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The Structure of Oxopentachloropropionatobis(triphenylphosphine)dirhenium(IV)[1a]

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The crystal and molecular structure of the compound $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$ reported recently by Rouschias and Wilkinson has been determined by means of single-crystal X-ray diffractometry. The molecular structure is essentially, though not in all respects, that postulated by Rouschias and Wilkinson. There are two octahedrally coordinated rhenium atoms with the octahedra joined on a common edge; the bridging atoms on this common edge are Cl and O. The propionato group fills one apical coordination position in each octahedron and the remaining positions in each are filled by two Cl atoms and a phosphorus atom. The phosphorus atoms are *trans* to the bridging chlorine atom. Neglecting the orientations of the phenyl rings and the β-carbon atom of $C_2H_5CO_2$, the structure has a virtual mirror plane containing the bridging O and Cl atoms and the carboxyl carbon atom. The quadrilateral formed by the two bridging atoms and the two rhenium atoms is practically planar, with an Re–Re distance of 2.522 ± 0.001 Å. The crystals, which were black, with tetragonal prismatic morphology ($\rho = 1.94$ g cm^{-3} at $\sim 23°$) belong to the tetragonal system with $a = 10.669 \pm 0.003$ Å and $c = 34.898 \pm 0.007$ Å. For $Z = 4$, $\rho_{\text{calcd}} = 1.945$ g cm^{-3}. The structure was solved by Patterson and Fourier methods and refined by least squares. Systematic absences indicated the space group to be $P4_1$ or $P4_3$. The use of 3156 *hkl* reflections and 446 $\bar{h}\bar{k}\bar{l}$ reflections permitted an unambiguous choice (for this particular crystal) of $P4_3$, for which final weighted and unweighted residuals of 0.050 and 0.044, respectively, were obtained.

Introduction

It has now been well established that the chemistry of rhenium in the oxidation state III is largely that of dinuclear[2-9] and trinuclear[10-20] metal atom cluster compounds, although a few mononuclear Re(III) complexes do appear to be adequately characterized.[21,22] Compounds containing rhenium in mean oxidation states between II and III also seem to involve strong Re–Re bonds.[23,24]

Very recently[25] it has been shown that the compound $La_4Re_6O_{19}$, which has rhenium in the mean oxidation state $+4^1/_3$, contains Re_2O_{10} groups, which are pairs of octahedra sharing an edge, with the Re–Re distance equal to 2.42 Å. The interpretation of this structure in terms of localized Re–Re bonding is not entirely straightforward, however, because the Re_2O_{10} groups are far from discrete. Instead they are extensively linked together by shared oxygen atoms and the substance has semimetallic electrical properties, indicative of considerable electron delocalization.

With the exception of the ternary oxide just mentioned, no Re–Re bonds are known in compounds in which the Re has an oxidation state greater than IV and compounds containing Re(IV) seem to have only a moderate tendency to form Re–Re bonds. Thus the best known Re(IV) species is the mononuclear $ReCl_6^{2-}$ ion. However, rhenium(IV) chloride[26] has a structure[8] in which there are chains of Re_2Cl_9 bioctahedra, with rhenium atoms occurring in pairs, separated by about 2.73 Å, and the $Re_2Cl_9^-$ ion[27] also has a bioctahedral structure[28] with an Re–Re distance of about 2.71 Å. Thus, the limited information available suggests that the borderline, in terms of oxidation state, between predominant and negligible tendency to metal–metal bond formation occurs around oxidation number IV for rhenium.

In view of the borderline nature of Re(IV) with respect to Re–Re bond formation, it was considered of interest to investigate the structure of the compound $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$ reported recently by Rouschias and Wilkinson.[29] These authors proposed structure I for the compound. This structure, which was quite speculative, would seem to require the

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[1] (a) Supported by the U. S. Atomic Energy Commission; (b) N. I. H. Predoctoral Fellow, 1965–1966.

[2] (a) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965); (b) F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

[3] B. G. Kuznetsov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1963).

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[5] F. A. Cotton, C. Oldham, and W. R. Robinson, *ibid.*, **5**, 1798 (1966).

[6] F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **6**, 214 (1967).

[7] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *ibid.*, **6**, 929 (1967).

[8] M. J. Bennett, F. A. Cotton, B. M. Foxman, and P. F. Stokely, *J. Am. Chem. Soc.*, **89**, 2759 (1967).

[9] M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).

[10] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); *Inorg. Chem.*, **2**, 1166 (1963).

[11] W. T. Robinson, J. B. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

[12] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

[13] F. A. Cotton and J. T. Mague, *Proc. Chem. Soc.*, 233 (1964); *Inorg. Chem.*, **3**, 1402 (1964).

[14] B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964).

[15] F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).

[16] F. A. Cotton and R. A. Walton, *ibid.*, **5**, 1802 (1966).

[17] B. R. Penfold and W. T. Robinson, *ibid.*, **5**, 1758 (1966).

[18] M. Elder and B. R. Penfold, *ibid.*, **5**, 1763 (1966).

[19] J. H. Hickford and J. E. Fergusson, *J. Chem. Soc.*, *A*, 113 (1967).

[20] M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, **7**, 1563 (1968).

[21] Some examples will be found in: (a) J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962); (b) N. F. Curtis, J. E. Fergusson, and R. S. Nyholm, *Chem. Ind.* (London), 625 (1958).

[22] There are other reports of mononuclear Re(III) complexes, but in many the structural conclusions lack adequate proof.

[23] F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 1257 (1967).

[24] M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 2866 (1966); *Proc. Roy. Soc.* (London), **A303**, 175 (1968).

[25] J. M. Longo and A. W. Sleight, *Inorg. Chem.*, **7**, 108 (1968); N. Morrow and L. Katz, American Crystallographic Association Meeting, Minneapolis, Minn., Aug 1967, Paper R-6.

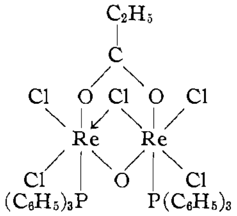
[26] F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).

[27] F. Bonati and F. A. Cotton, *ibid.*, **6**, 1353 (1967).

[28] F. A. Cotton and P. F. Stokely, unpublished observations.

[29] G. Rouschias and G. Wilkinson, *J. Chem. Soc.*, *A*, 465 (1966).

existence of a fairly short Re–Re separation and hence a high—possibly unprecedented—amount of Re(IV)–Re(IV) bonding. It seemed that a knowledge of the Re–Re distance and other structural features of this molecule might enable us significantly to refine our views concerning the influence of oxidation number on the tendency to metal–metal bond formation. This paper reports the results of the X-ray crystallographic study.



I

Experimental Section

Crystals of $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$ were prepared by a slight modification of the method of Rouschias and Wilkinson.[29] Propionic acid (25 ml) and $ReOCl_3[P(C_6H_5)_3]_2$[30] (2.0 g) were refluxed for 1 hr. The mixture was allowed to cool and the supernatant liquid was decanted. Black crystals, 0.9 g (56%), were collected, washed with propionic acid and pentane, and dried under vacuum. No $ReCl_4[P(C_6H_5)_3]_2$ was observed. *Anal.* Calcd for $Re_2Cl_5P_2O_3C_{39}H_{35}$: C, 40.26; H, 3.03; Cl, 15.24. Found: C, 40.8; H, 3.22; Cl, 16.0.

A preliminary optical examination showed the crystals to be tetragonal prisms. Single crystals were examined by Weissenberg and precession photography and found to belong to the tetragonal system. The unit cell parameters were determined at 23° as $a = 10.669 \pm 0.003$ Å and $c = 34.898 \pm 0.007$ Å from measurements on a General Electric manual diffractometer using Cu Kα radiation ($\lambda\alpha_1$ 1.5405 Å, $\lambda\alpha_2$ 1.5443 Å). The values quoted for a and c and corresponding uncertainties were obtained in a manner previously described by us.[20] The observed density, 1.94 ± 0.01 g cm^{-3}, measured by flotation in aqueous zinc bromide, agrees well with the calculated value of 1.945 g cm^{-3} for $Z = 4$, $V = 3972.4$ Å^3, and mol wt = 1163.4.

The observed Laue symmetry of 4/m and the systematic absences, $00l$ for $l \neq 4n$, observed on Weissenberg photographs of levels $hk0$ and $hk1$, and precession photographs of $h0l$, $h1l$, $h2l$, $0kl$, $1kl$, and $2kl$ suggested the enantiomorphic space groups $P4_1$ (C_4^2, no. 76) and $P4_3$ (C_4^4, no. 78).

The crystal used in the data collection was a tetragonal prism with dimensions of 0.06 × 0.06 × 0.11 mm. The crystal was aligned with its c axis coincident with the ϕ axis of the goniometer. Intensity data were collected on a General Electric quarter-circle automated XRD-6 diffractometer equipped with a Datex electronic system. Using nickel-filtered Cu Kα radiation, the intensities of 3938 independent reflections of the complete index set hkl and 554 related reflections of the index set $h\bar{k}\bar{l}$ (where the indices are ≥ 0), accessible within the sphere bounded by $(\sin\theta)/\lambda \leq 0.617$, were measured. The intensities were measured using a scintillation counter with the pulse height discriminator set to receive 95% of the Cu Kα radiation with the window centered on the Cu Kα peak. The crystal was placed 14.6 cm from the source and 17.9 cm from the 2° circular screening aperture; a moving-crystal, moving-counter (θ–2θ scan at 4°/min in 2θ) technique was employed. The integrated intensities ($I = P - B_1 - B_2$) were obtained from the total counts (P) of scan[31] from 2θ(calcd) − 1.33° to 2θ(calcd) + 1.33° and stationary background measurements (B_1, B_2) at the limits of each scan. A take-off angle of 2° was used, and the scan range of 2.66° conformed well with the mosaic spread of the crystal. Manual scans of the strongest reflections showed that the maximum counting rates never exceeded the linear response range of the scintillation counter. Every 6 hr during data collection the crystal orientation was checked, and three standard reflections were monitored. A random variation with time (±2% from the mean) of the standard reflections was consistent with the random instability of the X-ray equipment rather than decomposition. Of the 3938 independent reflections of the hkl set, 782 were rejected using two criteria: (1) $I \leq 0$; (2) $I/(P + B_1 + B_2)^{1/2} < 3$. The remaining 3156 reflections were corrected for Lorentz and polarization effects. Similarly, the 554 related reflections ($\bar{h}kl$) were processed and corrected as above; 108 of these reflections were rejected using the stated criteria.

All nonrejected data were corrected for absorption effects[32] ($\mu_{Cu} = 155.1$ cm^{-1}). An experimental absorption curve for the $00l$ reflections (obtained at $\chi = 90°$ upon rotation about the ϕ axis) and the calculated curve for the same reflections agreed well. The calculated transmission factors fell in the range 0.495–0.600. Only the 3156 independent reflections (complete index set hkl) were used in the structure solution and refinement.

