12)	-22(16)	5(9)
F(2)	-1941(23)	-2541(9)	-0158(10)	239(33)	35(5)	53(7)	-19(11)	6(15)	- 5(11)
F(3)	-2339(30)	-2315(12)	1849(16)	292(44)	53(7)	93(12)	-64(16)	11(24)	15(9)
F(4)	-0567(27)	-2873(9)	1204(14)	341(41)	37(5)	103(11)	-28(13)	-50(19)	9(7)
O(1)	-0400(35)	1991(14)	1631(20)	280(49)	61(9)	129(18)	73(17)	22(28)	-22(11)
O(2)	2162(38)	2506(14)	-0515(15)	339(56)	67(9)	84(11)	-40(21)	-16(23)	41(7)
O(3)	5391(22)	0701(12)	0031(12)	128(26)	70(8)	62(8)	-16(26)	11(28)	-16(14)
O(4)	4618(32)	2079(15)	1975(16)	285(45)	82(10)	74(12)	-57(18)	11(23)	-14(10)
O(5)	2703(26)	0368(18)	-1206(15)	127(30)	118(14)	63(10)	-48(20)	49(16)	-13(11)
O(6)	-1672(35)	1406(12)	-0908(15)	343(56)	43(7)	69(11)	34(19)	-48(22)	13(9)
O(7)	-2148(25)	0464(16)	1452(14)	120(30)	88(12)	62(10)	12(19)	35(16)	-13(11)
O(8)	0550(32)	0784(13)	2740(15)	276(51)	43(8)	61(11)	- 1(18)	26(22)	- 4(9)
O(9)	3814(26)	-0830(11)	0052(14)	214(35)	39(6)	94(11)	8(13)	25(18)	-22(14)
O(10)	5086(24)	-0163(16)	2460(16)	69(24)	102(13)	71(10)	11(18)	-43(14)	- 1(11)
C(1)	0631(59)	1713(18)	1350(26)	296(93)	15(10)	65(20)	47(27)	54(41)	- 1(13)
C(2)	2240(34)	2083(19)	-0043(17)	129(39)	82(14)	39(11)	-29(21)	-30(20)	-11(11)
C(3)	4218(35)	0904(16)	0355(18)	138(43)	39(9)	46(12)	-10(18)	-10(21)	14(9)
C(4)	3816(42)	1816(15)	1561(19)	285(54)	41(8)	48(13)	-91(16)	-21(26)	5(9)
C(5)	1905(31)	0391(16)	-0682(18)	56(35)	35(9)	44(13)	-24(17)	23(19)	- 5(10)
C(6)	-0834(30)	1053(13)	-0487(19)	202(35)	28(7)	106(14)	-19(13)	-56(18)	13(9)
C(7)	-1124(38)	0470(17)	1068(17)	176(48)	63(11)	44(10)	-18(22)	28(20)	-16(9)

Table V.II (continued)

ATOM	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(8)	1163(41)	0506(14)	2233(18)	284(56)	27(7)	55(12)	- 5(19)	2(25)	- 4(8)
C(9)	3080(35)	-0520(15)	0569(18)	163(43)	30(8)	57(12)	-42(18)	-71(19)	1(9)
C(10)	4002(42)	-0089(21)	2096(27)	100(51)	44(13)	60(21)	-59(25)	-19(31)	- 4(16)
C(11)	-1048(29)	-1417(14)	0429(16)	80(32)	35(8)	36(10)	- 8(32)	-13(33)	-24(16)
C(12)	-0510(29)	-1577(13)	1125(20)	68(32)	23(7)	76(14)	-21(13)	-21(19)	- 2(9)
C(13)	-2106(38)	-2062(14)	0439(22)	157(47)	21(7)	84(16)	-12(17)	13(26)	15(9)
C(14)	-1443(45)	-2249(19)	1196(27)	166(57)	38(11)	98(22)	-23(24)	13(34)	34(14)
Me(1)	-0484(44)	-1033(20)	2796(18)	254(60)	71(13)	36(12)	-36(25)	29(25)	-13(11)
Me(2)	2253(40)	-1881(18)	2084(26)	125(46)	40(11)	86(21)	3(22)	-13(31)	22(14)
Me(3)	-2629(33)	-0711(14)	-0924(23)	44(36)	37(12)	73(19)	-11(20)	-52(25)	6(14)
Me(4)	0547(35)	-1257(14)	-1083(19)	278(44)	29(7)	100(14)	10(17)	63(19)	0(9)

†Coefficients in the temperature expression: $\exp -10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + 2b_{12}hk + 2b_{13}h\ell + 2b_{23}k\ell)$

Table V.III

Bond distances (Å) and valence angles (degrees), with standard deviations in parentheses

Ru(1)-Ru(2)	2.831(3)	C(13)-F(1)	1.37(4)
Ru(1)-Ru(3)	2.831(3)	C(13)-F(2)	1.35(4)
Ru(1)-C(1)	1.95(5)	C(14)-F(3)	1.34(5)
Ru(1)-C(2)	1.95(3)	C(14)-F(4)	1.39(4)
Ru(1)-C(3)	1.88(3)		
Ru(1)-C(4)	1.89(3)	C(1)-O(1)	1.13(6)
		C(2)-O(2)	1.12(4)
Ru(2)-Ru(3)	2.858(6)	C(3)-O(3)	1.21(4)
Ru(2)-As(2)	2.417(4)	C(4)-O(4)	1.09(4)
Ru(2)-C(8)	1.87(3)	C(5)-O(5)	1.11(4)
Ru(2)-C(9)	1.90(3)	C(6)-O(6)	1.21(4)
Ru(2)-C(10)	1.91(4)	C(7)-O(7)	1.09(4)
		C(8)-O(8)	1.13(4)
Ru(3)-As(1)	2.417(3)	C(9)-O(9)	1.22(4)
Ru(3)-C(5)	1.93(3)	C(10)-O(10)	1.12(5)
Ru(3)-C(6)	1.83(3)		
Ru(3)-C(7)	2.00(3)	C(11)-C(12)	1.29(4)
		C(11)-C(13)	1.52(4)
As(1)-C(11)	1.92(3)	C(12)-C(14)	1.50(4)
As(1)-Me(3)	1.90(3)	C(13)-C(14)	1.43(6)
As(1)-Me(4)	1.94(3)		
As(2)-C(12)	1.96(3)		
As(2)-Me(1)	1.98(3)		
As(2)-Me(2)	1.90(3)		
Ru(2)-Ru(1)-Ru(3)	60.64(11)	Ru(3)-As(1)-C(11)	117(1)
Ru(2)-Ru(1)-C(1)	93(1)	Ru(3)-As(1)-Me(3)	120(1)
Ru(2)-Ru(1)-C(3)	78(1)	Ru(3)-As(1)-Me(4)	119(1)
Ru(2)-Ru(1)-C(4)	102(1)	C(11)-As(1)-Me(3)	101(1)
Ru(3)-Ru(1)-C(1)	81(1)	C(11)-As(1)-Me(4)	97(1)
Ru(3)-Ru(1)-C(2)	94(1)	Me(3)-As(1)-Me(4)	99(1)
Ru(3)-Ru(1)-C(3)	94(1)		
C(1)-Ru(1)-C(2)	92(1)	Ru(2)-As(2)-C(12)	119(1)
C(1)-Ru(1)-C(4)	92(2)	Ru(2)-As(2)-Me(1)	117(1)
C(2)-Ru(1)-C(3)	97(1)	Ru(2)-As(2)-Me(2)	117(1)
C(2)-Ru(1)-C(4)	105(1)	C(12)-As(2)-Me(1)	98(1)
C(3)-Ru(1)-C(4)	90(1)	C(12)-As(2)-Me(2)	98(1)
		Me(1)-As(2)-Me(2)	105(2)
Ru(1)-Ru(2)-Ru(3)	59.68(9)		
Ru(1)-Ru(2)-C(8)	80(1)	As(1)-C(11)-C(12)	137(2)
Ru(1)-Ru(2)-C(9)	98(1)	As(1)-C(11)-C(13)	132(2)
Ru(1)-Ru(2)-C(10)	102(1)	C(12)-C(11)-C(13)	91(2)
Ru(3)-Ru(2)-As(2)	102.48(11)		

Table V.III (continued)

Ru(3)-Ru(2)-C(8)	97(1)	As(2)-C(12)-C(11)	133(2)
Ru(3)-Ru(2)-C(9)	78(1)	As(2)-C(12)-C(14)	132(3)
As(2)-Ru(2)-C(8)	91(1)	C(11)-C(12)-C(14)	94(3)
As(2)-Ru(2)-C(9)	89(1)		
As(2)-Ru(2)-C(10)	97(1)	F(1)-C(13)-F(2)	103(3)
C(8)-Ru(2)-C(10)	91(2)	F(1)-C(13)-C(11)	116(2)
C(9)-Ru(2)-C(10)	94(2)	F(1)-C(13)-C(14)	116(3)
		F(2)-C(13)-C(11)	118(3)
Ru(1)-Ru(3)-Ru(2)	59.67(9)	F(2)-C(13)-C(14)	116(3)
Ru(1)-Ru(3)-C(5)	80(1)	C(11)-C(13)-C(14)	88(2)
Ru(1)-Ru(3)-C(6)	100(1)		
Ru(1)-Ru(3)-C(7)	94(1)	F(3)-C(14)-F(4)	103(3)
Ru(2)-Ru(3)-As(1)	101.80(12)	F(3)-C(14)-C(12)	117(3)
Ru(2)-Ru(3)-C(5)	97(1)	F(3)-C(14)-C(13)	121(3)
Ru(2)-Ru(3)-C(7)	76(1)	F(4)-C(14)-C(12)	115(3)
As(1)-Ru(3)-C(5)	90(1)	F(4)-C(14)-C(13)	116(3)
As(1)-Ru(3)-C(6)	101(1)	C(12)-C(14)-C(13)	86(3)
As(1)-Ru(3)-C(7)	94(1)		
C(5)-Ru(3)-C(6)	91(1)	Mean Ru-C-O	173
C(6)-Ru(3)-C(7)	95(1)		

Table V.IV

Equations of planes in the form $\ell X + mY + nZ = p$, where X, Y, Z are coordinates in Å, referred to orthogonal axes a, b, c.

	ℓ	m	n	p	maximum displacement (Å)
Ruthenium triangle (3 Ru atoms)	0.6940	-0.3306	-0.6396	-0.2223	0
Di-(tertiary arsine) (2 As and 4 C atoms)	0.7490	-0.5311	-0.3961	0.4677	0.06

Table V.V

Magnitudes (Å) of the principal axes of the thermal vibration ellipsoids of the heavy atoms.

