Summary

The vibrational spectra of hexachlorodisiloxane have been described in terms of D_{3h} symmetry. Since the experimental data do not discriminate between D_{3h} and D_{3d} symmetry, differences that would arise if the description were according to D_{3d} symmetry have been explicitly indicated. The data have been interpreted to indicate that the molecular skeleton is quasilinear and that the symmetric $SiCl_3$ stretching modes are coupled with the Si–O–Si stretching motion.

Acknowledgments.—The authors gratefully acknowledge the financial support given this research by the United States Air Force Systems Engineering Group under Contract No. F 33615-67-c-1381. Also appreciation to the National Science Foundation, which provided funds (Grant GP-7079) for the purchase of the He–Ne laser accessory for the Raman spectrophotometer, is expressed.

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The Structure of μ-Oxo-μ-chloro-di-μ-propionato-bis(chlorotriphenylphosphinerhenium). A New Metal–Metal Bond[1a]

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Received September 24, 1968

The crystal and molecular structures of one of the substances reported by Rouschias and Wilkinson to have the general formula $Re_2Cl_3(O_2CR)_2[P(C_6H_5)_3]_2$, namely, the one with R = C_2H_5, have been determined in an X-ray crystallographic study. It was found that the formula as previously given is incorrect, lacking one oxygen atom. The $Re_2OCl_3(O_2CC_2H_5)_2[P(C_6H_5)_3]_2$ molecule consists of two structurally equivalent Re atoms each surrounded by six ligand atoms at the vertices of a slightly distorted octahedron. The octahedra are joined on a common edge formed by bridging O and Cl atoms. The other two Cl atoms occupy positions *trans* to the bridging O atom, and the P atoms occupy positions *trans* to the bridging Cl atom. The pairs of vertices above and below the plane defined by these six ligand atoms and the two Re atoms are occupied by bridging bidentate C_2H_5COO groups. The symmetry of the two Re atoms and the ten atoms coordinated to them is C_{2v} neglecting small packing distortions. The Re–Re distance is 2.514 (1) Å. The entire structure is nearly identical with that of $Re_2OCl_5(O_2CC_2H_5)[P(C_6H_5)_3]_2$ except for the replacement of two Cl atoms by a propionato group. The crystals studied belong to space group $P2_1/c$ with dimensions $a = 14.059 \pm 0.003$ Å, $b = 17.477 \pm 0.003$ Å, $c = 17.556 \pm 0.003$ Å, and $\beta = 97.80 \pm 0.01°$. The observed and calculated densities were 1.81 ± 0.01 and 1.82 g cm^{-3} (for $Z = 4$), respectively. The structure was solved and refined using 2125 statistically significant independent reflections. Refinement was by a full-matrix, least-squares program in which the phenyl groups were treated as rigid bodies with separate isotropic temperature parameters for each carbon atom; anisotropic temperature parameters were used for Re, Cl, and P atoms. Final weighted and unweighted discrepancy indexes were 0.034 and 0.031, respectively. Mean values of bond lengths to rhenium atoms are (Å): Re–Cl(terminal), 2.360 (3); Re–Cl(bridge), 2.403 (3); Re–P, 2.455 (3); Re–O(carboxyl), 2.108 (5); Re–O(bridge), 1.916 (6).

Introduction

Dinuclear and trinuclear complexes of rhenium in oxidation state III have been well characterized.[2] Further, compounds containing rhenium in mean oxidation states between II and III appear to involve strong metal–metal interactions (Re–Re $\approx$ 2.29 Å).[3,4] Compounds containing rhenium in oxidation states near IV fall into two groups: (1) $La_4Re_6O_{19}$ (mean oxidation state $+4^1/_3$, Re–Re = 2.42 Å)[5] and $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$ (Re–Re = 2.52 Å);[2,6] and (2) $ReCl_4$ (Re–Re = 2.73 Å)[7] and $Re_2Cl_9^-$ (Re–Re = 2.71 Å).[8] In $Re^V{}_2Cl_{10}$, a dinuclear species, the metal–metal distance is quite long (3.74 Å),[9] consistent with the suggestion[2] that the border line, in terms of oxidation state, between pronounced and negligible tendency to metal–metal bond formation occurs around oxidation number IV for rhenium.