Solution and Refinement of Structure

The three-dimensional Patterson function[33] gave a set of ten unique vectors attributable to Re–Re interactions. A straightforward solution was not readily obtained; however, when the triclinic vector set was generated from the unique 4/m set, the solution became immediately obvious, with Re(1) placed at $x = 0.14$, $y = 0.32$; Re(2) at $x = 0.16$, $y = 0.36$; and Δz(Re–Re) = 0.07. A structure factor calculation (assuming space group $P4_1$) at this point, with phases based on the two rhenium atoms, gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.369$, where F_o is the observed and F_c the calculated structure factor; the weighted residual, $R_2 = \{\Sigma w \cdot [|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, using equal (unit) weights for all reflections was 0.412. For this and subsequent calculations, Re(1) was assigned a z coordinate of zero, and this parameter was held fixed throughout the course of the refinement.

One cycle of full-matrix, least-squares[34] refinement in which scale factor and positional and isotropic thermal parameters for the two rhenium atoms were varied reduced R_1 to 0.244 and R_2 to 0.311. A difference Fourier map at this stage revealed the positions of the five chlorine and two phosphorus atoms. It was noted that one of the seven "chlorine atoms," as they were temporarily designated, bridged the Re–Re bond, while the other six were terminal. Two more cycles of refinement reduced R_1 to 0.124 and R_2 to 0.165. A difference Fourier map at this point revealed the positions of the 36 phenyl carbon atoms, a bridging propionato group, and a bridging oxygen atom. At this

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(30) N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1054 (1964); *Inorg. Syn.*, **9**, 145 (1967).

(31) A modified version of D. P. Shoemaker's MIXG-2 MIT X-ray goniometer package (1962) was used to compute settings and prepare input for the automated diffractometer. It should be noted that for the above experiment, the conditions for multiple diffraction are maximized: W. A. Zachariasen, *Acta Cryst.*, **18**, 705 (1965). Since agreement between observed and calculated structure factors was later found to be very good, the effects are probably small in this case.

(32) Calculated using a local modification of the GONO9 program of W. C. Hamilton, goniostat absorption corrections (1960).

(33) Calculated using GINPUT-GENFOR, a Fourier series analysis program by R. B. Roof, Jr., D. R. Cromer, and A. C. Larson, Los Alamos Scientific Laboratory, 1965.

(34) C. T. Prewitt, a Fortran IV full-matrix crystallographic least-squares program, SFLS-5, 1966. The function minimized during refinement is $\Sigma w||F_c| - |F_o||^2$.

time, real and imaginary corrections[35] for anomalous scattering by Re, Cl, and P were included in the calculated structure amplitudes,[36] and refinement was continued in each of the enantiomorphous space groups $P4_1$ and $P4_3$. In the absence of anomalous scattering effects, there are two equally likely (and indistinguishable) solutions of the structure *for this particular crystal;* that is, the solution (obtained from the Patterson function) for space group $P4_1$ (enantiomer A) is equivalent to its inverse (enantiomer B) for space group $P4_3$. The set of coordinates for enantiomer B in space group $P4_3$ could be obtained, for example, by reflection of the enantiomer A structure in (001). Statistically one would expect to find an equal number of each of the above enantiomer–space group combinations. (It is important to note that structures involving the enantiomorphous pair—enantiomer B in space group $P4_1$ or enantiomer A in $P4_3$—are not under consideration here. In these the atoms are quite differently related to the unit cell, and it seems unlikely, though not impossible, that such crystals occur in the reaction product.) If anomalous scattering occurs, the two enantiomer–space group combinations are no longer equivalent,[37] and can be distinguished in several ways, the chief ones being: (a) by statistical tests on the crystallographic R factor; (b) by comparison of the observed F_{hkl} and $F_{\bar{h}\bar{k}\bar{l}}$ with the corresponding calculated structure amplitudes for both the enantiomer A and enantiomer B solutions; and (c) by an assessment of the relative stereochemical plausibilities of the two structures.

The essential features of this part of the refinement are summarized in Table I. Atomic scattering factors for Re are due to Cromer and Waber,[38] while, for the lighter atoms, those compiled by Ibers[39] were used.

From the data of Table I, it is readily seen that a significance test on the crystallographic R factors[40] allows *rejection,* with better than 99.5% confidence, of space group $P4_1$ (enantiomer A) as the correct solution. Further support for $P4_3$ (enantiomer B) as the correct choice is derived from a comparison of the calculated F_{hkl} and $F_{\bar{h}\bar{k}\bar{l}}$ with the corresponding observed structure amplitudes for each model at various stages in the refinement. The agreement for the cases in which there are significant differences between the calculated F_{hkl}'s and $F_{\bar{h}\bar{k}\bar{l}}$'s is excellent for only the $P4_3$ solution. In addition, from a chemical standpoint, the choice of enantiomer B is certainly the more likely one (see Table V and Discussion below).

TABLE I

SUMMARY OF THE STEPS IN LEAST-SQUARES REFINEMENTS[a]

Remarks	Space group $P4_1$ (enantiomer A) R_1	Space group $P4_1$ (enantiomer A) R_2	Space group $P4_3$ (enantiomer B) R_1	Space group $P4_3$ (enantiomer B) R_2	Ratio[c] $R_2(P4_1)/R_2(P4_3)$
(1) All atom parameters varied (isotropic temperature factors); equal (unit) weights	0.0556	0.0642	0.0527	0.0609	1.054
(2) All atom parameters varied (anisotropic temperature factors for Re, Cl and P; isotropic temperature factors for other atoms); empirical weighting scheme[b]	0.0456	0.0525	0.0438	0.0503	1.025
(3) Structure factor calculation only; parameters of step 2 used to calculate R_1 and R_2 for index set hkl and partial index set $\bar{h}\bar{k}\bar{l}$	0.0477	0.0576	0.0445	0.0512	1.125

[a] Each set of residuals, R_1 and R_2, listed are those obtained when the indicated type of refinement was cycled to convergence (individual parameter change less than ~0.3 esd). [b] The empirical weighting scheme was chosen according to Cruickshank's criterion that $w||F_o| - |F_c||^2$ should be constant. The details are as follows: for $|F_o| < 74.0$, $w^{-1} = 53.2 - 0.488|F_o|$; for $74.0 \leq |F_o| < 235.0$, $w^{-1} = 0.0977|F_o| + 9.77$; for $|F_o| \geq 235.0$, $w^{-1} = 1.07|F_o| - 218.2$. Anisotropic temperature factors were of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. *Cf.* D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press Inc., New York, N. Y., 1965, p 114. [c] For rejection of the hypothesis that enantiomer A is the correct solution a value for this ratio of >1.001 is necessary.

A final electron density difference map showed no features higher than 0.6 e⁻/Å³ (near the rhenium atoms) and 0.3–0.4 e⁻/Å³ elsewhere. Many of the smaller peaks (~0.3 e⁻/Å³) were near positions where hydrogen atoms attached to the phenyl rings would be expected to lie; however, a structure factor calculation including phenyl hydrogen atoms and one cycle of least-squares refinement varying carbon atom parameters *only* showed no change in R_1 or R_2. Since a full-matrix refinement varying positional and thermal parameters for all 81 atoms was impossible owing to storage limitations, this phase of the structure solution was abandoned. It is worthwhile to note, however, that the data are probably of good enough quality for a complete refinement if computer limitations were not a factor. Calculation of the structure factors for the rejected reflections gave no $|F_c|$ greater than twice the minimum observable.

Table II lists the observed and calculated structure amplitudes, $10|F_o|$ and $10|F_c|$, respectively, each in electrons; data are included for both the hkl and $\bar{h}\bar{k}\bar{l}$ sets. Final atomic fractional coordinates and isotropic temperature factors are shown in Table III. Anisotropic temperature factors are given in Table IV. Estimated standard deviations quoted in Tables III and IV were obtained from the inverse matrix of the final least-squares refinement cycle.

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(35) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(36) C. T. Prewitt, Ph.D. Thesis, Massachusetts Institute of Technology, 1962, p 163. The formulas used to calculate the dispersion-corrected real and imaginary parts of the structure factor are (neglecting temperature factors)

$$A = \sum_{\substack{\text{all} \\ \text{atoms}}} \{(f_0 + \Delta f')\cos\phi - \Delta f''\sin\phi\}$$

$$B = \sum_{\substack{\text{all} \\ \text{atoms}}} \{(f_0 + \Delta f')\sin\phi + \Delta f''\cos\phi\}$$

where $\phi = 2\pi(hx + ky + lz)$.

(37) Indeed, the "enantiomers" are no longer that but are dimensionally different structures.

(38) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(39) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(40) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

Results

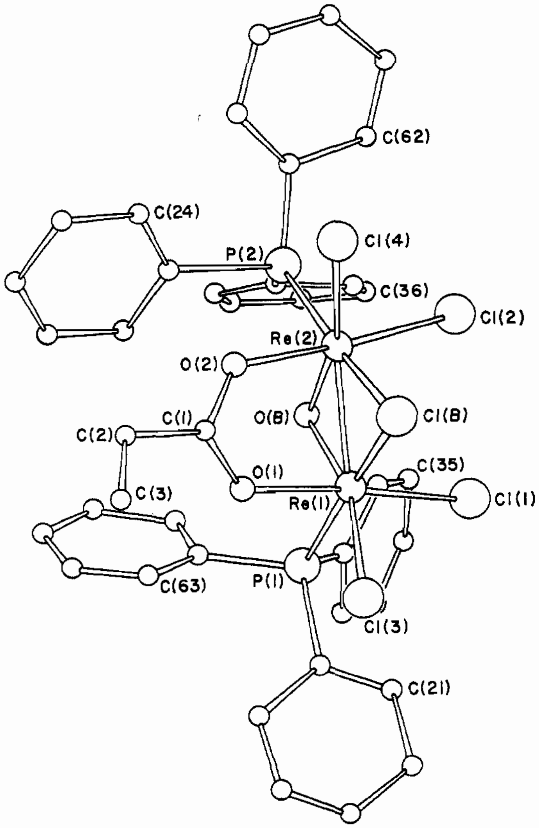

Figure 1.—A perspective drawing of the molecular structure of $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$. The atom numbering system is also illustrated.