	Axis 1	Axis 2	Axis 3
Ru(1)	0.18	0.23	0.27
Ru(2)	0.16	0.21	0.25
Ru(3)	0.16	0.20	0.25
As(1)	0.16	0.20	0.25
As(2)	0.17	0.22	0.27

DISCUSSION

In the same way that $LFe_3(CO)_{10}$ is related to $Fe_3(CO)_{12}$,[18] the complex $LRu_3(CO)_{10}$ is related to $Ru_3(CO)_{12}$.[35] As shown in Figure V.1, one carbonyl group on each of two ruthenium atoms is replaced by the arsenic atoms of the di-(tertiary arsine)ligand. Since ligands of lower acceptor strengths than the carbonyl group are less efficient at removing π-antibonding electron density from the metal cluster, metal-metal bonds between atoms having carbonyl groups replaced by these ligands would be expected to be longer than metal-metal bonds involving atoms having only carbonyl groups. This effect has been observed previously, and is in evidence in the present structure. The bond distances Ru(1)-Ru(2) and Ru(1)-Ru(3), (both 2.831(3) Å) are significantly shorter than Ru(2)-Ru(3), (2.858(6) Å).

Although both ^1H and ^{19}F n.m.r. spectra consist of singlet resonances, the mean plane of the di-(tertiary arsine) ligand is in fact twisted 18.4° with respect to the plane of the ruthenium triangle. This implies either that this twist is a result of packing forces (the plane of the ligand being co-planar with the ruthenium triangle in solution), or that the ligand is flexing in solution and assumes a stationary configuration upon crystallization. As in $L_2Ru_3(CO)_8$, the twisting of the ligand again causes Ru-Ru-C angles for axial carbonyls to change from nearly 90° in $Ru_3(CO)_{12}$ to the severely skewed configurations shown

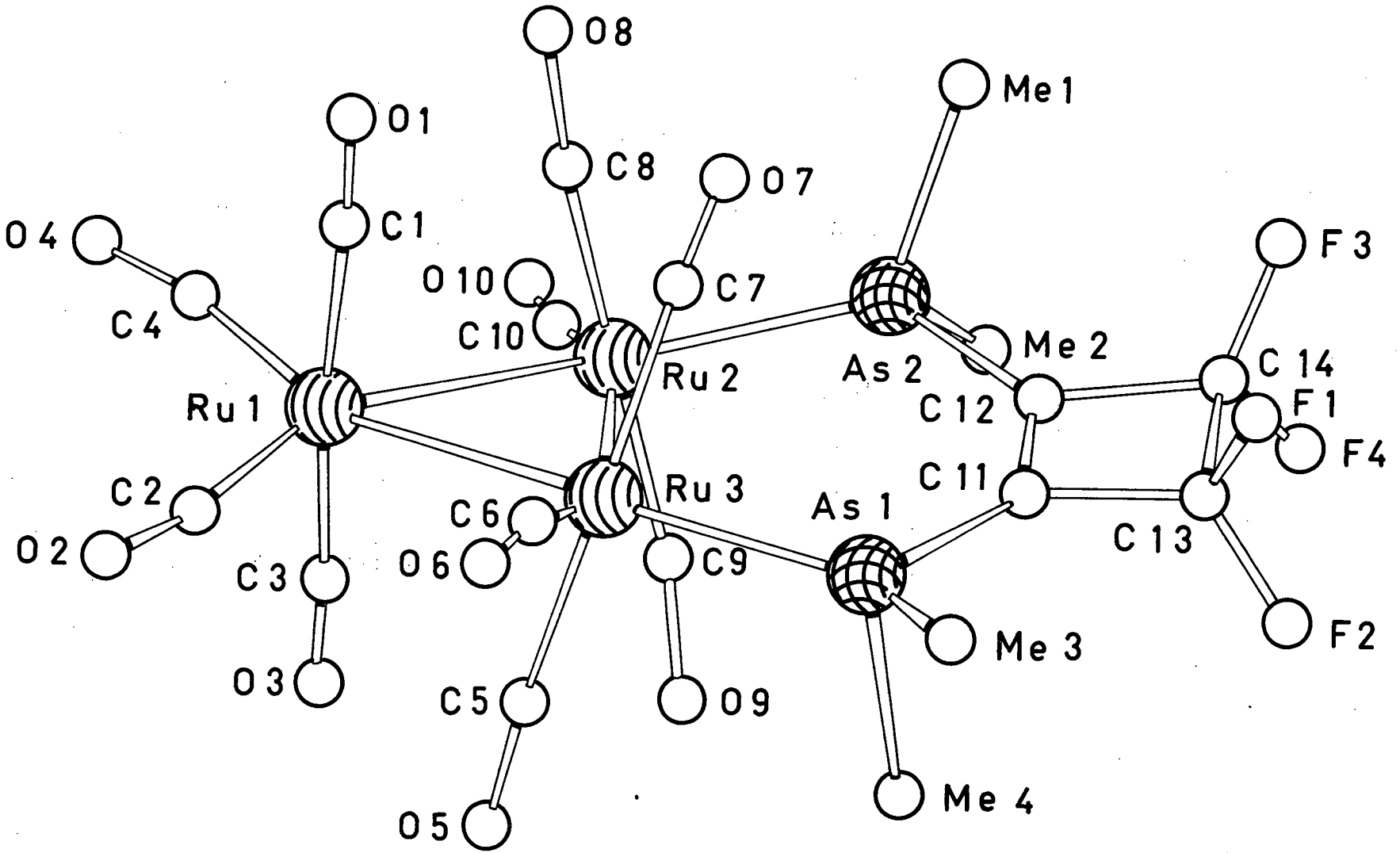

Figure V.1 Molecular structure of $LRu_3(CO)_{10}$.

in Figure V.2. Mean Ru-C and C-O bond distances are in excellent agreement with previously reported values[36-40,42,43] and Ru-C-O angles (mean 172.8°, σ(mean) 1.3°))are significantly non-linear as in most carbonyl complexes.

Ru-As bond distances (both 2.417 Å) are in good agreement with the values 2.401 and 2.413 Å found for $L_2Ru_3(CO)_8$ and are within the range 2.308 to 2.472 Å reported for $Ru((Ph_2AsC_6H_4)_3As)Br_2$.[41] Ru-As-C angles are again larger than C-As-C angles (averages 118.2 and 99.7° respectively) due to the steric effect of the ruthenium atom (*cf.* Figure III.4).

The dimensions of the di-(tertiary arsine) ligand are essentially identical to those in other similar structures.[32] The double bond in the cyclobutene ring (1.29 Å) is retained and other carbon-carbon distances are reasonable. Carbon-fluorine bond distances (mean 1.36 Å) are also as expected.

The extent of anisotropy of the thermal vibrations of the heavy atoms is shown in Table V.V. The principal axes of vibration show no regularities in orientation with respect to intramolecular vectors.

Intermolecular van der Waals contacts ranging from 2.96 to 3.48 Å are shown in the a-axis projection of the structure in Figure V.3.

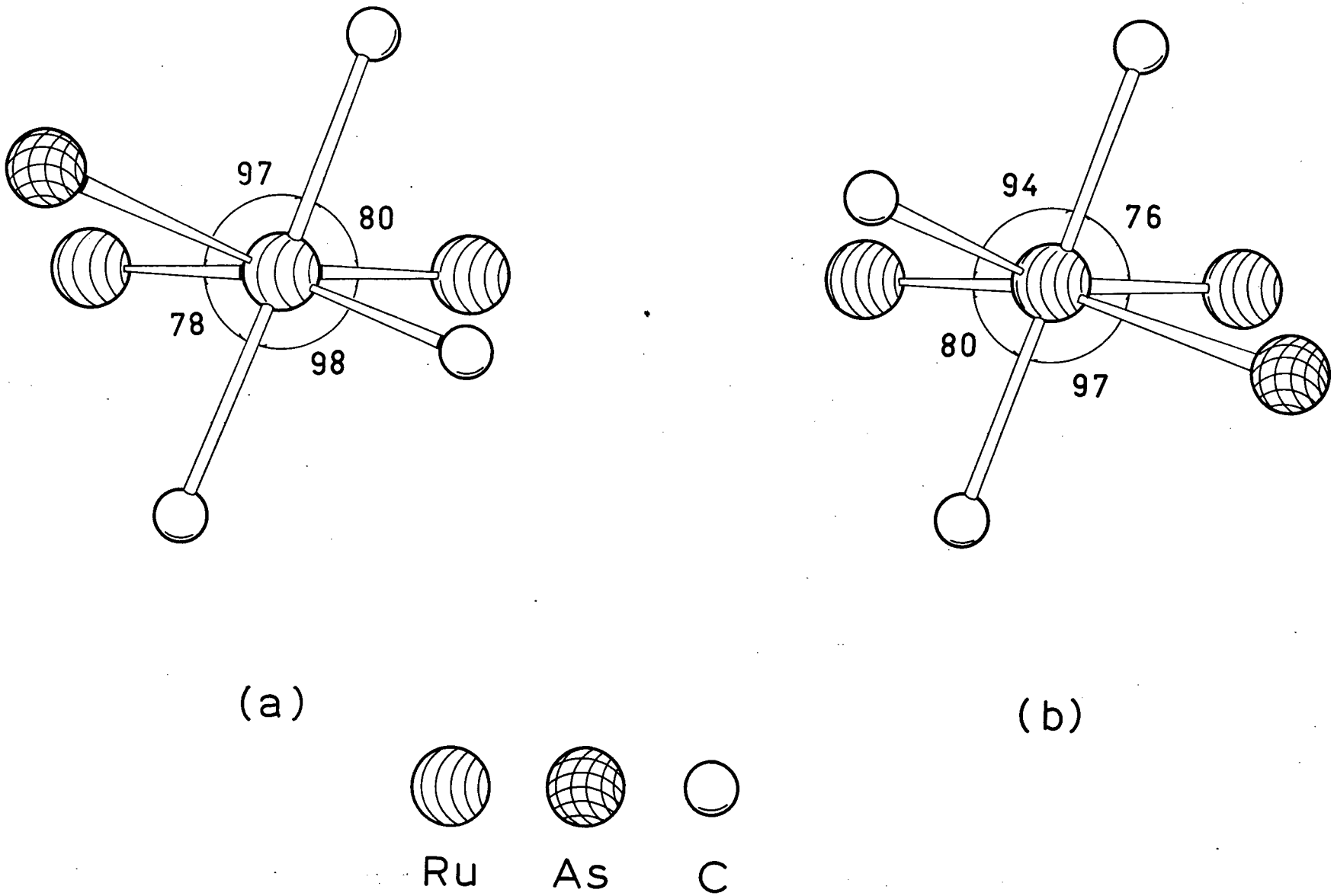

Figure V.2 Co-ordination around (a) Ru(2) and (b) Ru(3) of $LRu_3(CO)_{10}$.