As part of our continuing study of polynuclear

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(1) (a) Supported in part by the U. S. Atomic Energy Commission; (b) Massachusetts Institute of Technology; (c) Oregon Graduate Center; (d) NIH Predoctoral Fellow, 1965–1966.

(2) F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, **7,** 1784 (1968). The opening paragraph of this paper is remiss in omitting to mention the very recent papers by G. Rouchias and G. Wilkinson, *J. Chem. Soc.*, 993 (1967); 489 (1968), in which a number of new mononuclear Re(III) complexes are reported.

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

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

(5) 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.

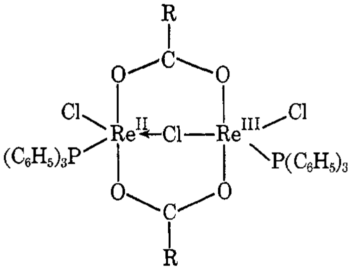
(6) G. Rouschias and G. Wilkinson, *J. Chem. Soc.*, *A*, 465 (1966).

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

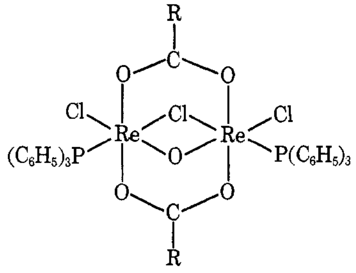
(8) F. A. Cotton and P. F. Stokely, unpublished observations.

(9) K. Mucker, G. S. Smith, and Q. Johnson, *Acta Cryst.*, **B24,** 874 (1968).

rhenium complexes in various oxidation states, it was considered of interest to investigate the structure of compounds of the type $Re_2Cl_3(RCO_2)_2[P(C_6H_5)_3]_2$, reported recently by Rouschias and Wilkinson.[6] In order to reduce the number of crystallographically distinct atoms to be located, we first attempted the preparation of phenyldiethylphosphine analogs of Wilkinson and Rouchias' compounds; however, none of these was crystallographically suitable, and the structural study was therefore carried out on the triphenylphosphine compounds. Rouschias and Wilkinson postulated structures which they wrote as I for these compounds, which have rhenium in the formal mean oxidation state 2.5. The structure determination which forms the subject of this paper has led us to reformulate the compounds as $Re_2OCl_3(RCO_2)_2[P(C_6H_5)_3]_2$ having structures of type II (which is rather similar to the structure of $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$)[2] and formal mean oxidation states for rhenium of 3.5.



I



II

Experimental Section

$Re_2OCl_3(C_2H_5CO_2)_2[PC_6H_5(C_2H_5)_2]_2$.—The preparation of several phenyldiethylphosphine analogs of the Rouschias and Wilkinson triphenylphosphine complexes was attempted. The experimental procedure was essentially that of Rouschias and Wilkinson, except that *trans*-$ReOCl_3[PC_6H_5(C_2H_5)_2]_2$[10] was used instead of the triphenylphosphine complex. The results of many experiments led to the conclusion that *trans*-$ReOCl_3[PC_6H_5(C_2H_5)_2]_2$ reacts with various carboxylic acids, either in presence of air or in an atmosphere of nitrogen, to form mixtures of $Re_2OCl_3(RCO_2)_2[PC_6H_5(C_2H_5)_2]_2$ and $ReCl_4[PC_6H_5(C_2H_5)_2]_2$. No compound analogous to the $Re_2OCl_5(RCO_2)[P(C_6H_5)_3]_2$ was observed.