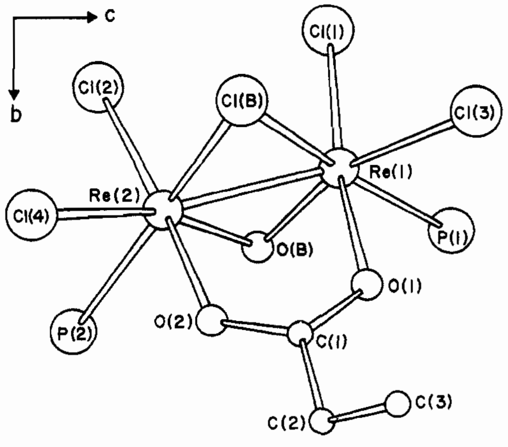

Figure 2.—Projection down [100] of the inner coordination sphere of $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$.

The structure (enantiomer B, space group $P4_3$) is depicted in Figures 1 and 2, which also show the numbering scheme used in Tables V–VII, where the intramolecular dimensions are presented. In the figures, all atoms associated solely with Re(1) have been assigned odd serial numbers, and all atoms associated solely with Re(2) have been assigned even serial numbers. Analogously, phenyl rings 1, 3, and 5 are attached to P(1), while rings 2, 4, and 6 are attached to P(2). The numbering scheme for the phenyl carbon atoms is arranged so that each carbon atom has a label C(*mn*), in which *m* is the atom sequence number and *n* is the ring number. For example, the carbon atoms attached directly to P(1) are C(11), C(13), and C(15). In Figure 1, only one carbon atom on each ring has been labeled; the other labels may be determined using this label and the foregoing rule.

Table VIII gives the equations for two important planes in the inner coordination sphere and the distances of the atoms from the planes. Root-mean-square vibrational amplitudes and their direction cosines have been omitted from this report, since the observed complex thermal motion of the heavy atoms afforded no useful chemical or structural insight.

Discussion

Effect of Anomalous Scattering.—Ueki, Zalkin, and Templeton[41] have recently discussed the serious coordinate errors that can result from the neglect of the imaginary component, $\Delta f''$, of the anomalous scattering in structure solutions involving polar space groups. As these authors have pointed out, unless the $\Delta f''$ contribution (which is always positive) is considered, the anomalous scatterer will appear to be closer to the X-ray source and detector than it actually is. Consequently, if the origin is fixed by an anomalous scatterer in a polar space group, the other atoms will undergo shifts to compensate for this. In the sense of the crystallographic point symmetry (4, as opposed to Laue symmetry 4/m) we have collected an incomplete set of data; the point group symmetry demands collection of both index sets *hkl* and $hk\bar{l}$ (where *h*, *k*, and *l* are all ≥ 0). The coordinate error introduced by neglect of $\Delta f''$ in the refinement of polar structures with this type of incomplete data set has been termed *polar dispersion error*;[42] further, similar errors, of smaller magnitude, will be introduced if incorrect or inaccurate $\Delta f''$ corrections are used in the refinement.

Cruickshank and McDonald[43] have recently discussed polar dispersion errors in detail. In particular, they found that an estimate of Δz, the coordinate error introduced by including $\Delta f''$ in the calculations and choosing the *incorrect* structure model (for example, enantiomer A in our case), is given by

$$\Delta z = \frac{2}{\pi S_{\max}}\left(\frac{\Delta f''}{|f|}\right)_{^1/_2 S_{\max}}$$

where $S = (2 \sin \theta)/\lambda$, $|f|$ is the modulus of the complex atomic scattering factor, and the quantity $(\Delta f''/|f|)$ is taken as the phase shift due to anomalous scattering, evaluated at $S = {}^1/_2 S_{\max}$. Use of this formula predicts shifts in the *z* coordinate (with reference to Re(1)) of 0.081 Å for light atoms, 0.027 Å for chlorine atoms, and 0.041 Å for phosphorus atoms. The average observed shifts were 0.084, 0.028, and 0.036 Å, respectively. A rather surprising fact is that a similar formula predicts

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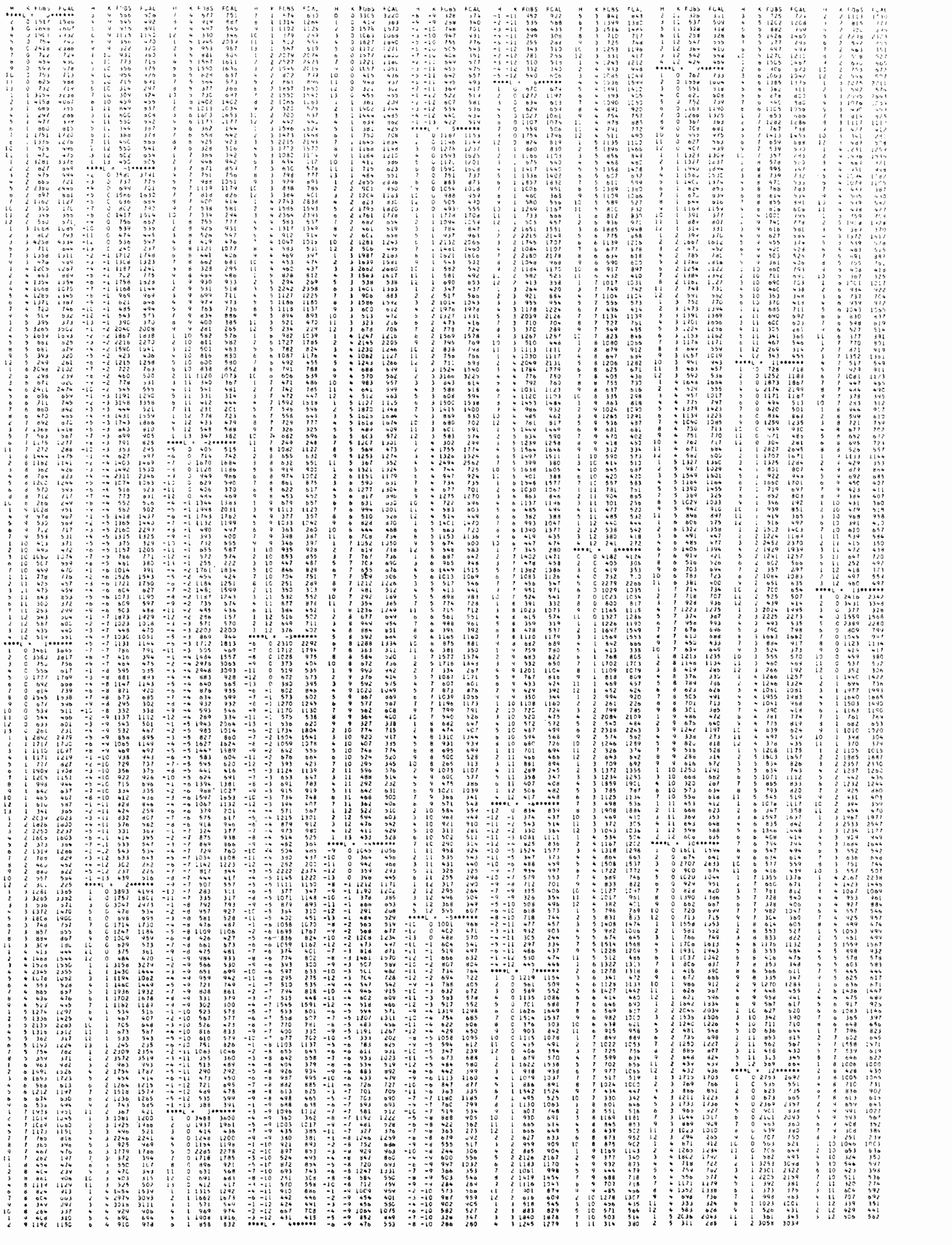
(41) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **20**, 836 (1966).

(42) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1767 (1966).

(43) D. W. J. Cruickshank and W. S. McDonald, *Acta Cryst.*, **23**, 9 (1967).

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) (IN ELECTRONS) FOR $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$



in this case an error in the z coordinate of an oxygen atom of 0.014 Å if the correction, $\Delta f'' = 0.1$ electron, is neglected.

Table V contains the principal bond lengths for enantiomers A and B (in the space groups $P4_1$ and $P4_3$, respectively) in the inner coordination sphere, grouped into what one would normally expect to be *chemically* equivalent pairs. For enantiomer A, the lighter atoms are shifted so that (expected) chemically equivalent bond lengths are different by as much as 0.12 Å; for

TABLE II (*Continued*)