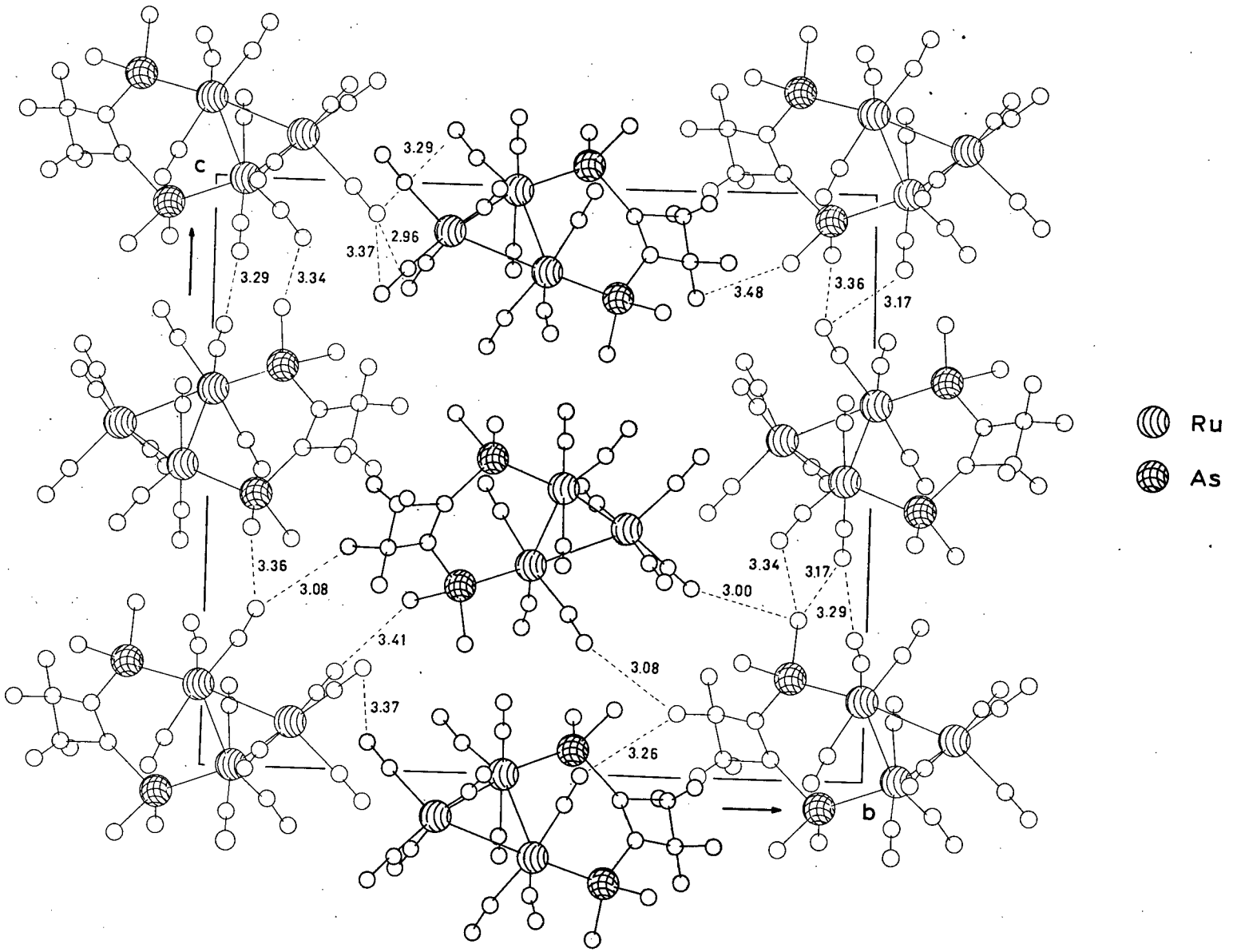

Figure V.3 Projection of unit cell down a-axis.

VI. THE STRUCTURE DETERMINATION OF $Me_2AsCF_2CF(CF_3)AsMe_2 \cdot Mo(CO)_4$

STRUCTURE ANALYSIS

The coordinates of the molybdenum and arsenic atoms in space group $\underline{C}2/\underline{c}$ were derived from the Patterson function and improved with two cycles of full-matrix refinement, using scattering factors from ref.26. A difference synthesis phased on the refined parameters revealed the positions of all twenty-one carbon, oxygen, and fluorine atoms.

One cycle of full-matrix least-squares refinement with minimization of $\Sigma \underline{w}\Delta^2$ using unit weights for all observed reflections and isotropic thermal paremeters for all atoms reduced $\underline{R}$ to 0.116. Converting to anisotropic temperature factors for molybdenum, arsenic, and fluorine atoms and refining for one cycle reduced $\underline{R}$ to 0.083. At this point, observed reflections were assigned weights from the following scheme.

$$\underline{w} = \{\underline{A} + \underline{B}|\underline{F}_o| + \underline{C}|\underline{F}_o|^2 + \underline{D}|\underline{F}_o|^3\}^{-1}$$

where $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$ are calculated by least-squares treatment to give best fit to constant $\underline{w}\Delta^2$ over all $|\underline{F}_o|$. Two cycles of refinement (142 variables) using this weighting scheme with $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$ equal to 7.1341, 1.5458, -0.0186 and 0.00008 respectively (unobserved reflections are excluded from refinement but included in final structure factor calculation), reduced $\underline{R}$ and $\underline{R}_w$ to 0.073 and 0.094 for observed reflections and 0.085 and 0.148 for all data. At final convergence, all parameter shifts were small

fractions of their standard deviations. A final difference Fourier revealed residuals of ±1.5 e/Å^3 around the heavy atoms which can only be explained as random experimental error. Measured and calculated structure factors are given in Table VI.I. Table VI.II gives the final positional and thermal parameters with standard deviations calculated from the inverse matrix of the last refinement cycle. Bond distances and valence angles are in Table VI.III; standard deviations of these quantities take into account the standard deviations of the unit cell parameters. Table VI.IV shows the extent of anisotropy of the thermal motion of the molybdenum, arsenic, and fluorine atoms. The anisotropy is large for the fluorine atoms, particularly those of the trifluoromethyl group, and the bond distances should be increased somewhat by corrections for libration. However, since the carbon and oxygen atoms were refined isotropically, no corrections were made. Although bond length comparisons within the present molecule are valid, detailed comparisons with distances in other molecules should take account of possible libration corrections.

Table VI.I

Final measured and calculated structure factors. Unobserved reflections have an asterisk after the $|F_o|$ value.

H	K	OBS	CALC
**** L = 0****			
4	0	501	639
6	0	47	40
8	0	69	75
10	0	317	371
12	0	226	240
14	0	234	253
16	0	233	247
18	0	93	95
20	0	111	110
22	0	30	23
3	1	160	177
5	1	66	71
7	1	57	56
9	1	7*	5
11	1	13	19
13	1	114	122
15	1	32	32
17	1	81	82
19	1	0*	7
21	1	41	39
23	1	12*	14
0	2	130	85
2	2	67	37
4	2	72	62
6	2	34	39
8	2	19	29
10	2	26	34
12	2	157	160
14	2	0*	8
16	2	89	86
18	2	23	20
20	2	20	16
22	2	10*	15
1	3	159	148
3	3	29	16
5	3	226	236
7	3	111	124
9	3	61	58
11	3	143	150
13	3	84	85
15	3	55	47
17	3	70	77
19	3	39	35
21	3	20	24
0	4	238	214
2	4	117	107
4	4	13	20
6	4	157	162
8	4	131	116
10	4	138	139
12	4	35	40
14	4	70	73
16	4	45	40
18	4	23	22
20	4	59	53
22	4	0*	8
1	5	135	132
3	5	355	340
5	5	146	142
7	5	377	350
9	5	212	201
11	5	185	179
13	5	114	115
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-4	4	33	31
-2	4	65	67
0	4	41	42
2	4	27	14
-9	5	32	32
-7	5	51	44
-5	5	106	107
-3	5	89	87
-1	5	118	116

Table VI.II

Final positional (fractional × 10^4) and thermal parameters,

with standard deviations in parentheses

ATOM	x	y	z	B or b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23} †
Mo	1503(1)	1128(2)	1863(2)	22(1)	66(2)	77(2)	0(1)	8(1)	1(1)
As(1)	1563(1)	2939(2)	2675(2)	28(1)	63(2)	83(3)	- 1(1)	6(1)	- 3(2)
As(2)	0840(1)	1960(2)	0112(2)	24(1)	81(2)	73(3)	0(1)	4(1)	7(2)
F(1)	0328(9)	3159(16)	1540(21)	47(6)	159(20)	299(32)	19(8)	78(12)	25(20)
F(2)	0396(9)	3916(15)	-0236(17)	59(6)	139(17)	171(21)	46(9)	- 27(10)	39(15)
F(3)	1460(7)	3969(13)	0505(17)	36(4)	113(14)	216(23)	6(6)	35(8)	71(15)
F(4)	1441(10)	5343(14)	2357(29)	50(7)	81(13)	512(56)	14(9)	2(15)	-48(22)
F(5)	0775(13)	5515(17)	0955(24)	86(10)	118(18)	286(35)	29(11)	17(15)	42(21)
F(6)	0680(13)	4909(17)	2533(28)	102(11)	115(18)	455(51)	24(12)	156(22)	- 5(25)
C(1)	2134(12)	1379(22)	1161(25)	6.9(6)					
C(2)	2014(11)	0691(21)	3245(25)	6.3(6)					
C(3)	1430(9)	-0220(19)	1193(20)	5.1(6)					
C(4)	0917(11)	0826(21)	2679(24)	6.3(6)					
C(5)	0682(15)	3327(28)	0663(32)	8.8(8)					
C(6)	1109(13)	3859(23)	1399(28)	7.6(7)					
C(7)	1010(16)	4916(29)	1860(33)	8.5(8)					
Me(1)	0073(14)	1565(27)	-0416(29)	8.7(8)					
Me(2)	1055(13)	2251(25)	-1364(29)	8.4(8)					
Me(3)	1333(15)	3248(29)	4113(34)	9.9(9)					
Me(4)	2249(14)	3645(26)	2903(31)	8.9(8)					
O(1)	2529(9)	1517(18)	0749(20)	9.4(6)					
O(2)	2331(9)	0453(18)	4112(21)	9.5(6)					
O(3)	1372(8)	-1066(16)	0848(19)	8.2(5)					
O(4)	0572(10)	0590(18)	3206(21)	9.8(6)					

†Coefficients in the temperature expression: $\exp -10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + 2b_{12}hk + 2b_{13}h\ell + 2b_{23}k\ell)$

Table VI.III

Bond distances (Å) and valence angles (degrees), with standard deviations in parentheses