A crystallographically suitable sample of $Re_2OCl_3(C_2H_5CO_2)_2[PC_6H_5(C_2H_5)_2]_2$ was obtained by recrystallization of the crude product from warm *n*-butyl chloride and data collection was begun on a manual General Electric XRD-5 diffractometer. The crystals were mounted in sealed capillaries because of their marked instability; nonetheless, decomposition was quite rapid, and it was estimated that at least eight crystals would be needed for the complete data collection if each crystal were rejected when the intensities of the standard reflections dropped to 85% of their initial values. At this point (after collection of ~700 data) it was decided that data collection with the more stable triphenylphosphine derivative would be preferable. Crystal and analytical data for the phenyldiethylphosphine derivative are given here. Crystal data: monoclinic, space group $P2_1$ or $P2_1/m$; $a = 9.845$, $b = 14.661$, $c = 11.597$ Å; $\beta = 97.98°$ (22°). *Anal.* Calcd for $C_{26}H_{40}O_5P_2Cl_3Re_2$: C, 32.08; H, 4.14; Cl, 10.93. Found: C, 30.8; H, 4.40; Cl, 10.9.

$Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$.—The compound was prepared under the conditions outlined in Rouschias and Wilkinson's preparation of "$Re_2Cl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$." The data collection was carried out on a very small acicular crystal, approximately 0.01 cm long and 0.003 cm in maximum width, with a roughly hexagonal cross section. Precession photographs (levels $h0l$ through $h2l$ and $h,k,2h$) showed the crystal to be monoclinic and mounted along the $10\bar{2}$ reciprocal axis. The systematic absences, $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, uniquely determined the space group[11] to be $P2_1/c$ (C_{2h}^5, no. 14). Predominant faces included {100}, {010}, {111}, $\{1\bar{1}1\}$, and two others which were not identified.

The crystal was moved to a computer-controlled[12] Picker four-circle diffractometer where attempts to align the crystal along the needle axis indicated it to be very nearly coincident with the $20\bar{3}$ reciprocal axis. Unit cell parameters at 21°, derived from least-squares refinement of the observed values for 2θ, ω, and χ for 12 centered reflections, measured at a takeoff angle of 1°, were found to be $a = 14.059 \pm 0.003$, $b = 17.477 \pm 0.003$, $c = 17.556 \pm 0.003$ Å; $\cos \beta = -0.1529 \pm 0.002$ (λ(Cu $K\beta_1$) 1.39217 Å). The observed density, 1.813 ± 0.010 g cm^{-3}, measured by flotation in aqueous zinc bromide at 25°, agrees well with the calculated value of 1.816 g cm^{-3} for $Z = 4$, $V = 4262.9$ Å^3, and $M = 1165.5$. For $Z = 4$ in space group $P2_1/c$ no symmetry constraints are placed on the molecule.

Collection of intensity data was planned to include a complete sphere of intensity data having θ(Cu $K\alpha$) $\leq 47.5°$. Data were collected in consecutive quadrants so that an interruption after one or more quadrants would not necessarily require starting again. Nickel-filtered Cu $K\alpha$ radiation was used, with a takeoff angle of 4° and the pulse-height discriminator set to accept 95% of the Cu $K\alpha$ radiation, when centered on the $K\alpha$ peak. The moving-crystal, moving-counter technique was used, with a 2θ scan rate of 1°/min and scan range of ($1.50° + \triangle$), where $\triangle$ is the 2θ separation of the Cu $K\alpha_1$ and Cu $K\alpha_2$ peaks at the 2θ value for the reflection concerned; this conformed well with the mosaic spread of the crystal. The crystal–source and crystal–detector distances were each approximately 24 cm; 1.5-mm diameter incident and exit beam collimators were used without further restriction on the aperture. There was no evidence for overlapping peaks. Background counts of 10 sec each were measured at the extremes of each 2θ scan. The observed intensities, $A[P - (t/20)B]$, where A is the correction factor for the attenuators inserted for those reflections having counting rates which would otherwise exceed the linear counting range of the detector, P is the number of counts during the scan, B is the sum of the background counts, and t is the counting time for the scan in seconds.