H	K	FOBS	FCAL
****L = 14******			
1	0	1375	1383
2	0	619	525
3	0	4140	4028
5	0	807	864
7	0	1265	1229
8	0	458	467
9	0	531	478
10	0	647	673
12	0	434	421
1	1	2157	2135
2	1	1899	1841
3	1	794	793
4	1	2040	1989
5	1	2675	2656
6	1	532	640
7	1	1076	1056
8	1	966	902
10	1	591	542
11	1	390	376
1	2	1686	1710
2	2	3249	3167
3	2	1146	1120
4	2	1861	1546
5	2	407	294
6	2	865	885
8	2	627	645
9	2	381	391
11	2	303	287
1	3	1432	1356
2	3	1168	1217
3	3	472	390
4	3	2041	2061
5	3	639	624
6	3	1195	1155
7	3	703	626
9	3	413	334
10	3	449	362
1	4	1017	1034
2	4	2111	2092
3	4	1342	1391
4	4	509	574
6	4	885	946
7	4	773	801
8	4	564	505
9	4	445	398
10	4	429	371
1	5	1732	1695
3	5	519	488
4	5	649	700
5	5	1536	1544
7	5	652	630
1	6	1235	1240
2	6	482	510
3	6	990	1105
4	6	1618	1625
6	6	363	382
7	6	804	817
9	6	377	251
10	6	355	371
2	7	1000	1004
3	7	966	1024
4	7	413	414
5	7	566	579
6	7	798	772
9	7	416	469
1	8	727	675
2	8	1371	1355
3	8	447	318
4	8	598	611
5	8	1016	1074
7	8	373	283
8	8	294	252
9	8	543	554
1	9	1091	1070
2	9	397	356
3	9	579	579
4	9	809	867
7	9	701	738
8	9	497	447
2	10	640	624
3	10	508	492
4	10	607	626
6	10	799	652
2	11	693	685
3	11	456	439
4	11	411	380
5	11	361	380
1	12	473	474
****L = 15******			
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2	0	2246	2297
3	0	859	870
4	0	1350	1339
5	0	2131	2117
6	0	678	666
7	0	695	645
8	0	833	770
9	0	516	538
10	0	342	291
11	0	494	509
12	0	263	285
1	1	2400	2366
2	1	1530	1568
3	1	2118	2041
4	1	2044	1972
5	1	1297	1293
6	1	1197	1220
7	1	975	1008
9	1	630	571
11	1	301	257
12	1	271	303
1	2	1077	1179
2	2	1605	1595
3	2	1575	1567
4	2	1462	1412
5	2	632	671
6	2	1510	1512
7	2	1114	1080
10	2	355	365
1	3	2139	2137
2	3	2710	2693
3	3	718	790
4	3	1138	1059
5	3	1526	1467
6	3	713	706
7	3	445	406
8	3	657	645
10	3	550	322
11	3	667	263
1	4	1999	1976
2	4	1173	1203
3	4	1130	1132
4	4	911	970
5	4	658	651
6	4	416	527
7	4	966	933
8	4	729	718
9	4	439	403
1	5	1014	983
3	5	1361	1326
4	5	1136	1099
6	5	662	693
7	5	711	729
9	5	562	558
1	6	362	403
2	6	1118	1088
3	6	1068	1021
4	6	526	558
5	6	917	716
6	6	842	787
8	6	393	384
1	7	960	972
2	7	1052	1032
4	7	1337	1359
5	7	909	934
7	7	361	306
8	7	548	543
10	7	265	291
1	8	945	965
2	8	490	469
3	8	1159	1155
4	8	735	686
6	8	571	529
7	8	567	612
9	8	299	230
1	9	431	372
2	9	907	860
3	9	910	936
5	9	764	789
6	9	419	463
7	9	377	390
8	9	318	311
1	10	833	831
2	10	701	656
4	10	434	474
5	10	502	540
7	10	361	426
3	11	513	561
4	11	449	528
1	12	397	385
2	12	353	422
****L = 16******			
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2	0	1850	1833
4	0	2208	2188
5	0	1118	1169
6	0	1557	1510
7	0	864	838
8	0	733	660
9	0	661	650
10	0	503	509
11	0	442	404
12	0	311	248
1	1	322	332
2	1	2165	2118
3	1	2090	2090
4	1	1665	1617
6	1	777	721
7	1	778	750
8	1	716	711
11	1	324	328
12	1	240	243
1	2	2812	2873
2	2	440	389
3	2	530	437
4	2	1154	1123
5	2	2271	2241
6	2	1068	1022
7	2	1139	1058
9	2	471	396
10	2	317	343
11	2	428	378
12	2	447	454
1	3	1136	1161
2	3	693	667
3	3	2120	2095
5	3	409	374
7	3	927	826
8	3	717	832
9	3	577	542
1	4	1549	1533
2	4	727	676
3	4	1137	1098
4	4	762	815
5	4	1084	1058
6	4	1443	1493
7	4	368	380
11	4	447	444
1	5	637	661
2	5	1813	1733
3	5	514	555
4	5	1062	1036
5	5	637	622
6	5	797	777
7	5	721	702
8	5	710	663
9	5	349	368
1	6	1138	1135
2	6	463	427
3	6	714	776
4	6	1149	1178
5	6	992	1024
6	6	834	847
7	6	482	413
9	6	467	423
10	6	335	325
1	7	358	261
2	7	921	869
3	7	1460	1476
5	7	591	640
6	7	847	895
8	7	360	286
9	7	301	354
1	8	949	915
2	8	955	943
3	8	492	468
4	8	671	689
5	8	765	773
6	8	540	579
9	8	260	256
1	9	918	910
3	9	756	751
4	9	728	695
5	9	407	428
6	9	653	683
7	9	368	301
8	9	355	417
2	10	717	715
3	10	882	914
6	10	294	286
1	11	627	653
2	11	386	367
3	11	378	386
4	11	255	189
5	11	652	646
1	12	261	278
2	12	573	598
****L = 17******			
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2	0	1772	1767
3	0	1263	1284
4	0	2085	2072
5	0	1511	1507
6	0	894	809
9	0	931	965
10	0	715	713
11	0	421	343
1	1	1421	1471
2	1	1993	1979
3	1	1356	1296
4	1	597	586
5	1	1297	1228
6	1	1921	1806
7	1	651	605
8	1	422	450
10	1	591	506
11	1	376	392
12	1	567	596
1	2	873	861
2	2	1264	1303
3	2	1625	1600
4	2	1650	1606
5	2	1612	1379
6	2	608	587
8	2	816	790
9	2	508	500
10	2	361	429
11	2	294	320
1	3	1873	1921
2	3	1612	1622
4	3	366	400
5	3	812	811
6	3	1492	1444
7	3	1365	1342
8	3	418	413
9	3	403	358
10	3	461	438
11	3	404	417
1	4	567	503
2	4	1141	1134
3	4	914	927
4	4	1167	1214
5	4	955	899
6	4	728	720
9	4	594	510
10	4	468	441
11	4	346	376
1	5	1413	1442
2	5	937	924
3	5	814	821
4	5	553	533
5	5	670	694
6	5	1152	1199
7	5	872	840
8	5	706	749
9	5	327	219
2	6	507	459
3	6	1447	1440
4	6	502	441
5	6	1122	1242
7	6	339	368
8	6	412	432
9	6	426	449
1	7	1384	1371
2	7	731	757
3	7	694	738
4	7	451	453
5	7	532	589
6	7	464	361
7	7	750	760
9	7	444	427
1	8	387	400
2	8	465	502
3	8	1008	1041
4	8	1047	1055
5	8	745	777
6	8	589	638
8	8	516	519
9	8	315	388
1	9	442	458
2	9	1228	1164
6	9	742	724
8	9	487	540
2	10	416	427
4	10	691	693
5	10	442	435
6	10	351	391
1	11	797	790
2	11	343	365
3	11	377	372
4	11	258	275
****L = 18******			
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2	0	467	497
3	0	1807	1783
4	0	1206	1180
5	0	764	684
6	0	1019	967
7	0	948	918
8	0	1060	1035
10	0	392	432
1	1	1246	1319
2	1	660	620
3	1	776	746
4	1	1324	1358
5	1	1327	1262
6	1	997	983
7	1	753	668
8	1	550	595
9	1	378	410
10	1	767	730
11	1	600	597
1	2	705	713
2	2	1668	1682
3	2	1249	1234
4	2	1047	971
6	2	585	577
7	2	1121	1083
8	2	636	521
9	2	826	811
1	3	667	719
2	3	963	972
4	3	1360	1311
5	3	1018	1026
6	3	1097	1055
7	3	891	878
9	3	909	875
10	3	357	267
11	3	748	757
1	4	504	584
2	4	1757	1726
3	4	625	579
4	4	444	454
5	4	450	412
6	4	582	610
7	4	1077	1074
8	4	1242	1186
9	4	545	492
1	5	1626	1667
3	5	938	995
4	5	1023	1038
5	5	801	847
6	5	1083	1018
7	5	729	752
10	5	819	801
1	6	1187	1139
2	6	877	835
3	6	656	657
4	6	1230	1236
6	6	710	723
7	6	593	619
8	6	804	779
9	6	404	386
10	6	250	242
1	7	448	411
2	7	990	964
3	7	838	822
4	7	483	495
5	7	1348	1343
6	7	595	567
9	7	390	382
1	8	371	373
2	8	914	988
3	8	519	543
4	8	616	666
5	8	597	620
6	8	513	524
7	8	638	653
1	9	797	783
2	9	683	617
3	9	482	539
4	9	695	723
6	9	404	382
7	9	532	608
1	10	835	787
2	10	578	591
3	10	533	480
4	10	309	277
5	10	272	311
6	10	580	597
2	11	632	626
3	11	363	448
4	11	257	281
****L = 19******			
1	0	1525	1496
2	0	1830	1758
3	0	936	930
5	0	1297	1228
6	0	1110	1077
7	0	844	842
9	0	532	524
10	0	733	704
11	0	503	497
1	1	519	473
2	1	505	448
3	1	1215	1189
4	1	1242	1268
5	1	1354	1347
7	1	536	488
8	1	824	764
9	1	890	868
10	1	663	618
11	1	640	623
1	2	766	756
2	2	1515	1464
3	2	753	755
4	2	510	435
5	2	571	520
6	2	1103	1098
7	2	798	794
8	2	1026	1037
9	2	610	608
11	2	703	708
1	3	850	830
2	3	614	621
3	3	918	882
4	3	855	835
5	3	1085	1064
6	3	684	656
7	3	706	654
8	3	557	544
9	3	820	806
10	3	717	703
1	4	1826	1804
2	4	328	311
3	4	1022	1071
4	4	362	385
5	4	535	577
6	4	980	980
7	4	1390	1362
8	4	771	767
9	4	546	517
10	4	657	646
11	4	353	373
1	5	906	847
2	5	902	945
3	5	998	1021
4	5	1098	1086
5	5	948	975
8	5	872	870
9	5	640	651
2	6	1700	1714
3	6	447	406
4	6	424	485
6	6	1078	1066
7	6	847	883
8	6	495	498
9	6	423	415
10	6	481	556
1	7	466	432
2	7	551	615
3	7	716	707
4	7	1440	1436
6	7	738	751