Mo-C(1)	1.96(3)	C(1)-O(1)	1.20(3)
Mo-C(2)	1.90(3)	C(2)-O(2)	1.18(3)
Mo-C(3)	1.94(3)	C(3)-O(3)	1.19(3)
Mo-C(4)	1.96(3)	C(4)-O(4)	1.20(3)
Mo-As(1)	2.573(4)		
Mo-As(2)	2.569(7)	C(5)-C(6)	1.40(4)
		C(6)-C(7)	1.54(4)
As(1)-Me(3)	1.92(4)	C(5)-F(1)	1.50(4)
As(1)-Me(4)	1.92(3)	C(5)-F(2)	1.37(4)
As(1)-C(6)	2.06(3)	C(6)-F(3)	1.51(4)
As(2)-Me(1)	1.95(3)	C(7)-F(4)	1.24(4)
As(2)-Me(2)	1.94(3)	C(7)-F(5)	1.34(4)
As(2)-C(5)	1.99(4)	C(7)-F(6)	1.26(4)
C(1)-Mo-As(1)	90(1)	As(2)-C(5)-F(1)	106(2)
C(1)-Mo-As(2)	92(1)	As(2)-C(5)-F(2)	113(2)
C(1)-Mo-C(2)	87(1)	As(2)-C(5)-C(6)	118(3)
C(1)-Mo-C(3)	90(1)	F(1)-C(5)-F(2)	108(3)
C(4)-Mo-As(1)	90(1)	F(1)-C(5)-C(6)	99(3)
C(4)-Mo-As(2)	93(1)	F(2)-C(5)-C(6)	112(3)
C(4)-Mo-C(2)	88(1)		
C(4)-Mo-C(3)	89(1)	As(1)-C(6)-C(7)	113(2)
As(1)-Mo-C(2)	90(1)	As(1)-C(6)-F(3)	104(2)
As(1)-Mo-As(2)	82.1(2)	As(1)-C(6)-C(5)	111(2)
As(2)-Mo-C(3)	95(1)	C(7)-C(6)-F(3)	108(3)
C(3)-Mo-C(2)	92(1)	C(7)-C(6)-C(5)	121(3)
		F(3)-C(6)-C(5)	97(3)
Mo-As(1)-Me(3)	121(1)		
Mo-As(1)-Me(4)	119(1)	C(6)-C(7)-F(4)	113(3)
Mo-As(1)-C(6)	108(1)	C(6)-C(7)-F(5)	110(3)
Me(3)-As(1)-C(6)	106(1)	C(6)-C(7)-F(6)	113(3)
Me(3)-As(1)-Me(4)	102(2)	F(4)-C(7)-F(5)	106(3)
Me(4)-As(1)-C(6)	98(1)	F(4)-C(7)-F(6)	110(3)
		F(5)-C(7)-F(6)	105(3)
Mo-As(2)-Me(1)	123(1)		
Mo-As(2)-Me(2)	122(1)	Mo-C(1)-O(1)	178(3)
Mo-As(2)-C(5)	106(1)	Mo-C(2)-O(2)	178(3)
Me(1)-As(2)-C(5)	95(1)	Mo-C(3)-O(3)	176(2)
Me(1)-As(2)-Me(2)	103(1)	Mo-C(4)-O(4)	176(2)
Me(2)-As(2)-C(5)	102(1)		

Table VI.IV

Magnitudes (Å) of the principal axes of the thermal vibration ellipsoids of anisotropic atoms.

	Axis 1	Axis 2	Axis 3
Mo	0.22	0.24	0.26
As(1)	0.23	0.24	0.30
As(2)	0.21	0.27	0.28
F(1)	0.26	0.37	0.49
F(2)	0.19	0.38	0.51
F(3)	0.24	0.32	0.42
F(4)	0.25	0.39	0.61
F(5)	0.29	0.44	0.53
F(6)	0.26	0.37	0.65

DISCUSSION

The molecule 1,2-bis(dimethylarsino)hexafluoropropanemolybdenum tetracarbonyl (Figure VI.1) is derived from molybdenum hexacarbonyl[44,45] by replacement of two carbonyl groups by the arsenic atoms of the chelating di-(tertiary arsine) ligand. The co-ordination around molybdenum remains essentially octahedral. The five atoms C(2), C(3), Mo, As(1) and As(2) are situated in the least-squares plane given in Table VI.V with C(1) and C(4) equally spaced above and below this plane. The As-Mo-As angle is 82.1°, and the other angles at molybdenum are in the range 87-95° (Table VI.III). The Mo-C bond distances, 1.90-1.96(3), mean 1.94 Å, and the C-O bond lengths, 1.18-1.20(3), mean 1.19 Å, are similar to values reported previously.[46-52] The Mo-C-O groupings are almost exactly linear, 176-178(3)°.

The Mo-As bond distance appears to be measured for the first time, the mean value being 2.572(4) Å. This distance is close to that which would be predicted from a knowledge of other metal-arsenic bond lengths, and from differences in covalent radii; *e.g.* the Fe-As bond distance is 2.30 Å, the Mo-Mo distances in various compounds[49-52] average 3.25 Å, and the unbridged Fe-Fe distance in $Fe_3(CO)_{12}$ is 2.65 Å,[18] giving a predicted Mo-As bond length of (2.30 + ½(3.25 - 2.65)) = 2.60 Å.

The As-Me bond lengths are 1.92-1.95(3), mean 1.93 Å, and the As-C (fluorocarbon) bond distances are 1.99(4)

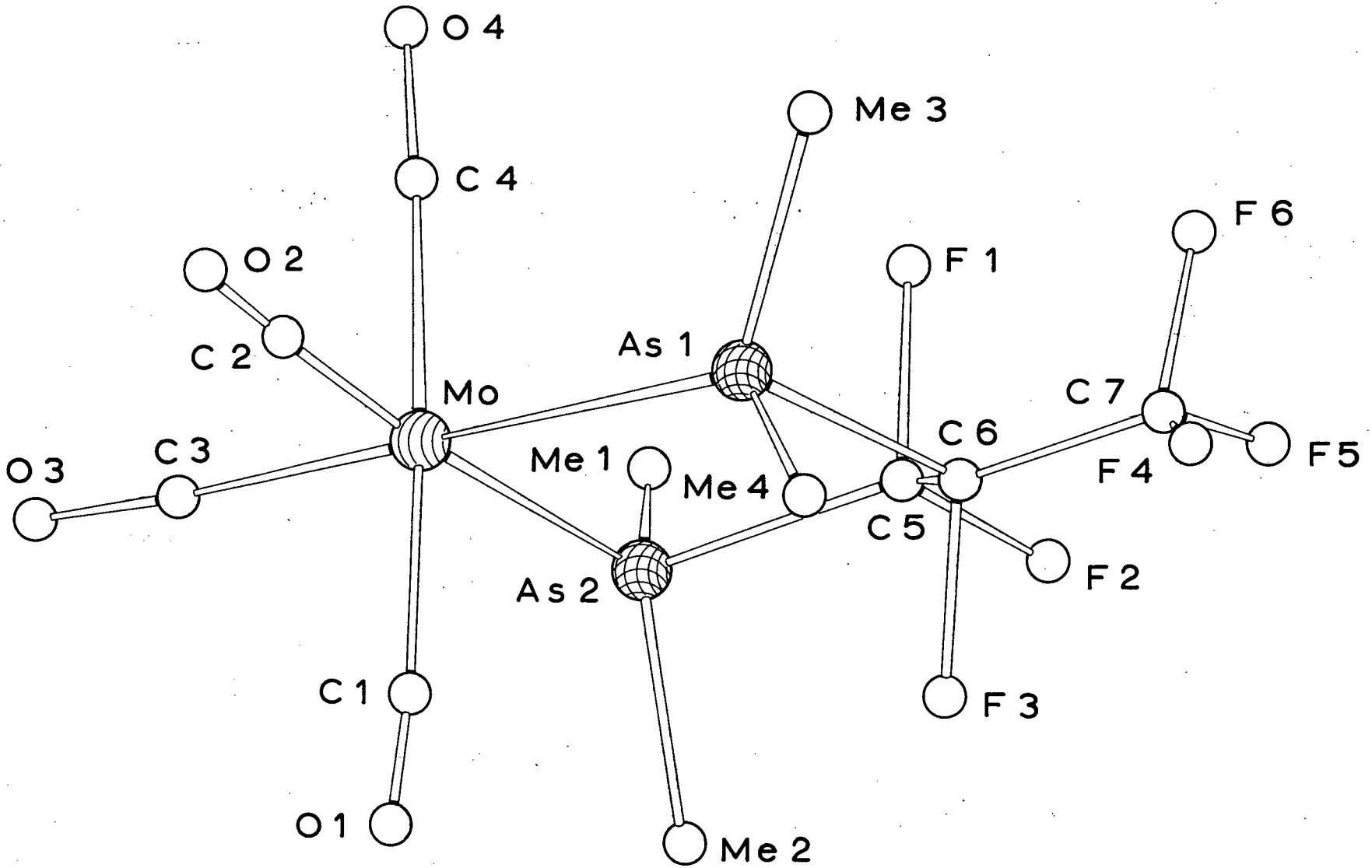


Figure VI.1 Molecular structure of L'Mo(CO)$_4$.

Table VI.V

(a.) Equation of weighted mean plane of Mo, As(1), As(2), C(2) and C(3) in the form $\ell X' + mY + nZ' = p$ where X', Y, Z' are coordinates in Å, referred to the orthogonal axes a, b, c^*.

ℓ	m	n	p	maximum displacement (Å)
0.8801	0.1876	-0.4361	2.2605	0.03

(b.) Direction cosines of the vector C(5)-C(6) referred to the orthogonal axes a, b, c^*.

(0.6333, 0.5014, 0.5895)

and 2.06(3), mean 2.03 Å; the mean values of the two types of As-C bond are significantly different. The angles at arsenic which involve the molybdenum atom are larger than the angles involving only carbon atoms. The Mo-As-C(fluorocarbon) angles, 106 and 108(1)°, are probably influenced by their presence in the five-membered ring, but the Mo-As-Me angles, 119-123 mean 121°, are all significantly larger than the tetrahedral angle, presumably as a result of the steric influence of the $Mo(CO)_4$ group. There are two distinct Me-As-C(fluorocarbon) angles at each arsenic atom, 98 and 106(1)° at As(1), and 95 and 102(1)° at As(2), probably as a result of differing steric interactions between the two methyl groups at each arsenic and the fluorocarbon.