Three standard reflections were measured every 50 reflections. During collection of the first two quadrants of intensity data (forms hkl, $hk\bar{l}$ and the center-of-symmetry-related $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}l$) a slow but significant decrease in the intensities of these standards was observed. The decrease appeared to be 2θ dependent (12,0,4, $2\theta = 91.37°$, showed a maximum decrease of 10%; $\bar{1}92$, $2\theta = 48.30°$, a maximum of 4%; and 100, $2\theta = 6.36$, a maximum of 2%) which was not corrected by realignment of the

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[10] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

[11] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962.

[12] The Busing and Levy programs for four-circle diffractometers (*Acta Cryst.*, **22,** 457 (1967)), programmed for the PDP8/s computer by Howard Coliadas, were used for all phases of diffractometer control and data collection.

crystal. Consequently, data collection was not continued beyond this point and the data were subsequently processed without correction for this effect.

A total of 8428 reflections had been measured, of which 4233 were accepted as significant according to the criteria: (a) $I > 0$ and (b) $I \geq 3\sigma(I)$ (all reflections required to be absent by the symmetry elements of the space group had been measured and none were accepted under these criteria, confirming choice of space group). The observed intensities were corrected for Lorentz and polarization effects and the values for equivalent pairs of reflections were averaged, giving a total of 2125 observed independent reflections. Absorption corrections ($\mu = 133.7$ cm^{-1}) were then applied; calculated transmission factors ranged from 0.200 to 0.353.

Solution and Refinement of the Structure

The appearance of only one peak on the Harker line $(0, v, ^1/_2)$ indicated that both rhenium atoms had approximately the same y coordinate. A solution was readily obtained, with Re(1) at $x = 0.11$, $y = 0.08$, $z = 0.20$ and Re(2) at $x = 0.28$, $y = 0.08$, $z = 0.17$. A structure factor calculation at this point, with phases based on the two rhenium atoms, gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.316$, where F_o is the observed and F_c the calculated structure factor. The weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, using a weighting scheme similar to that of Doedens and Ibers,[13] was 0.382.

One cycle of full-matrix, least-squares refinement in which scale factors and isotropic thermal parameters were varied for the two rhenium atoms led to $R_1 = 0.275$ and $R_2 = 0.355$. A difference Fourier map at this stage revealed the positions of three chlorine, two phosphorus, four oxygen, and eighteen phenyl carbon atoms. It was noted that the oxygen atoms were part of two *trans*-carboxylato groups bridging the Re–Re bond and also that one of the chlorine atoms bridged the metal–metal bond. In fact, at this stage the geometry was not unlike that in $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$. A peak of the same electron density as the carboxylate oxygen atoms and in an acceptable position for a bridging oxygen atom also appeared on this map. A reformulation of the compound now appeared necessary, but it was temporarily delayed until a further electron density difference map, at a lower R value, could be obtained. Two additional cycles of full-matrix, least-squares refinement with contributions included from all atoms located above, except the "bridging oxygen" atom, gave $R_1 = 0.130$ and $R_2 = 0.189$. A difference Fourier map at this point revealed the positions of the remaining eighteen phenyl carbon atoms and the six propionato carbon atoms. The bridging oxygen atom was the most prominent feature on the map. There also appeared to be indications of disorder of the β-carbon atoms; however, further least-squares refinement in which occupancy factors were varied for these atoms (in addition to the usual parameters) indicated that the disorder was slight. The secondary positions were refined to occupancy factors of <0.1, with rather high (~11 Å^2) temperature factors. Furthermore, neither the α- nor the β-carbon atoms of either propionato group had unusually high temperature factors. Therefore the disordered model was abandoned, and the β-carbon atoms at the principal positions were refined with fixed occupancy factors of 1.0.