7	7	501	448
8	7	459	460
9	7	406	398
1	8	1083	1110
2	8	662	728
3	8	478	571
5	8	479	487
6	8	652	702
7	8	502	523
8	8	474	525
1	9	405	392
3	9	746	755
4	9	392	403
5	9	770	753
7	9	463	450
1	10	831	809
2	10	299	307
3	10	483	549
5	10	342	396
6	10	449	472
1	11	382	334
4	11	570	597
****L = 20******			
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2	0	479	424
4	0	1086	1060
5	0	1282	1279
6	0	917	859
7	0	657	667
9	0	998	968
11	0	1007	1015
1	1	540	532
2	1	728	687
3	1	1263	1270
4	1	877	864
7	1	1156	1130
8	1	1126	1078
9	1	651	690
10	1	437	368
11	1	405	392
1	2	967	978
2	2	346	289
4	2	453	425
5	2	954	892
6	2	1313	1270
8	2	351	270
9	2	452	394
10	2	1115	1082
11	2	470	439
1	3	944	942
2	3	769	770
3	3	1033	1051
4	3	783	752
6	3	833	801
7	3	579	635
8	3	1653	1614
1	4	843	823
2	4	958	936
3	4	1030	1081
5	4	1099	1075
6	4	915	933
7	4	497	512
9	4	788	770
10	4	710	715
1	5	665	636
2	5	984	929
3	5	1130	1119
4	5	382	357
5	5	454	450
7	5	1278	1237
8	5	508	525
9	5	962	941
1	6	1201	1253
2	6	968	937
4	6	1058	1032
5	6	1266	1290
6	6	431	390
7	6	611	598
9	6	632	628
1	7	751	727
2	7	667	635
3	7	988	952
4	7	440	448
6	7	824	828
7	7	499	516
8	7	981	937
9	7	279	315
1	8	779	726
2	8	561	461
3	8	932	880
4	8	690	719
5	8	324	283
6	8	926	919
1	9	877	878
4	9	581	654
5	9	319	326
7	9	453	544
2	10	544	584
3	10	363	380
5	10	490	465
2	11	405	434
3	11	248	273
****L = 21******			
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2	0	421	359
3	0	1342	1289
4	0	938	874
5	0	551	501
6	0	970	954
7	0	929	901
8	0	367	332
9	0	712	586
10	0	947	920
1	1	957	1005
2	1	575	505
4	1	391	440
5	1	589	651
6	1	968	951
7	1	639	624
8	1	1031	994
9	1	847	850
10	1	351	355
11	1	574	602
1	2	389	353
2	2	484	546
3	2	576	512
4	2	843	871
5	2	712	704
6	2	622	598
7	2	761	706
8	2	1178	1120
9	2	712	704
10	2	562	451
11	2	760	742
1	3	527	569
2	3	1084	1110
3	3	994	1028
6	3	963	976
7	3	1058	1033
8	3	512	418
9	3	566	570
10	3	927	884
11	3	352	362
1	4	859	893
3	4	573	539
4	4	1111	1120
5	4	581	605
6	4	503	465
7	4	824	832
8	4	889	862
9	4	704	703
10	4	465	446
1	5	660	657
2	5	1397	1366
3	5	658	579
4	5	616	588
5	5	965	956
6	5	733	673
7	5	774	730
8	5	973	970
9	5	522	542
10	5	263	205
1	6	951	912
2	6	832	784
3	6	1369	1345
4	6	374	393
5	6	693	686
6	6	896	928
7	6	576	563
8	6	501	472
9	6	665	638
1	7	719	742
3	7	624	583
4	7	998	1016
5	7	456	454
6	7	471	458
7	7	717	720
8	7	373	360
9	7	473	531
1	8	661	658
2	8	864	868
4	8	387	497
5	8	888	935
7	8	350	368
8	8	490	540
1	9	412	344
2	9	648	654
3	9	816	801
4	9	318	166
5	9	408	349
6	9	612	640
7	9	282	344
1	10	454	467
3	10	376	279
4	10	473	530
1	11	498	549
2	11	387	403
****L = 22******			
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2	0	1105	1050
3	0	698	648
4	0	531	487
5	0	644	616
5	0	579	616
6	0	465	474
7	0	460	348
8	0	1473	1437
11	0	253	301
1	1	1067	1066
2	1	549	569
4	1	574	598
6	1	986	959
7	1	751	756
9	1	445	438
10	1	1104	1073
11	1	556	576
1	2	829	853
2	2	350	406
3	2	915	956
4	2	554	533
5	2	462	451
6	2	375	261
7	2	1475	1458
8	2	431	521
9	2	1004	982
11	2	349	376
1	3	875	877
2	3	560	584
3	3	341	334
5	3	1553	1568
6	3	618	550
7	3	603	557
9	3	879	865
1	4	624	583
2	4	1302	1296
3	4	844	866
4	4	679	716
6	4	760	738
7	4	730	760
8	4	1103	1070
9	4	708	716
1	5	723	694
2	5	364	292
3	5	873	853
4	5	1466	1461
5	5	457	507
6	5	1157	1140
10	5	941	964
1	6	1179	1125
2	6	539	513
3	6	457	421
4	6	793	761
5	6	387	404
6	6	393	286
7	6	520	487
8	6	1108	1121
9	6	267	313
2	7	1105	1118
3	7	715	784
5	7	926	929
6	7	730	734
7	7	485	495
2	8	345	302
3	8	835	816
4	8	704	666
7	8	742	786
1	9	725	708
2	9	353	351
3	9	547	531
4	9	669	679
5	9	514	542
6	9	321	339
1	10	548	565
2	10	431	442
1	11	335	380
****L = 23******			
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2	0	833	811
3	0	471	431
4	0	765	756
5	0	704	712
6	0	576	484
7	0	789	740
9	0	687	616
10	0	697	683
1	1	1129	1197
2	1	1010	993
4	1	338	254
5	1	732	741
6	1	1172	1142
7	1	871	880
8	1	661	675
9	1	497	562
10	1	303	287
11	1	506	501
1	2	750	753
2	2	607	646
3	2	781	783
4	2	929	905
5	2	930	857
6	2	1110	1066
9	2	730	692
10	2	454	463
1	3	594	549
2	3	660	641
3	3	869	806
4	3	661	684
5	3	485	472
6	3	946	924
7	3	1377	1277
9	3	738	728
10	3	585	580
2	4	435	324
3	4	1056	1046
4	4	1335	1345
5	4	806	804
6	4	528	529
7	4	457	489
8	4	643	605
9	4	522	492
10	4	470	525
1	5	1071	1049
2	5	922	963
5	5	892	870
6	5	866	823
7	5	482	468
8	5	847	841
9	5	636	608
3	6	1072	1120
5	6	732	659
6	6	649	661
7	6	596	631
8	6	292	303
9	6	608	645
1	7	1239	1234
3	7	703	757
4	7	443	458
5	7	493	457
6	7	511	546
7	7	687	672
1	8	458	408
2	8	673	652
3	8	416	504
4	8	846	814
5	8	701	659
2	9	871	864
3	9	390	380
6	9	514	533
1	10	352	365
3	10	439	445
4	10	478	571
1	11	645	668
****L = 24******			
0	0	1674	1740
1	0	347	334
2	0	725	722
3	0	589	518
4	0	550	542
5	0	967	878
6	0	772	742
7	0	847	793
8	0	340	355
9	0	728	695
1	1	722	794
2	1	1060	1051
3	1	955	1004
6	1	497	445
7	1	843	848
8	1	893	854
9	1	637	546
1	2	1156	1173
2	2	676	722
4	2	761	741
5	2	1033	996
6	2	1442	1485
7	2	409	393
9	2	406	419
10	2	794	778
1	3	825	826
2	3	531	520
3	3	966	935
4	3	1012	958
6	3	814	842
7	3	464	485
8	3	1019	1024
1	4	667	603
2	4	855	753
3	4	879	861
4	4	923	883
5	4	1075	1097
6	4	1068	1049
9	4	343	371
10	4	493	499
1	5	674	603
2	5	971	909
3	5	1053	1026
4	5	552	590
6	5	344	278
7	5	774	793
9	5	732	707
1	6	950	940
2	6	460	524
3	6	377	381
4	6	892	917
5	6	794	779
7	6	656	634
8	6	335	328
9	6	557	605
1	7	568	321
3	7	751	748
5	7	517	576
6	7	349	296
7	7	302	330
8	7	645	695
1	8	479	492
2	8	726	706
3	8	843	786
4	8	592	556
6	8	536	553
1	9	575	493
3	9	402	328
4	9	711	740
5	9	451	464
6	9	287	352
2	10	600	582
3	10	368	516
4	10	252	287
****L = 25******			
1	0	1534	1504
2	0	1254	1226
5	0	944	870
6	0	1138	1109
7	0	722	736
8	0	430	469
10	0	425	428
1	1	698	714
2	1	1187	1025
3	1	1011	1033
4	1	1015	1054
5	1	770	728
6	1	540	494
7	1	498	505
8	1	370	347
9	1	672	645
1	2	1130	1158
2	2	489	506
3	2	868	874
5	2	836	846
6	2	925	893
7	2	1051	996
8	2	710	744
1	3	984	1027
2	3	813	883
3	3	970	962
4	3	1193	1205
5	3	844	841
8	3	488	435
9	3	515	478
10	3	513	527
1	4	1212	1237
2	4	384	399
3	4	831	842
5	4	988	990
6	4	638	626
7	4	800	815
8	4	338	439
9	4	362	359
1	5	815	708
3	5	1166	1164
4	5	842	983
5	5	780	787
6	5	451	424
8	5	713	673
9	5	419	421
1	6	767	746
2	6	1190	1160
6	6	854	846
7	6	309	305
8	6	362	329
2	7	690	666
4	7	892	923
6	7	366	259
8	7	415	500
1	8	841	863
2	8	629	636
3	8	425	431
5	8	402	447
6	8	443	472
7	8	419	431
3	9	840	828
5	9	614	682
1	10	595	599
2	10	430	404
3	10	347	353
****L = 26******			
1	0	1640	1610
3	0	1563	1551
4	0	375	358
6	0	675	676
7	0	752	720
8	0	392	341
9	0	309	286
10	0	458	453
1	1	1457	1538
2	1	398	288
3	1	519	586
4	1	1140	810
5	1	1360	1293
6	1	527	602
7	1	806	743
8	1	325	231
10	1	580	580
1	2	429	336
2	2	1622	1664
3	2	819	850
4	2	752	803
6	2	431	439
7	2	889	845
8	2	429	441
9	2	411	464
2	3	639	594
4	3	1219	1212
5	3	884	850
6	3	1007	941
9	3	312	232
1	4	725	732
2	4	1328	1318
3	4	1084	1052
4	4	503	384
5	4	644	596
6	4	573	479
7	4	661	640
8	4	473	501
9	4	392	378
1	5	1510	1485
2	5	413	391
3	5	394	398
4	5	536	517
5	5	865	812
6	5	587	629
7	5	410	399
9	5	277	298
1	6	1054	1081
2	6	589	567
3	6	914	931
4	6	676	675
7	6	483	454
8	6	504	509
2	7	750	798
3	7	435	439