A table of α (the dihedral angle between the plane

containing the ring carbon atoms and the metal atom and the plane containing the ring nitrogen atoms and the metal atom) and β (the angle between the nitrogen atoms as one looks down the carbon-carbon bond) has been compiled for a number of $M(en)_3$ complexes. Average values of α and β are 24.8 and 48.6° respectively.[53] The five-membered ring in $L'Mo(CO)_4$ is non-planar with C(5) and C(6) displaced by -0.40 and 0.14 Å respectively from the As-Mo-As plane, so that the C-C bond is twisted 23.2° with respect to the central plane of the molybdenum octahedron (*cf.* 24.8° average of values from ref.53). A view along the C-C bond is shown in Figure VI.2. The arrangement is staggered, with the *trans* dihedral angles all being close to 180° (178, 175, and 179°). The As-C-C-As dihedral angle (47°, *cf.* 48.6°, average from ref. 53) is reduced from an ideal 60° as a result of the formation of the chelate ring. The one trifluoromethyl and three fluorine substituents of the C-C bond may be classified as axial or equatorial with respect to the chelate ring; the bulkier trifluoromethyl group occupies a less sterically-hindered equatorial position (Figures VI.1 and VI.2).

The bond distances and valence angles in the fluorocarbon group (Table VI.III) show some unusual and interesting features. The C-F(axial) bond distances are 1.50 and 1.51(4), mean 1.51(3) Å, the C-F(equatorial) bond length is 1.37(4) Å, and the C-F(trifluoromethyl) bonds

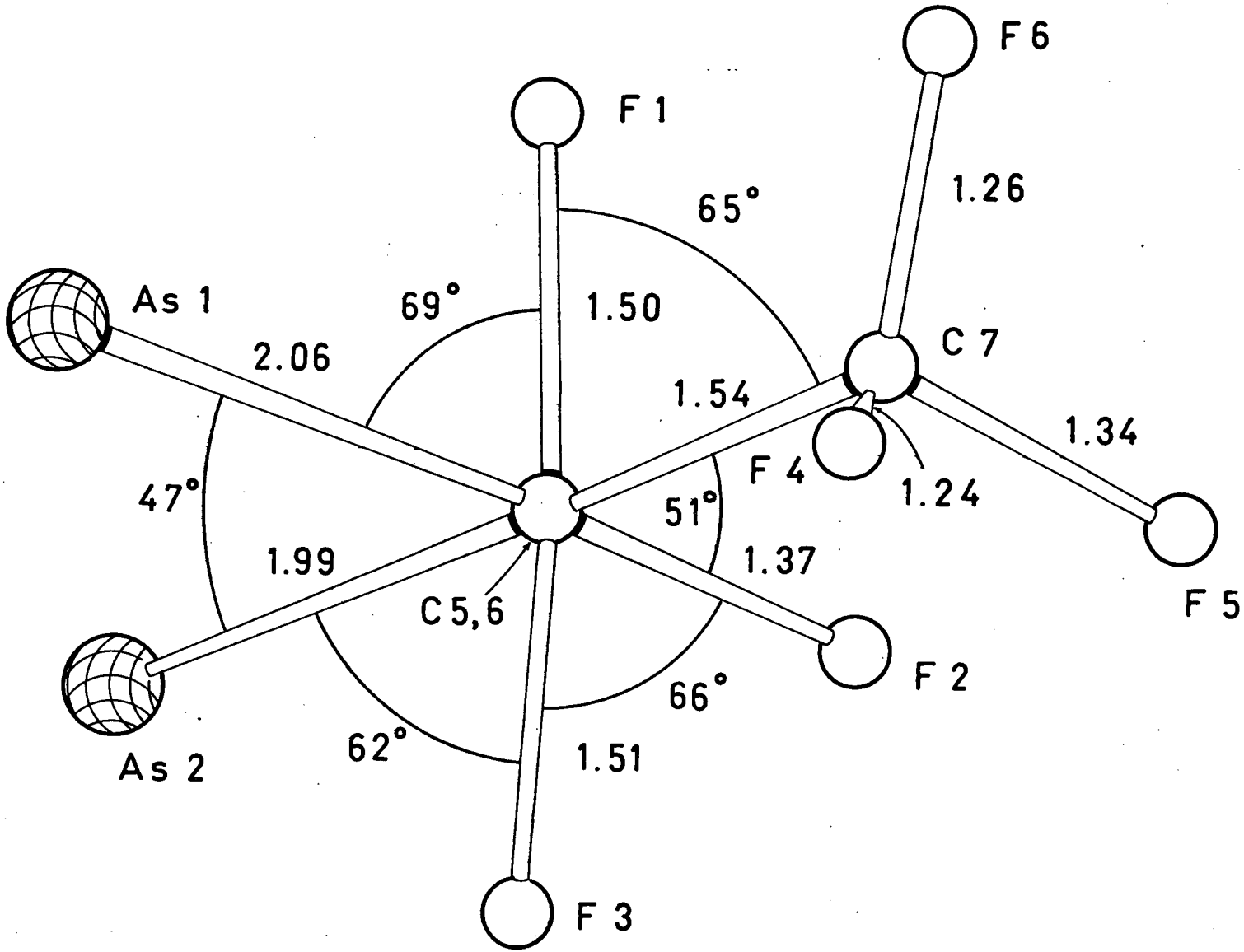
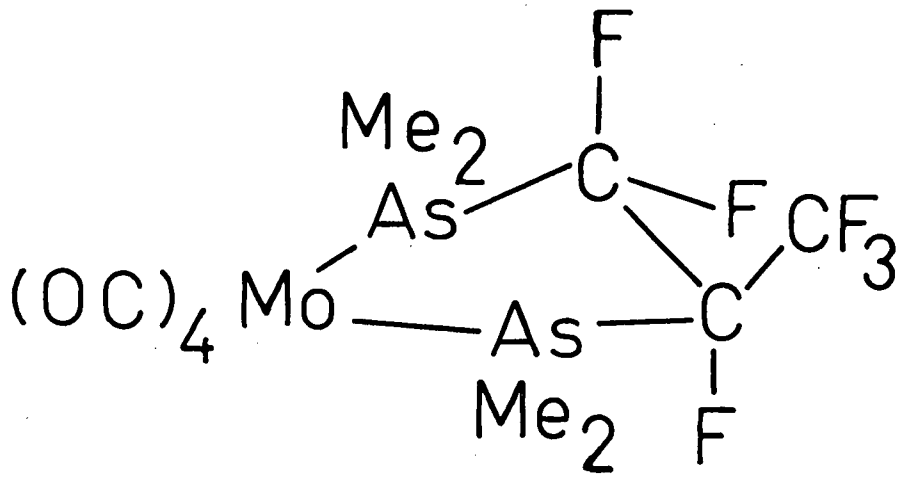


Figure VI.2 View of bond distances and dihedral angles around C(5)-C(6) bond.

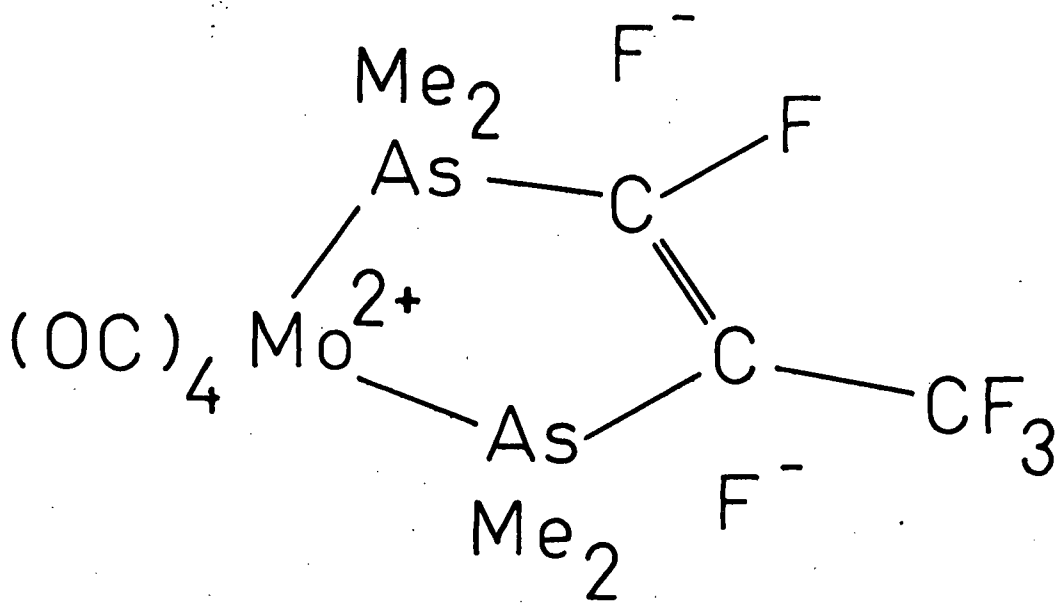
measure 1.24, 1.26, and 1.34(4), mean 1.28(2) Å. The normal C-F bond distance[54] is 1.33 Å. The equatorial and trifluoromethyl C-F bond lengths do not differ significantly from the normal value; the equatorial C-F bond cannot be claimed to be significantly longer than the trifluoromethyl bonds, as it differs from the mean trifluoromethyl length by only 2σ and from the longest observed trifluoromethyl bond by only 0.5σ. The C-F(axial) bonds are however very significantly longer than a normal C-F bond (by 6σ), than the C-F(equatorial) bond (by 2.8σ), and than the mean of the C-F(trifluoromethyl) bonds (by 6σ).

The C-C bond distance is 1.40(4) Å, significantly shorter (by 3.5σ) than a normal C-C single bond (1.54 Å). The valence angles at C(5) and C(6) are also informative. Those angles not involving the axial fluorine atoms are all greater than the tetrahedral value, range 111-121(3), mean 115°; the angles involving the axial fluorines are correspondingly less than the tetrahedral value, with the C-C-F(axial) angles being 97 and 99(3)°.

All of these unusual features are explicable in terms of a bonding system which, in valence bond language, contains a contribution not only from the normal structure Ia (Figure VI.3), but also from the structure Ib, which involves donation of molybdenum non-bonding d-electrons, *via* the arsenic 4d orbitals, into orbitals of the fluorocarbon group. The molecular dimensions are best explained by an equal contribution of the two canonical forms Ia and



Ia



Ib

Figure VI.3 Proposed bonding scheme to account for anomalous observations.

Ib to the resonance hybrid; the C-C bond thus has 50% double bond character, in agreement with the observed distance of 1.40 Å, and the angles not involving F(axial) would be expected to be about midway between the tetrahedral (110°) and trigonal (120°) values, as observed (mean 115°). The C-F(axial) bond distance would be predicted to be considerably longer than a normal single bond (1.33 Å) as a result of the contribution of the no-bond structure, Ib, again as observed (1.51 Å). In molecular orbital terminology, the chelate ring contains a delocalized π-bond system, which involves a filled molybdenum 4d orbital, empty arsenic 4d orbitals, and an orbital on each carbon atom which approximates a p orbital, normal to an approximate sp^2 σ-bonding system.