After all nonhydrogen atoms had been located, refinement was continued using a version of Prewitt's SFLS5 full-matrix, least-squares program modified by B. M. Foxman and M. J. Bennett for least-squares refinement of phenyl rings as rigid bodies. The rigid-body program as used here was limited to planar rigid bodies, *e.g.*, the six carbon atoms of a phenyl group. The program operates as follows. Coordinates for the individual atoms are generated in the XY plane of an internal Cartesian coordinate system. Rotation of the body in the course of refinement is measured by the angles D, E, and F (in radians) about the axes X, Y, and Z, respectively, of the local coordinate system. For a regular polygon it is customary to place the origin at the center of the polygon. An isotropic temperature factor is varied for each atom.

The rigid-body parameters for three of the phenyl rings were generated from the positional coordinates of the carbon atoms obtained in the previous cycle, assuming an ideal distance of 1.397 Å from the center of gravity of the ring to each carbon atom. For the other three rings, rigid-body parameters were generated directly from the Fourier coordinates. Three cycles of refinement of scale factors, coordinates, and isotropic temperature factors for all six phenyl rigid bodies resulted in convergence of the isotropic refinement with $R_1 = 0.043$ and $R_2 = 0.049$. At this point contributions from the phenyl hydrogen atoms were included in the structure factors; the hydrogen atoms were fixed at the calculated distance (1.08 Å) from the carbon atoms and shifted after each cycle in accordance with the shifts of the carbon atoms. Each hydrogen atom was assigned an isotropic temperature factor 1.1 times that of the carbon atom to which it was attached. Two more cycles of refinement led to $R_1 = 0.040$ and $R_2 = 0.047$. Finally, anisotropic temperature factors (suggested by features on difference maps) in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were assigned to the Re, Cl, and P atoms. Two more cycles of full-matrix, least-squares refinement resulted in convergence, with $R_1 = 0.032$ and $R_2 = 0.042$. On the final cycle of least-squares refinement, no parameter change was greater than 0.2 esd. Several reflections, *viz.*, 020, 011, 111, 11$\bar{1}$, 021, 002, and 102, which showed evidence of serious extinction effects, were rejected from the final cycles of refinement but were included in the calculation of the above values of R_1 and R_2. When these reflections were also omitted from the calculation of the residuals, the values obtained were $R_1 = 0.031$ and $R_2 = 0.034$.

A final difference Fourier map contained a peak of 0.9 e$^-$/Å^3 (about one-fourth the peak density for carbon atoms on earlier Fourier maps), about 1.5 Å from C(5), and only small ($\leq$0.5 e$^-$/Å^3) seemingly random features

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(13) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). Our weighting scheme differs only in that p, "the uncertainty factor," was assigned a value of 0.045.

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10), IN ELECTRONS, FOR $Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$