4	7	406	420
5	7	339	389
6	7	441	418
2	8	490	474
3	8	602	549
5	8	532	537
1	9	625	642
3	9	412	467
4	9	635	730
1	10	441	445
****L = 27******			
1	0	1280	1249
2	0	1559	1522
3	0	708	730
4	0	1116	1031
5	0	1144	1120
8	0	670	639
9	0	469	404
10	0	320	359
1	1	964	1046
2	1	1169	1189
3	1	1166	1212
4	1	862	820
5	1	618	643
6	1	1070	1011
7	1	537	463
8	1	519	514
9	1	371	399
1	2	881	934
2	2	630	655
3	2	1155	1155
4	2	1058	1078
5	2	769	697
8	2	501	437
10	2	386	416
1	3	1061	1079
2	3	1256	1280
4	3	674	596
5	3	1055	1020
6	3	668	658
7	3	623	589
8	3	501	481
1	4	881	890
2	4	922	890
3	4	782	682
4	4	1231	1213
5	4	573	564
8	4	354	355
9	4	490	492
1	5	699	727
2	5	948	951
3	5	1004	969
4	5	464	452
6	5	539	567
7	5	554	549
1	6	400	495
2	6	1007	1050
3	6	768	756
4	6	448	412
5	6	664	632
1	7	1114	1156
3	7	348	318
5	7	357	289
7	7	514	549
2	8	330	243
3	8	500	497
4	8	689	711
5	8	274	199
6	8	435	463
2	9	569	631
2	10	380	440
****L = 28******			
0	0	2137	2275
2	0	621	561
3	0	377	270
4	0	1415	1405
5	0	363	354
6	0	1229	1169
7	0	422	386
9	0	367	332
1	1	1085	1149
2	1	1548	1583
3	1	888	906
4	1	873	881
6	1	446	434
7	1	516	431
8	1	650	625
1	2	1450	1545
2	2	344	377
3	2	525	462
4	2	516	529
5	2	1266	1231
6	2	565	528
7	2	351	158
8	2	319	328
1	3	1316	1408
2	3	611	621
3	3	1785	1847
4	3	505	540
7	3	775	765
9	3	396	369
1	4	925	937
2	4	872	902
3	4	527	583
4	4	439	391
5	4	675	630
6	4	679	679
1	5	618	658
2	5	1475	1495
3	5	352	256
4	5	952	963
5	5	518	509
8	5	546	540
1	6	654	700
4	6	612	619
6	6	336	301
7	6	493	523
2	7	458	446
3	7	823	861
6	7	529	566
1	8	635	599
2	8	543	519
4	8	300	219
5	8	569	547
1	9	500	533
2	9	297	252
4	9	580	624
****L = 29******			
1	0	1239	1193
2	0	1375	1406
3	0	399	480
4	0	594	623
5	0	1093	1039
7	0	385	365
8	0	738	717
9	0	424	464
1	1	935	1043
2	1	778	814
3	1	1065	1057
4	1	774	832
5	1	509	536
6	1	742	741
7	1	427	425
8	1	453	414
9	1	466	396
1	2	781	837
2	2	572	481
3	2	1560	1657
4	2	960	965
5	2	355	244
6	2	795	748
7	2	389	374
9	2	457	454
1	3	1060	1071
2	3	1155	1217
3	3	440	473
4	3	580	496
5	3	875	860
6	3	605	563
8	3	333	343
1	4	1100	1089
2	4	850	829
3	4	850	854
4	4	1020	996
5	4	532	491
6	4	339	406
8	4	382	357
1	5	589	580
2	5	499	533
3	5	1043	1054
4	5	543	386
6	5	638	615
7	5	540	505
1	6	1046	1027
2	6	748	741
3	6	637	640
5	6	534	535
6	6	403	353
1	7	713	697
2	7	520	545
4	7	368	414
5	7	583	615
3	8	487	492
4	8	550	537
2	9	490	491
3	9	346	444
****L = 30******			
1	0	1352	1257
2	0	360	259
3	0	1645	1643
4	0	382	334
7	0	737	705
8	0	415	341
9	0	546	536
1	1	1202	1253
2	1	439	425
3	1	408	402
4	1	684	753
5	1	1107	1071
6	1	598	522
7	1	588	529
8	1	379	356
1	2	797	723
2	2	1555	1608
3	2	690	704
4	2	1062	1109
6	2	619	606
8	2	505	487
9	2	308	321
1	3	666	743
2	3	595	624
3	3	352	372
4	3	1149	1120
5	3	770	714
6	3	755	678
1	4	672	608
2	4	892	893
3	4	1248	1316
4	4	592	569
5	4	332	255
6	4	358	349
8	4	332	323
1	5	929	931
2	5	402	415
3	5	394	291
4	5	349	437
5	5	708	707
6	5	305	244
7	5	345	306
1	6	755	788
3	6	746	776
4	6	516	539
6	6	359	291
7	6	437	485
1	7	339	355
2	7	603	583
3	7	413	428
5	7	321	367
6	7	397	433
1	8	425	405
2	8	633	601
3	8	455	458
1	9	414	475
2	9	280	314
****L = 31******			
1	0	1215	1201
2	0	1090	1075
3	0	419	415
4	0	399	354
5	0	699	697
6	0	519	522
7	0	909	837
8	0	436	496
1	1	696	703
2	1	698	744
3	1	1154	1186
4	1	783	796
5	1	849	823
6	1	372	340
8	1	349	340
9	1	639	659
1	2	598	649
2	2	1011	1086
3	2	666	693
4	2	366	329
5	2	525	559
6	2	513	521
7	2	686	689
1	3	634	628
2	3	1064	1059
3	3	791	796
4	3	1101	1123
5	3	747	830
8	3	317	362
1	4	747	741
2	4	721	698
3	4	618	623
5	4	455	456
6	4	447	441
7	4	512	544
1	5	421	432
3	5	771	827
4	5	608	649
5	5	793	771
1	6	355	402
2	6	915	942
3	6	332	206
5	6	443	437
6	6	582	612
2	7	391	392
4	7	780	801
5	7	360	359
1	8	661	673
2	8	454	487
3	8	457	442
****L = 32******			
0	0	1782	1892
2	0	820	791
4	0	938	892
5	0	604	600
6	0	659	619
1	1	366	302
2	1	1066	1053
3	1	608	706
4	1	595	566
6	1	361	336
7	1	742	686
8	1	655	619
1	2	1020	1030
2	2	369	318
4	2	605	654
5	2	998	956
6	2	731	746
1	3	899	884
2	3	501	595
3	3	1013	1079
4	3	656	661
8	3	487	531
2	4	398	437
3	4	337	193
4	4	555	515
5	4	830	860
6	4	628	608
2	5	834	769
3	5	529	564
4	5	687	683
7	5	576	617
1	6	577	554
4	6	689	708
5	6	401	429
6	6	410	453
1	7	434	459
2	7	617	636
3	7	637	605
5	7	268	283
1	8	422	577
2	8	440	472
3	8	462	499
****L = 33******			
1	0	853	807
2	0	676	585
3	0	445	413
4	0	551	531
5	0	337	391
6	0	509	413
7	0	300	304
8	0	469	482
1	1	602	596
2	1	754	756
3	1	461	450
5	1	553	531
6	1	837	852
7	1	565	522
8	1	507	467
1	2	417	426
3	2	715	823
4	2	665	710
5	2	749	710
8	2	410	437
1	3	567	557
2	3	644	644
3	3	490	489
5	3	377	323
6	3	777	783
7	3	507	531
2	4	491	545
3	4	477	445
4	4	1010	979
5	4	596	567
6	4	286	246
1	5	574	611
2	5	358	374
3	5	469	451
5	5	442	434
6	5	605	636
3	6	718	751
4	6	453	469
5	6	576	646
1	7	906	980
3	7	284	357
1	8	350	412
2	8	250	249
****L = 34******			
1	0	411	365
3	0	619	666
4	0	513	470
5	0	363	355
6	0	562	588
7	0	335	309
8	0	682	715
1	1	724	735
2	1	326	280
4	1	484	533
5	1	634	618
6	1	646	646
7	1	415	351
1	2	441	501
2	2	467	460
3	2	672	683
4	2	394	358
6	2	335	290
7	2	674	632
2	3	369	363
4	3	461	372
5	3	761	791
6	3	342	311
7	3	317	298
1	4	385	417
2	4	326	364
3	4	686	707
4	4	378	455
5	4	386	426
6	4	494	487
1	5	607	546
3	5	316	320
4	5	492	508
5	5	618	422
6	5	740	770
1	6	645	635
4	6	381	375
2	7	459	519
3	7	537	553
****L = 35******			
1	0	422	430
2	0	346	317
3	0	534	454
4	0	537	473
5	0	703	727
7	0	708	679
2	1	319	178
5	1	630	591
5	1	340	392
2	2	481	462
4	2	505	443
5	2	410	437
6	2	581	597
7	2	341	391
1	3	313	269
3	3	461	507
4	3	393	383
5	3	313	331
6	3	428	397
1	4	661	674
3	4	350	357
4	4	482	462
5	4	345	362
6	4	375	344
2	5	628	682
4	5	355	453
5	5	644	652
1	6	381	286
2	6	287	348
3	6	272	304
1	7	512	536
****L = 36******			
0	0	330	338
5	0	803	825
7	0	294	302
1	1	328	248
3	1	383	439
4	1	542	565
7	1	757	798
4	2	470	534
6	2	561	556
1	3	535	469
2	3	469	444
4	3	528	576
6	3	440	435
2	4	552	590
5	4	508	477
1	5	389	366
3	5	530	496
4	5	275	318
1	6	614	650
2	6	328	423
1	7	349	385
****L = 37******			
1	0	330	256
2	0	521	481
3	0	459	382
6	0	531	537
3	1	522	446
4	1	509	522
5	1	340	393
6	1	347	353
2	2	457	512
3	2	400	437
5	2	459	463
6	2	393	441
3	3	562	531
4	3	327	342
5	3	309	269
1	4	641	680
4	4	293	326
5	4	302	334
1	5	419	461
2	5	424	478
3	5	390	406
4	5	302	277
2	6	430	496
****L = 38******			
1	0	350	324
3	0	712	664
5	0	446	429
6	0	335	342
1	1	486	537
2	1	494	510
4	1	343	401
5	1	526	526
6	1	466	487
1	2	301	318
2	2	448	470
3	2	606	620
4	2	411	360
4	3	514	501
5	3	513	499
2	4	411	474
3	4	530	573
1	5	369	332
3	5	283	354
1	6	403	503
****L = 39******			
1	0	568	540
2	0	465	435
4	0	549	501
1	1	536	575
2	1	436	443
3	1	638	612
1	2	314	336
2	2	276	234
3	2	487	549
4	2	596	607
5	2	420	421
1	3	490	496
2	3	563	603
2	4	410	413
3	4	269	315
1	5	510	525
2	5	380	443
****L = 40******			
0	0	986	1066
2	0	616	622
4	0	623	624
2	1	750	794
3	1	628	634
4	1	402	433
1	2	750	813
1	3	521	549
2	3	364	340
3	3	598	645
****L = 41******			
1	0	801	793
2	0	683	661
1	1	409	439
2	1	423	435
3	1	525	541
1	2	294	364
2	2	502	525
3	2	381	413
1	3	579	595
2	3	522	559
****L = 42******			
1	0	594	604
1	2	284	333
1	1	727	765
2	1	327	301