It is difficult to predict what distance would be expected for the C-F(axial) bonds on the basis of the above bonding scheme. However, since the bonds have a predicted total bond order of 0.5, the distance would be longer than the single bond distance (1.33 Å) by <u>approximately</u> 0.14 Å, which is the shortening noted in the C-C bond for a related change in bond order. This is in agreement with the observed value of 1.51 Å.

More reliable comparison may be made with $CHF{=}CF{\cdot}Mn(CO)_5$ in which long C-F bonds, 1.48(2) Å, have been observed.[55] These long bonds have been rationalized in terms of structures involving $Mn^{+}{=}\overset{||}{C}\ \ F^{-}$. Another comparable structure is $Mn(CO)_5CF_3$ where i.r. spectra have been interpreted [56] in terms of weak

C-F bonds resulting from resonance structures of the type $Mn^{+}=CF_2 \quad F^{-}$. Contributions from structures of this type have been supported by the observance of a short $Mo-C_3F_7$ in $\pi-C_5H_5Mo(CO)_3C_3F_7$,[47] although no related abnormalities were found in the C-F bonds. The situation in the present compound is similar, but with the added feature that the carbon atom is not directly bonded to the metal, so that any effect must be transmitted through the arsenic atoms.

It is well known that in a metal complex, the metal atom tends to reduce a high formal negative charge by back-donation of electrons into non-bonding or anti-bonding orbitals of the ligands. It would appear that the ligand in the present compound is able to function in this back-donation by virtue of the presence of the C-F bonds in the axial positions. Such bonding appears to be able to force C-F bonds into a favourable axial position even in compounds where steric factors favour an equatorial position for the fluorine atom. In $Me_2AsCHFCH_2AsMe_2 \cdot Cr(CO)_4$ for example, n.m.r. studies[57] indicate an axial fluorine atom.

At first glance, this model appears to have the undesirable feature that the positive charge on the molybdenum might be expected to cause Mo-C bonds to be longer and C-O bonds to be shorter than those of $Mo(CO)_6$ as a result of the unavailability of non-bonded metal electrons for back-bonding. Corresponding shifts of C-O stretching

frequencies to higher wavenumbers might also be expected. However, the charge distribution pictured in Figure VI.3.Ib can also be interpreted as a mechanism for increasing the π-acceptor strength of the di-(tertiary arsine) ligand to the level of the carbonyl group, in which case, no difference between the Mo-C and C-O bond lengths in $Mo(CO)_6$ and those in $L'Mo(CO)_4$ would be expected.

The $C-CF_3$ bond in the present compound, 1.54(4) Å, is a normal single bond, the C-C-F angles, 110-113(3)°, are slightly larger, and the F-C-F angles, 105-110(3)° slightly smaller than the tetrahedral value.

The thermal vibration ellipsoids for those atoms treated anisotropically (Table VI.IV) are in general oriented so that the maximum vibrations are in directions of least steric restraint, *i.e.* between or perpendicular to bonds.

The intermolecular packing appears to be governed solely by van der Waals interactions. A projection of the structure, with the shorter intermolecular distances, is shown in Figure VI.4.

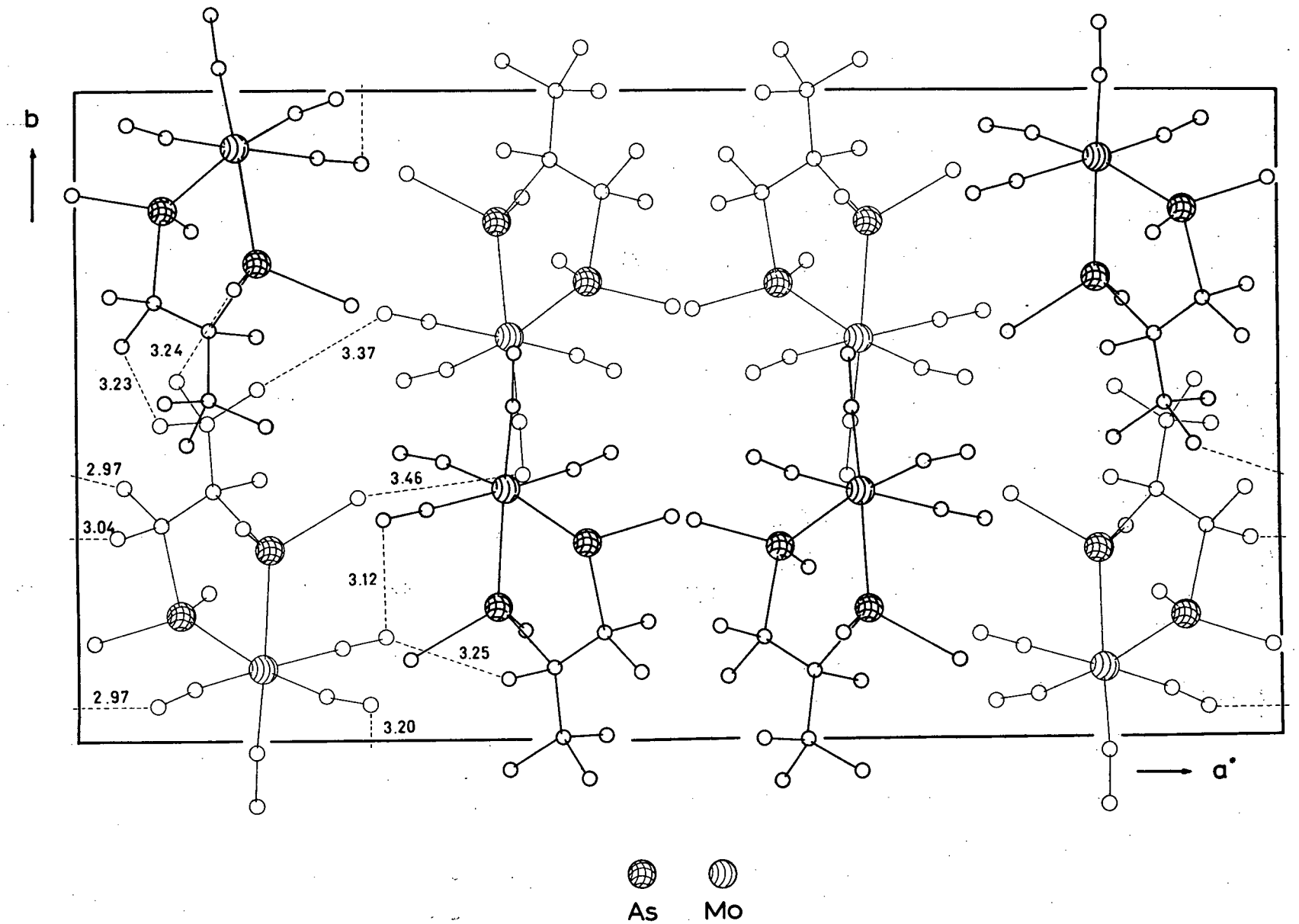


Figure VI.4 Projection of the unit cell down the c-axis.

VII. COMPUTER PROGRAMMING

A. PROGRAM "UPDATE"

During refinement by our full-matrix least-squares program, the residual quantity being minimized is $\Sigma \underline{w}\Delta^2$ where $\Delta = |\underline{F}_o - \underline{F}_c|$ and $\underline{w} = k/\sigma^2_{\underline{F}}$ (k is a constant and $\sigma_{\underline{F}}$ is the standard deviation in $\underline{F}$). The program can be made to assign standard deviations in $\underline{F}$'s from Cruickshank's equation[58]

$$\sigma^2_F = \underline{A} + \underline{B}|\underline{F}_o| + \underline{C}|\underline{F}_o|^2 + \underline{D}|\underline{F}_o|^3 \qquad (7.1)$$

A correct weighting scheme requires that $\Sigma \underline{w}\Delta^2$ be constant over local ranges of $|\underline{F}_o|$. Since all ranges can be made to have equal numbers of reflections, $\Sigma \underline{w}\Delta^2$ for a range is proportional to the mean $\underline{w}\Delta^2$, $\langle \underline{w}\Delta^2 \rangle$, of the range and we can say that the $\langle \underline{w}\Delta^2 \rangle$ for all ranges must be equal and make them all equal to $\langle \Delta^2 \rangle$ of the first range.

$$\langle \underline{w}\Delta^2 \rangle_i = \langle \Delta^2 \rangle_1 \qquad (7.2)$$

but since $\underline{w} = k/\sigma^2_{\underline{F}}$ (7.3)

$$\left(\frac{\langle \Delta^2 \rangle}{\sigma^2_{\underline{F}}} \right)_i = \frac{\langle \Delta^2 \rangle_1}{k} \qquad (7.4)$$

where $\sigma^2_{\underline{F}}$ is calculated for the mean $|\underline{F}_o|$ of the range.

Therefore, by transposing,

$$\left(\sigma^2_{\underline{F}}\right)_i = k \langle \Delta^2 \rangle_i / \langle \Delta^2 \rangle_1 \qquad (7.5)$$

and we must calculate $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$ for the best least-squares fit of

$\left(\sigma^2_{\underline{F}}\right)_i$ to k $<\Delta^2>_i/<\Delta^2>_1$ over NGRP ranges, where NGRP is input to the program from cards.

This leads to the familiar normal equations

$$\frac{\partial}{\partial \underline{A},\underline{B},\underline{C},\underline{D}} \sum_1^{NGRP} \{\underline{A} + \underline{B}<|\underline{F}_o|>_i + \underline{C}<|\underline{F}_o|>_i^{\,2} + \underline{D}<|\underline{F}_o|>_i^{\,3} - \frac{k<\Delta^2>_i}{<\Delta^2>_1}\}^2 = 0 \tag{7.6}$$

or in matrix notation,

$$\begin{pmatrix} NGRP & \sum_i <|\underline{F}_o|>_i & \sum_i <|\underline{F}_o|>_i^2 & \sum_i <|\underline{F}_o|>_i^3 \\ \sum_i <|\underline{F}_o|>_i & \sum_i <|\underline{F}_o|>_i^2 & \sum_i <|\underline{F}_o|>_i^3 & \sum_i <|\underline{F}_o|>_i^4 \\ \sum_i <|\underline{F}_o|>_i^2 & \sum_i <|\underline{F}_o|>_i^3 & \sum_i <|\underline{F}_o|>_i^4 & \sum_i <|\underline{F}_o|>_i^5 \\ \sum_i <|\underline{F}_o|>_i^3 & \sum_i <|\underline{F}_o|>_i^4 & \sum_i <|\underline{F}_o|>_i^5 & \sum_i <|\underline{F}_o|>_i^6 \end{pmatrix} \begin{pmatrix} \underline{A} \\ \underline{B} \\ \underline{C} \\ \underline{D} \end{pmatrix} =$$

$$k \begin{pmatrix} \sum_i <\Delta^2>_i/<\Delta^2>_1 \\ \sum_i <|\underline{F}_o|>_i <\Delta^2>_i/<\Delta^2>_1 \\ \sum_i <|\underline{F}_o|>_i^{\,2} <\Delta^2>_i/<\Delta^2>_1 \\ \sum_i <|\underline{F}_o|>_i^{\,3} <\Delta^2>_i/<\Delta^2>_1 \end{pmatrix} \tag{7.7}$$

or $\underline{\underline{T}}\ \underline{W}/k = \underline{S}$ (7.8) and $\underline{W}/k = \underline{\underline{T}}^{-1}\ \underline{S}$ (7.9)

and we solve for $\underline{A}/k$, $\underline{B}/k$, $\underline{C}/k$, and $\underline{D}/k$ by inverting $\underline{\underline{T}}$ and multiplying by $\underline{S}$.

The best choice of weights, which gives the lowest standard deviations in the derived parameters is $\underline{w} = 1/\sigma^2_{\underline{F}}$ so that if we can evaluate the constant k in (7.3) we can achieve the best weighting scheme by multiplying the

solution of the normal equations by k. It can be shown theoretically that the constant k is

$$\text{ERROR} = \Sigma \underline{w}\Delta^2/(\text{NREF}-\text{NV}) \qquad (7.10)$$

where NREF is the number of reflections and NV is the number of variables in the least-squares crystal structure refinement.

The program "UPDATE" can now be formulated in six stages (*cf.* Table VII.I).

i) read structure factor data and sort in order of increasing magnitude of $\underline{F}_o$. Subroutine ASORT(A,I,N,M,K) is an assembler-language routine which sorts the M by K fragment of the array A (which is dimensioned N by K) according to one-word keys located in the first column of the array. Each row is moved with its first element. For adaptation to this program, A is dimensioned 10,000 by 2 and M is set to NREF, the number of reflections read from the structure factor data. The array elements A(J,1) and A(J,2) contain $|\underline{F}_o|$ and $|\underline{F}_c|$, respectively, for the Jth reflection. At the completion of this stage of the program, we have an array A(NREF,2) which is sorted in order of increasing $|\underline{F}_o|$.

ii) determine the number of reflections in each range. The number of ranges desired (NGRP) is input to the program from cards. Each range is given NREF/NGRP reflections with additional single reflections added to the first few ranges if NREF/NGRP is not an integer.

Table VII.I

Listing of the program "UPDATE"

```
      REAL MDLSQ,MEANFO,MINFO,MAXFO,MWDLSQ,MINDLS
      REAL A(10,10),Y0(10),SIG(10),YC(10),STL(10),AC(10),A5(10)
      DIMENSION SUM(10),NUM(50),X(4,4)
      DIMENSION HJ(10),HK(10),HL(10),FSCALE(10),REFN(10),T(10),Y(4)
      REAL*8 X,Y,SUM,T
      INTEGER*2 HJ,HK,HL,FSCALE,REFN
  326 FORMAT(1X,'THIS DATA SET CANNOT BE FITTED TO A FOUR PARAMETER CURV
     1E')
  327 FORMAT(1X,'BY LEAST SQUARES METHODS WITHOUT NEGATIVE WEIGHTS')
   12 FORMAT(///' A = ',F15.9,' B = ',F15.9,' C = ',F15.9,' D = ',F15.9)
   23 FORMAT (///      F       SIGSQ        SQRTW  ',/)
   21 FORMAT(3X,F4.0,2F10.4)
   33 FORMAT(' ',///)
   39 FORMAT(4F10.1,2I5)
   40 FORMAT(1H ,F8.1,3H - ,F7.1,3X,F6.3,2X,F6.1,2X,F6.3,2X,F5.2,2X,F6.3
     1,2X,I5)
   41 FORMAT(/22H       TOTAL                ,F6.3,2X,F6.1,2X,F6.3,2X,F5.2,2X,
     1F6.3,2X,I5)
   42 FORMAT(' ',21X'   R     MEAN FO   RW      MEAN     ERROR      NREF'/46
     1X,'WDELSQ'/)
  192 FORMAT(///'WEIGHTING PARAMETERS CORRECTED FOR F SQUARED')
      READ(5,38) FIN1,FIN2,FMAX,NV,NGRP
      RNGRP=NGRP
      JKP=0
      DO 200 IJ=1,10
  200 SUM(IJ)=0.
      NREF=0
C
C     READ STRUCTURE FACTOR DATA AND SORT IN ORDER OF INCREASING
C     MAGNITUDE OF FOBS
C
      DO 1 JOB=1,1000
      READ(2,END=99) (YO(K),SIG(K),YC(K),STL(K),AC(K),A5(K),K=1,10),
     1(HJ(L),HK(L),HL(L),FSCALE(L),REFN(L),L=1,10)
      DO 1 I=1,10
      IF(HJ(I).GE.99) GO TO 99
      IF(Y0(I)) 1,1,4234
 4234 NREF=NREF+1
      A(NREF,1)=YC(I)
    2 A(NREF,2)=YC(I)
    1 CONTINUE
   99 CALL ASORT(A,1,10000,NREF,2)
C
C     DETERMINE NUMBER OF REFLECTIONS IN EACH RANGE
C
      XNREF=NREF
      INREF=NREF/NGRP
      IF=NREF-(NGRP*INREF)
      DO 3 J=1,NGRP
      IF(J-IF) 4,4,5
    5 NUM(J)=INREF
      GO TO 3
    4 NUM(J)=INREF+1
    3 CONTINUE
C
C     CALCULATE WEIGHTING ANALYSIS INFORMATION
C
      SSDLTA = 0.0
      SSUMFO=0.0
      DO 6 J=1,NGRP
      SUMFO=0.
      SDELTA=0.
      DLSQ=0.
      KP=NUM(J)
      DO 7 I=1,KP
      DELTA=ABS(A(JKP+I,1)-A(JKP+I,2))
      DLTASQ=DELTA*DELTA
      DLSQ=DLSQ+DLTASQ
      SDELTA=SDELTA+DELTA
      SUMFO=SUMFO+A(JKP+I,1)
      WRITE(4) DLTASQ,A(JKP+I,1)
      IF(I.EQ.1) MINFO=A(JKP+I,1)
    7 IF(I.EQ.NUM(J)) MAXFO=A(JKP+I,1)
      MDLSQ=DLSQ/NUM(J)
      IF(J.EQ.1)     MINDLS=MDLSQ
      MEANFO=SUMFO/NUM(J)
      R=SDELTA/SUMFO
      MDLSQ= MDLSQ/MINDLS
      SSUMFO=SSUMFO+SUMFO
      SSDLTA=SSDLTA+SDELTA
      JKP=JKP+KP
    6 WRITE(3) MINFO,MAXFO,MEANFO,R,MDLSQ
      ENDFILE 3
      REWIND 3
C
C     CALCULATE MATRIX ELEMENTS FOR LEAST SQUARES CALCULATION AND SOLVE
C     FOR WEIGHTING SCHEME PARAMETERS
C
      DO 8 JOB=1,NGRP
      READ(3,END=16) E,F,B,G,AN
      T(1)=B
      SUM(1)=SUM(1)+T(1)
      DO 15 J=2,6
      JM1=J-1
      T(J)=T(JM1)*B
      SUM(J)=SUM(J)+T(J)
   15 CONTINUE
      T(7)=AN
      SUM(7)=SUM(7)+T(7)
      DO 14 L=8,10
      LM1=L-1
      T(L)=T(LM1)*B
      SUM(L)=SUM(L)+T(L)
   14 CONTINUE
    8 CONTINUE
   16 CONTINUE
      REWIND 3
      X(1,1)=RNGRP
      DO 18 K=2,4
      KM1=K-1
   18 X(1,K)=SUM(KM1)
      DO 9 K=2,4
    9 X(2,K)=SUM(K)
      X(3,3)=SUM(4)
      X(3,4)=SUM(5)
      X(4,4) = SUM(6)
      DO 11 I=2,4
      IM1=I-1
      DO 11 J=1,IM1
   11 X(I,J)=X(J,I)
      DO 10 K=1,4
      KP4=K*4
   10 Y(K)=SUM(KP6)
      CALL SOLTN(X,Y,4,4,DET,&99)
      REWIND 4
C
C     CALCULATE WEIGHTING ANALYSIS INFORMATION USING NEW WEIGHTING
C     SCHEME PARAMETERS
C
      XT=NREF-NV
      SWDLSQ=0.0
      DO 401 J=1,100
      READ(4,END=402) DLTASQ,FO
      SIGSQ=Y(1)+Y(2)*FO+Y(3)*FO*FO+Y(4)*FO*FO*FO
      W=1.0/SIGSQ
      WDLSQ=W*DLTASQ
  401 SWDLSQ=SWDLSQ+WDLSQ
  402 TERR=(SWDLSQ/XT)
      DO 191 IJK=1,4
  191 Y(IJK)=TERR*Y(IJK)
      WRITE(6,192)
      WRITE(6,12) (Y(I),I=1,4)
      WRITE(6,33)
      WRITE(6,42)
      REWIND 4
      SWDLSQ=0.0
      SWFOSQ=0.
      DO 31 J=1,NGRP
      WDLSQ=0.0
      WFO=0.
      WFOSQ=0.
      KP=NUM(J)
      DO 32 I=1,KP
      READ(4) DLTASQ,FO
      SIGSQ=Y(1)+Y(2)*FO+Y(3)*(FO**2)+Y(4)*(FO**3)
      IF(SIGSQ.LE.0.0) GO TO 305
      W=1.0/SIGSQ
      WFOSQ=WFOSQ+W*FO*FO
   32 WDLSQ=WDLSQ+W*DLTASQ
      MWDLSQ=WDLSQ/NUM(J)
      READ(3) MINFO,MAXFO,MEANFO,R,MDLSQ
      ERROR=SQRT(MDLSQ/XT)*RNGRP)
      WTOR=SQRT(WDLSQ/WFOSQ)
      WRITE(6,40) MINFO,MAXFO,R,MEANFO,WTOR,MWDLSQ,ERROR,NUM(J)
      SWDLSQ=SWDLSQ+WDLSQ
      SWFOSQ=SWFOSQ+WFOSQ
   31 CONTINUE
      TNREF=SSUMFO/XNREF
      TR=SSDLTA/SSUMFO
      TWTOR=SQRT(SWDLSQ/SWFOSQ)
      TNWDS=SWDLSQ/XNREF
      TERR=SQRT(SWDLSQ/XT)
      WRITE(6,41) TR,TNREF,TWTOR,TNWDS,TERR,NREF
C
C     CALCULATE W AND SIGMA AS FUNCTION OF FOBS
C
      IF (FIN1 .LT. 0.0) FIN1=5.0
      IF (FIN2 .LT. 0.0) FIN2=10.0
      IF (FMAX .LT. 0.0) FMAX=100.0
      IF (FLIM .LT. 0.0) FLIM=FMAX
      WRITE (6,20)
      F=FIN1
   22 SIGSQ=0.0
      DO 102 I=1,4
  102 SIGSQ=SIGSQ+Y(I)*F**(I-1)
      SQRTW=-0.
      IF(SIGSQ.LT.0.) GO TO 25
      SQRTW=SQRT(1.0/SIGSQ)
   25 WRITE (6,21) F,SIGSQ,SQRTW
      IF (F .GE. FMAX) GO TO 23
      IF (F .GE. FLIM ) GO TO 24
      F=F+FIN1
      GO TO 22
   24 F=F+FIN2
      GO TO 22
   23 CONTINUE
      GO TO 300
  305 WRITE(6,306)
      WRITE(6,307)
  300 STOP
      END
```

```
      SUBROUTINE SOLTN(A,B,N,M,DET,*)
C
C     SUBROUTINE TO SOLVE MATRIX EQUATION
C
      DIMENSION A(M,M),B(M)
      REAL*8 A,B
      REAL MULT
      DET=1.0
      DO 60 I=1,N
      DET=DET*A(I,I)
      IF(ABS(DET).LT.1.0E-6) GO TO 32
      DO 51 J=1,N
      IF(J.EQ.I) GO TO 51
      MULT=A(J,I)/A(I,I)
      IF(I.EQ.N) GO TO 53
      M=I+1
      DO 52 K=M,N
   52 A(J,K)= A(J,K)-A(I,K)*MULT
   53 B(J)=B(J)-B(I)*MULT
   51 CONTINUE
   60 CONTINUE
      DO 69 I=1,N
   69 B(I)=B(I)/A(I,I)
      RETURN
   32 WRITE(6,13)
   13 FORMAT(*DETERMINANT = ZERO, NO UNIQUE SOLUTION*)
      RETURN 1
      END
```