enantiomer B, the lighter atoms are shifted in the opposite direction, so that bond lengths of (expected) chemically equivalent pairs are, in general, more nearly equal. It would appear that a greater $\Delta f''$ for Re (Cromer's value = 5.37) would bring the bond lengths nearer to equality. It is estimated that a $\Delta f''$ in the range 7–8 electrons would reduce the discrepancies, assuming inherent mirror symmetry for the molecule, to within acceptable limits. Certainly one must exercise caution in making statements of this sort; Figure 1 shows that the chemically equivalent "halves" of the molecule are not without significant structural distortions. This will be discussed further below; however, it seems possible at this point that the

Table III

Final Atomic Coordinates[a] for $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$

Atom	x	y	z	B,[b] Å²
Re(1)	0.14245 (7)	0.31929 (7)	0.0[c]	
Re(2)	0.16479 (7)	0.37300 (7)	−0.07005 (3)	
Cl(1)	0.02508 (44)	0.13706 (37)	−0.00442 (16)	
Cl(2)	0.05397 (43)	0.20920 (42)	−0.09641 (14)	
Cl(3)	0.24923 (45)	0.24541 (53)	0.05404 (14)	
Cl(4)	0.30421 (44)	0.38031 (53)	−0.12291 (14)	
Cl(B)	0.30723 (39)	0.23102 (44)	−0.03933 (14)	
P(1)	−0.01730 (40)	0.40266 (40)	0.04460 (12)	
P(2)	0.04027 (41)	0.53269 (42)	−0.10641 (12)	
C(11)	−0.0025 (18)	0.3401 (17)	0.0936 (6)	3.32 (33)
C(21)	−0.0283 (21)	0.2185 (21)	0.0990 (7)	4.52 (42)
C(31)	−0.0128 (25)	0.1606 (25)	0.1358 (8)	5.97 (56)
C(41)	0.0264 (30)	0.2437 (32)	0.1646 (10)	7.60 (73)
C(51)	0.0528 (27)	0.3592 (28)	0.1595 (9)	6.75 (63)
C(61)	0.0408 (20)	0.4214 (21)	0.1228 (6)	4.51 (42)
C(12)	0.0356 (17)	0.5256 (17)	−0.1584 (5)	3.26 (32)
C(22)	0.0047 (19)	0.6340 (19)	−0.1787 (6)	4.08 (39)
C(32)	−0.0067 (25)	0.6206 (25)	−0.2206 (8)	5.81 (55)
C(42)	0.0082 (25)	0.5065 (25)	−0.2370 (7)	5.66 (53)
C(52)	0.0389 (26)	0.3967 (26)	−0.2176 (8)	5.95 (58)
C(62)	0.0486 (21)	0.4063 (20)	−0.1778 (7)	4.44 (42)
C(13)	−0.0111 (17)	0.5711 (17)	0.0465 (5)	3.27 (32)
C(23)	−0.1122 (21)	0.6419 (20)	0.0317 (6)	4.45 (42)
C(33)	−0.1072 (26)	0.7761 (26)	0.0327 (8)	6.13 (58)
C(43)	−0.0009 (26)	0.8348 (26)	0.0482 (9)	6.20 (58)
C(53)	0.1006 (26)	0.7608 (26)	0.0645 (8)	6.22 (57)
C(63)	0.0955 (21)	0.6306 (21)	0.0610 (7)	4.65 (43)
C(14)	0.1110 (17)	0.6793 (17)	−0.0956 (6)	3.30 (34)
C(24)	0.2007 (21)	0.7307 (21)	−0.1205 (7)	4.67 (43)
C(34)	0.2675 (25)	0.8424 (25)	−0.1105 (8)	5.93 (55)
C(44)	0.2302 (28)	0.9049 (27)	−0.0759 (9)	7.03 (65)
C(54)	0.1425 (28)	0.8561 (29)	−0.0511 (9)	6.95 (67)
C(64)	0.0828 (19)	0.7425 (20)	−0.0612 (6)	4.28 (41)
C(15)	−0.1777 (17)	0.3646 (17)	0.0347 (5)	3.07 (32)
C(25)	−0.2202 (16)	0.3359 (15)	−0.0032 (5)	3.06 (30)
C(35)	−0.3441 (18)	0.3112 (19)	−0.0088 (6)	3.85 (38)
C(45)	−0.4315 (19)	0.3161 (18)	0.0211 (6)	3.90 (37)
C(55)	−0.3899 (20)	0.3424 (20)	0.0563 (6)	4.35 (40)
C(65)	−0.2661 (19)	0.3681 (19)	0.0642 (6)	3.96 (38)
C(16)	−0.1300 (18)	0.5383 (19)	−0.0968 (6)	3.77 (36)
C(26)	−0.1962 (20)	0.4278 (20)	−0.1025 (6)	4.25 (40)
C(36)	−0.3337 (21)	0.4337 (22)	−0.1007 (7)	4.70 (43)
C(46)	−0.3869 (23)	0.5432 (23)	−0.0907 (7)	5.27 (49)
C(56)	−0.3199 (25)	0.6477 (25)	−0.0833 (8)	5.87 (54)
C(66)	−0.1882 (20)	0.6528 (20)	−0.0871 (6)	4.29 (41)
C(1)	0.3044 (18)	0.5400 (18)	−0.0159 (6)	3.59 (36)
C(2)	0.3836 (20)	0.6578 (20)	−0.0069 (7)	4.77 (44)
C(3)	0.4746 (23)	0.6333 (23)	0.0237 (7)	5.53 (51)
O(1)	0.2580 (11)	0.4746 (11)	0.0104 (3)	3.06 (22)
O(2)	0.2811 (11)	0.5187 (11)	−0.0514 (4)	3.17 (22)
O(B)	0.0473 (10)	0.4238 (11)	−0.0329 (3)	2.52 (20)

[a] Estimated standard deviations (in parentheses) in this and following tables occur in the last significant digit in each case.
[b] Thermal parameters for Re, Cl, and P are given in Table IV.
[c] Parameter fixed in polar space group.

apparent nonequivalence of the bonds is not completely due to packing considerations.

There appears to be some uncertainty as to whether the value of $\Delta f''$ depends upon the number of anomalous scatterers in the unit cell; however, current thought indicates that this is not an important factor.[44-46] The need for more accurate values of $\Delta f''$ and its angular dependence and/or experimental verification of current literature values is apparent. Ueki, Zalkin, and Templeton[41] compared their X-ray determination of thorium nitrate pentahydrate with the results of a neutron diffraction study of the same compound[47] and estimated that $\Delta f''$ should be greater than theoretical values[35,48] by 1.0–1.6 electrons. On the other hand, there has been experimental confirmation of the $\Delta f''$ values of both light and heavy atoms.[49]

Description of the Structure.—The crystal structure, which consists of normally packed, discrete dinuclear molecules, is defined by the unit cell dimensions, the space group symmetry operations, and the positional parameters given in Table II. Figure 1 shows the over-all molecular structure and numbering scheme; in Figure 2 only the inner coordination about the rhenium atoms is shown. The shorter intermolecular contacts appear to be normal and are not listed; there are no rhenium atom intermolecular contacts at distances of less than 4.5 Å. As in the structure of $ReNCl_2(P(C_6H_5)_3)_2$,[50] the crystal packing is mainly dependent upon the intermolecular interactions of the phenyl rings. Principal intramolecular distances and angles, as derived from the data of Table II, are given in Table VI.[51] The effects of different packing environments for the chemically related "halves" of the molecule are seen in the marked discrepancies between related pairs of Cl–Re–P, Re–P–C, C–P–C, and P–C–C_{para} angles.

The molecular structure as a whole possesses neither crystallographic nor virtual symmetry higher than C_1. However, the inner coordination sphere (Figure 2) has effective mirror symmetry if one ignores atom C(3) of the propionato group and keeps in mind the previous discussion of anomalous scattering. The dinuclear molecular unit consists of coordination octahedra which share an edge. In effect, the short Re–Re bond is triply bridged by a chlorine atom, an oxygen atom, and a propionato group. For the sake of simplicity, the weighted averages of (presumably) chemically equivalent bond lengths will be used in the following discussion of bond lengths. The major structural features may now be discussed.

The Re–Re distance, 2.522 Å, definitely indicates direct metal-to-metal bonding. It is close to the distances 2.43–2.51 Å found in trinuclear halorhenium(III) structures,[10,13,17,18,20] in which the rhenium–rhenium bond order is generally agreed[52,53] to be 2, regardless of whether an MO or a VB analysis of the bonding is used. It is to be noted that this bond length is unaffected by the $\Delta f''$ corrections since both rhenium atoms experience the same phase shift due to anomalous scattering.

Thus, one of the principal questions prompting this

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(44) R. Parthasarathy, *Acta Cryst.*, **15**, 41 (1962).

(45) J. M. Bijvoet, *ibid.*, **15**, 620 (1962).

(46) S. R. Hall and E. N. Maslen, *ibid.*, **20**, 383 (1966).

(47) J. C. Taylor, M. H. Mueller, and R. L. Hitterman, *ibid.*, **20**, 842 (1966).

(48) C. H. Dauben and D. H. Templeton, *ibid.*, **8**, 841 (1955).

(49) See ref 44–46 and references therein.

(50) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(51) Distances and angles were calculated using updated versions of the programs MGEOM by J. S. Wood and DISTAN by D. P. Shoemaker.

(52) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

(53) J. E. Fergusson, B. R. Penfold, M. Elder, and B. H. Robinson, *J. Chem. Soc.*, 5500 (1965).

TABLE IV

ANISOTROPIC TEMPERATURE FACTORS (× 10^5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Equiv isotropic B
Re(1)	540 (7)	554 (7)	52 (1)	80 (5)	−3 (2)	−4 (2)	2.50
Re(2)	511 (6)	598 (7)	50 (1)	−34 (6)	4 (2)	−19 (2)	2.50
Cl(1)	1020 (45)	479 (33)	96 (5)	−68 (32)	43 (13)	8 (11)	3.84
Cl(2)	810 (42)	692 (40)	74 (4)	−169 (33)	−19 (10)	−34 (10)	3.48
Cl(3)	797 (45)	1283 (58)	68 (4)	333 (41)	0 (11)	88 (12)	4.26
Cl(4)	757 (44)	1318 (60)	67 (4)	−73 (40)	64 (10)	−34 (12)	4.24
Cl(B)	637 (37)	794 (45)	72 (4)	151 (34)	−16 (10)	−27 (10)	3.34
P(1)	602 (38)	646 (39)	36 (3)	94 (31)	−12 (8)	−9 (9)	2.48
P(2)	658 (41)	677 (41)	48 (4)	−71 (32)	9 (9)	19 (10)	2.80

TABLE V

VARIATIONS IN PRINCIPAL BOND LENGTHS

	Space group $P4_1$ enantiomer A	Space group $P4_3$ enantiomer B	Wtd av[a]
Re(1)–Cl(1)	2.320	2.318	2.312 (3)
Re(2)–Cl(2)	2.312	2.302	
Re(1)–Cl(3)	2.321	2.340	2.356 (4)
Re(2)–Cl(4)	2.389	2.371	
Re(1)–Cl(B)	2.437	2.421	2.411 (3)
Re(2)–Cl(B)	2.388	2.399	
Re(1)–P(1)	2.451	2.474	2.490 (3)
Re(2)–P(2)	2.523	2.506	
Re(1)–O(B)	1.948	1.896	1.889 (8)
Re(2)–O(B)	1.827	1.882	
Re(1)–O(1)	2.075	2.097	2.095 (8)
Re(2)–O(2)	2.066	2.092	

[a] Weighted averages used in this table, Table VII, and the text were computed according to "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958, p S1.