iii) the following five quantities are calculated for each range and stored temporarily on a data file.

MINFO, MAXFO, and MEANFO, the minimum, maximum and mean $|\underline{F_o}|$ in the range.

$\underline{R}$, the discrepancy index $\Sigma|\Delta|/\Sigma|\underline{F_o}|$ for the range.

MDLSQ, the ratio $\langle\Delta^2\rangle_i/\langle\Delta^2\rangle_1$

iv) the quantities MEANFO and MDLSQ are used to set up the matrix of normal equations and the system is solved for $\underline{A}/k$, $\underline{B}/k$, $\underline{C}/k$, and $\underline{D}/k$. SOLTN is a subroutine for solving matrix equations.

v) using these values for $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$, the constant ERROR is evaluated and each of the four weighting scheme parameters is multiplied by this value. Using these corrected values of $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$, a table of MINFO, MAXFO, $\underline{R}$, MEANFO, WTDR, MWDLSQ, ERROR, and NUM(J) is compiled and printed for each range.

$$\text{WTDR} = \{\Sigma\underline{w}\Delta^2/\Sigma\underline{wF_o^2}\}^{1/2}$$

$$\text{MWDLSQ} = \langle\underline{w}\Delta^2\rangle$$

NUM(J) = number of reflections in the Jth range.

vi) $\underline{w}$ and σ^2 are calculated and printed as a function of $\underline{F_o}$ in steps of FIN1 from FIN1 to FLIM and in steps of FIN2 from FLIM to FMAX where FIN1, FLIM, FIN2, and FMAX are input to the program from cards. Sometimes because of bad fit, the values of σ^2 are negative and should be adjusted by small changes to the weighting parameters before being used in structure refinement.

B. PROGRAM "ORTEP"

During the course of the work for this thesis, the Oak Ridge National Laboratory thermal ellipsoid plot program, ORTEP,[59] was made compatible with our existing programs and implemented on the IBM 360/67 by the author.

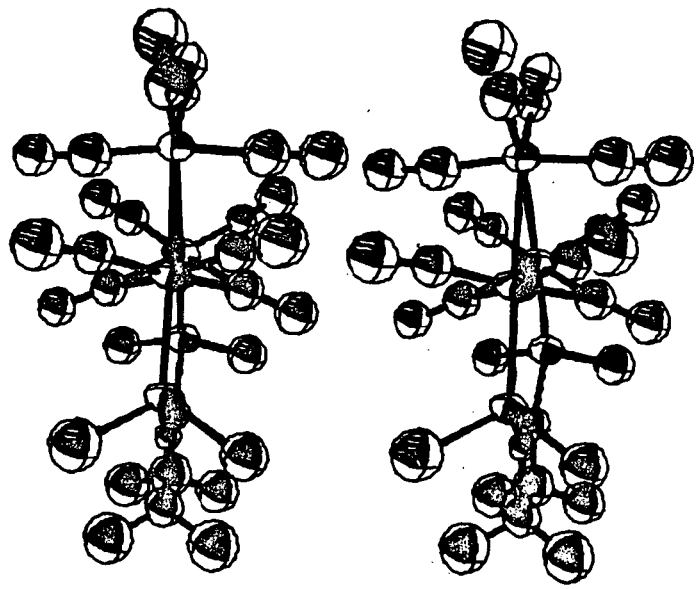
Stereo views of the four structures in this thesis are given in Figure VII.1 as plotted by ORTEP. Atoms are represented by 50% probability ellipsoids of thermal vibration.

Figure VII.1

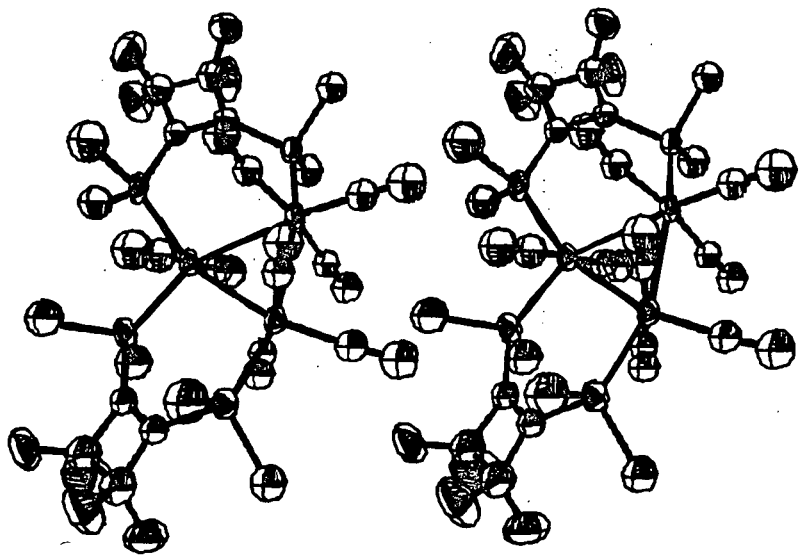
Stereo views of

(a) $LFe_3(CO)_{10}$ (c) $LRu_3(CO)_{10}$

(b) $L_2Ru_3(CO)_8$ (d) $L'Mo(CO)_4$

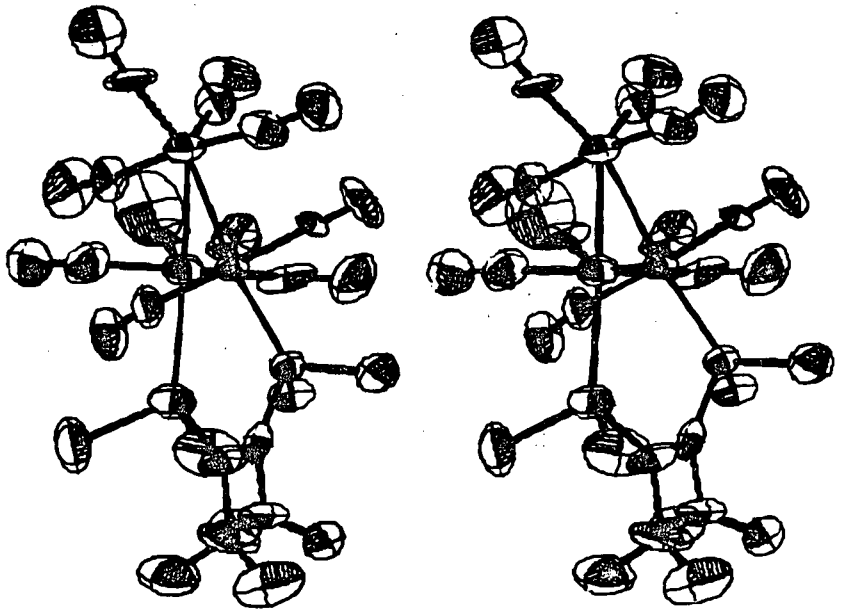


(a)

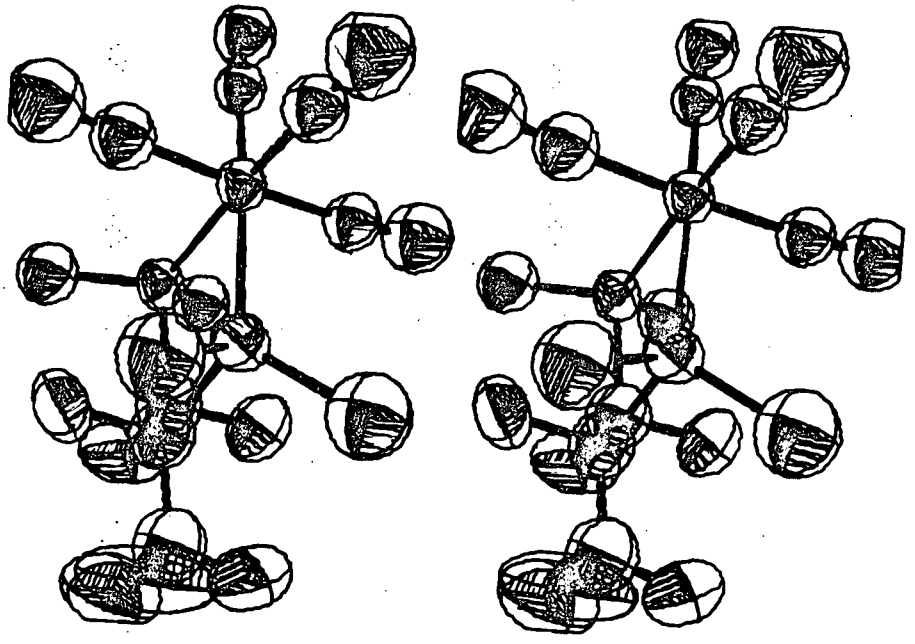


(b)

Figure VII.1 (continued)



(c)



(d)

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