TABLE VI

PRINCIPAL MOLECULAR DIMENSIONS

Bond distances, Å		Intramolecular nonbonded contacts, Å	
Re(1)–Re(2)	2.522 (1)	Re(1)–C(1)	2.973
Re(1)–Cl(1)	2.318 (4)	Re(2)–C(1)	2.994
Re(2)–Cl(2)	2.302 (5)	Re(1)–O(2)	3.151
Re(1)–Cl(3)	2.340 (5)	Re(2)–O(1)	3.169
Re(2)–Cl(4)	2.371 (5)	Re(1)–Cl(2)	3.687
Re(1)–Cl(B)	2.421 (4)	Re(2)–Cl(1)	3.715
Re(2)–Cl(B)	2.399 (4)	Cl(1)–Cl(3)	3.349
Re(1)–P(1)	2.474 (4)	Cl(2)–Cl(4)	3.364
Re(2)–P(2)	2.506 (4)	Cl(1)–P(1)	3.341
Re(1)–O(B)	1.896 (11)	Cl(3)–P(1)	3.318
Re(2)–O(B)	1.882 (11)	Cl(2)–P(2)	3.472
Re(1)–O(1)	2.097 (11)	Cl(4)–P(2)	3.302
Re(2)–O(2)	2.092 (12)	Cl(1)–Cl(2)	3.316
P(1)–C(11)	1.84 (2)	Cl(1)–Cl(B)	3.399
P(1)–C(13)	1.80 (2)	Cl(2)–Cl(B)	3.365
P(1)–C(15)	1.79 (2)	Cl(1)–O(B)	3.226
P(2)–C(12)	1.82 (2)	Cl(2)–O(B)	3.186
P(2)–C(14)	1.78 (2)		
P(2)–C(16)	1.85 (2)		
C(1)–O(1)	1.25 (2)		
C(2)–O(2)	1.28 (2)		
C(1)–C(2)	1.55 (3)		
C(2)–C(3)	1.47 (3)		

Interbond angles, deg			
Cl(1)–Re(1)–P(1)	88.4 (2)	Re(1)–P(1)–C(11)	113.3 (6)
Cl(2)–Re(2)–P(2)	92.4 (2)	Re(1)–P(1)–C(13)	110.9 (6)
Cl(1)–Re(1)–Cl(3)	92.0 (2)	Re(1)–P(1)–C(15)	117.0 (6)
Cl(2)–Re(2)–Cl(4)	92.1 (2)	Re(2)–P(2)–C(12)	119.5 (6)
Cl(3)–Re(1)–P(1)	87.1 (2)	Re(2)–P(2)–C(14)	105.4 (6)
Cl(4)–Re(2)–P(2)	85.2 (2)	Re(2)–P(2)–C(16)	116.8 (7)
P(1)–Re(1)–O(1)	90.7 (3)	C(11)–P(1)–C(13)	108.9 (8)
P(2)–Re(2)–O(2)	88.1 (3)	C(31)–P(1)–C(51)	105.6 (9)
Cl(3)–Re(1)–Cl(B)	88.4 (2)	C(51)–P(1)–C(11)	100.3 (8)
Cl(4)–Re(2)–Cl(B)	88.3 (2)	C(12)–P(2)–C(14)	105.9 (9)
Re(2)–Re(1)–Cl(1)	100.2 (1)	C(14)–P(2)–C(16)	110.5 (9)
Re(1)–Re(2)–Cl(2)	99.6 (1)	C(16)–P(2)–C(12)	98.9 (9)
Cl(B)–Re(2)–O(2)	87.4 (4)	C(1)–C(2)–C(3)	111 (2)
Cl(B)–Re(1)–O(1)	88.8 (3)	P(1)–C(11)–C(41)	178 (1)
Cl(1)–Re(1)–Cl(B)	91.6 (2)	P(1)–C(13)–C(43)	179 (1)
Cl(2)–Re(2)–Cl(B)	91.4 (2)	P(1)–C(15)–C(45)	177 (1)
Re(2)–Re(1)–O(1)	86.1 (3)	P(2)–C(12)–C(42)	175 (1)
Re(1)–Re(2)–O(2)	85.6 (3)	P(2)–C(14)–C(44)	177 (1)
Re(1)–O(B)–Re(2)	83.8 (5)	P(2)–C(16)–C(46)	174 (1)
Re(1)–Cl(B)–Re(2)	63.1 (1)		

study, that is, whether Re–Re bonding would occur in this Re(IV) compound, is clearly answered. Such a bond does occur and has a strength comparable to that of a double bond according to the criterion of distance. However, this remark is not to be taken literally, nor should the metal–metal interaction be oversimplified in any other way. Each Re(IV) species individually has three 5d electrons left after metal–ligand bonding. Since the dinuclear molecule is reported to be diamagnetic,[29] a complete description of the metal–metal interaction must account for the pairing up of six electron spins. Besides direct metal–metal bonding, indirect (*i.e.*, superexchange) coupling of spins, intraatomic coupling of spins, and direct but weak (as in Cu(II) and Cr(II) carboxylate dimers) interatomic coupling of spins are all possible contributors to an over-all description of the metal–metal interaction. It must also be borne in mind that the presence of bridging atoms here undoubtedly imposes constraints on the metal–metal distance so that a bond order–bond length relationship of the type which is valid for species with little or no bridging[54] cannot be applied uncritically in the present case.

With regard to the bridging ligands, it is notable that in this one molecule there is found each one of the types which occur separately in other polynuclear rhenium species, *viz*, halogen, oxygen, and carboxyl. The single bridging atoms Cl(B) and O(B) lie in environments similar to those observed in other rhenium cluster compounds. Thus, the Re–Cl(B) distance, 2.411 Å, and Re(1)–Cl(B)–Re(2) angle, 63.1°, are quite similar to the corresponding distances and angles in Re_3Cl_9,[13] for example, which are 2.46 (4) Å and

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(54) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

TABLE VII

C–C BOND DISTANCES (Å) IN THE TRIPHENYLPHOSPHINE GROUPS[a]

C(11)–C(21)	1.34 (3)	C(14)–C(24)	1.40 (3)
C(21)–C(31)	1.43 (3)	C(24)–C(34)	1.43 (3)
C(31)–C(41)	1.40 (4)	C(34)–C(44)	1.44 (3)
C(41)–C(51)	1.28 (5)	C(44)–C(54)	1.38 (4)
C(51)–C(61)	1.45 (3)	C(54)–C(64)	1.41 (4)
C(61)–C(11)	1.41 (3)	C(64)–C(14)	1.41 (2)
C(12)–C(22)	1.40 (3)	C(15)–C(25)	1.43 (2)
C(22)–C(32)	1.47 (3)	C(25)–C(35)	1.36 (3)
C(32)–C(42)	1.36 (4)	C(35)–C(45)	1.40 (2)
C(42)–C(52)	1.39 (4)	C(45)–C(55)	1.33 (2)
C(52)–C(62)	1.40 (3)	C(55)–C(65)	1.38 (3)
C(62)–C(12)	1.45 (3)	C(65)–C(15)	1.40 (2)
C(13)–C(23)	1.41 (3)	C(16)–C(26)	1.39 (3)
C(23)–C(33)	1.43 (4)	C(26)–C(36)	1.47 (3)
C(33)–C(43)	1.40 (4)	C(36)–C(46)	1.35 (3)
C(43)–C(53)	1.46 (4)	C(46)–C(56)	1.35 (4)
C(53)–C(63)	1.40 (4)	C(56)–C(66)	1.41 (3)
C(63)–C(13)	1.40 (3)	C(66)–C(16)	1.41 (3)

[a] See footnote *a* in Table V; weighted average = 1.403 (5) Å.

TABLE VIII

BEST WEIGHTED LEAST-SQUARES PLANES[a]

Atoms	Plane	Eq
Re(1)–Re(2)–O(1)–O(2)–C(1)–C(2)	1	$-0.8030x + 0.5929y + 0.0604z = 0.8000$
Re(1)–Re(2)–O(B)–Cl(B)	2	$0.5949x + 0.7675y + 0.2388z = 3.5165$

Distances of Atoms from Planes (Å)

Atoms	Plane 1	Atoms	Plane 2
Re(1)	−0.001	Re(1)	0.002
Re(2)	0.000	Re(2)	0.000
O(1)	0.014	O(B)	−0.021
O(2)	−0.035	Cl(B)	−0.002
C(1)	−0.025		
C(2)	0.061		

[a] Calculated using the method outlined in "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1962, p 93.

61 (2)°. Similarly, the Re–O(B) distance, 1.889 Å, is comparable to the Re–O distance of 1.95 (4) Å, observed in $La_4Re_6O_{19}$.[25] In $K_4Re_2OCl_{10}$,[55] where the Re–O–Re linkage is linear, the distance is 1.86 (1) Å, and it has been suggested that there is considerable double-bond character.[56]

The carboxylate bridge system differs slightly in some of its dimensions from that found in $Re_2(O_2CC_6H_5)_4Cl_2$.[9] In that compound the Re–O distances are 2.018 (5) Å while here they are 2.095 Å. Also, the Re–Re–O angles are slightly acute (86°). Since the Re–Re distance here (2.522 Å) is appreciably greater than that in $Re_2(O_2CC_6H_5)_4Cl_2$ (2.235 Å), the acute angles and at least part of the apparent weakening of the Re–O bonds are obviously attributable to the fact that the Re–Re distance somewhat exceeds the optimum "bite" of the carboxyl group. The C–O and C–C distances in the propionato group are normal.

Calculations of the weighted least-squares best planes (Table VIII) show that the two sets of atoms, *viz.*, O(1), O(2), Re(1), Re(2), C(1), C(2) and O(B), Cl(B), Re(1), Re(2), involved in the bridging, each form planar groups with no appreciable deviations. The angle between these planes is 94.7°.

The mean Re–P bond length, 2.490 Å, lies within the range of rhenium–phosphorus bonds in accurately determined structures such as $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$ (2.490 (5), 2.442 (4), 2.469 (5) Å),[57] $ReNCl_2(P(C_6H_5)_3)_2$ (2.448 (2) Å),[50] and $Re_2Cl_6(P(C_2H_5)_3)_2$ (2.45 (1) Å).[8] Within the $(C_6H_5)_3P$ ligands the mean bond distances (P–C, 1.813 (8) Å, and C–C, 1.403 (5) Å) agree well with those in $P(C_6H_5)_3$ itself.[58] There are significant distortions in the C–P–C and P–C–C_{para} angles, however, presumably because of packing forces.

The mean Re–Cl distances are very similar to those in other rhenium compounds.[8,55] The longer bond distance, 2.355 Å, occurs for the Re–Cl bond *trans* to the strong Re–O(B) bond, while the shorter distance, 2.310 Å, occurs for the Re–Cl bond *trans* to a carboxylate oxygen atom.

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