H	L	FOBS	FCAL
K = 0**			
1	0	1885	1893
2	0	526	691
3	0	2659	2689
4	0	951	1045
5	0	4789	5024
6	0	2896	2528
7	0	1352	1399
8	0	1665	1613
10	0	765	693
11	0	803	810
12	0	1112	1097
13	0	1544	1573
0	2	4646	5650
1	2	4053	4489
1	-2	2404	2607
2	2	1042	998
2	-2	878	885
3	2	1659	1611
3	-2	1579	1601
4	-2	415	365
5	2	2480	2553
5	-2	2630	2651
6	2	4472	4745
6	-2	749	734
7	2	1435	1415
7	-2	2742	2798
8	2	1296	1322
9	2	856	871
10	-2	1740	1748
11	2	1885	1906
11	-2	996	1045
12	2	1014	1009
12	-2	2162	2098
13	-2	1067	1136
0	4	2120	2136
1	4	2283	2409
1	-4	2361	2573
2	4	2171	2165
2	-4	1354	1340
3	4	1655	1713
3	-4	956	993
4	4	560	582
4	-4	2622	2808
5	4	868	900
5	-4	862	856
6	4	3602	3774
6	-4	3210	3465
7	4	1981	2077
7	-4	2779	2839
8	4	636	662
8	-4	591	603
9	4	1210	1257
9	-4	2108	2142
11	4	1227	1202
11	-4	2090	2166
12	4	1933	1880
12	-4	2079	1973
0	6	2264	2282
1	-6	1648	1595
2	6	2250	2294
2	-6	1479	1514
3	-6	2942	3177
4	6	1057	1074
4	-6	2945	2904
5	6	2069	2032
5	-6	3338	3578
6	6	606	606
6	-6	3142	3287
7	6	1548	1586
7	-6	1053	1121
8	-6	1137	1208
9	6	1325	1318
9	-6	1575	1690
10	-6	1369	1370
11	-6	2356	2421
13	-6	660	708
0	8	2839	2819
1	8	1273	1232
1	-8	438	539
2	8	1692	1678
2	-8	1723	1729
3	8	2599	2559
3	-8	2851	2977
4	8	855	872
4	-8	698	710
5	8	1008	1042
5	-8	3182	3327
6	8	769	793
7	8	905	871
8	8	1785	1714
10	-8	1190	1168
11	-8	968	677
12	-8	967	906
1	10	1736	1788
2	-10	1435	1451
3	10	2144	2100
3	-10	736	753
4	10	910	908
4	-10	2537	2614
5	10	661	638
5	-10	1109	1214
6	10	636	541
6	-10	992	948
8	10	2233	2225
9	10	1043	1048
9	-10	967	967
10	-10	1790	1791
0	12	1214	1197
1	12	1293	1248
2	12	1523	1509
2	-12	635	655
3	12	1048	1050
3	-12	1036	1042
4	12	957	934
4	-12	1518	1591
6	-12	649	611
7	12	1019	1033
9	-12	1866	1858
1	-14	920	918
2	14	1709	1676
2	-14	798	713
3	14	682	659
3	-14	1554	1609
4	14	1188	1209
4	-14	1271	1257
8	-14	1770	1645
9	-14	1158	1046
2	-16	1478	1497
3	-16	1176	1214
5	-16	792	727
K = 1**			
1	0	3036	3088
2	0	776	711
3	0	1357	1332
4	0	546	559
6	0	2139	2124
7	0	1947	2006
8	0	548	454
11	0	1150	1150
12	0	788	707
0	1	1494	1290
1	1	4362	4788
1	-1	3921	4361
2	1	2953	2976
2	-1	562	584
3	-1	1576	1901
4	1	1932	1961
4	-1	1160	1118
5	1	1128	1098
6	1	2781	2805
6	-1	3373	3583
7	1	3457	3489
7	-1	1461	1484
8	-1	952	955
9	-1	609	598
11	-1	1294	1321
12	1	1580	1560
12	-1	1120	1109
13	-1	888	886
0	2	2417	2577
1	2	955	771
1	-2	1891	1741
2	2	1723	1789
3	2	1481	1429
3	-2	936	957
4	2	812	754
4	-2	1306	1297
5	2	1623	1657
5	-2	815	684
6	2	1043	962
6	-2	2491	2600
7	2	1659	1709
7	-2	499	481
8	2	669	735
8	-2	690	673
11	-2	1092	1087
12	2	1232	1213
13	-2	633	556
0	3	3446	3524
1	-3	1385	1486
2	3	2032	2077
2	-3	2278	2268
3	3	829	836
3	-3	1636	1515
4	-3	400	389
5	3	3088	3186
5	-3	1632	1603
6	-3	2106	2186
7	3	2582	2610
7	-3	1670	1623
8	3	1928	1858
9	-3	846	822
10	-3	1759	1746
11	-3	1334	1321
12	3	1615	1581
13	-3	1171	1129
0	4	2583	2512
1	4	892	878
1	-4	870	885
2	4	1514	1508
2	-4	1226	1239
3	-4	1497	1511
4	4	634	604
4	-4	660	642
5	4	1889	1922
5	-4	1638	1702
6	4	987	983
6	-4	1324	1378
7	4	1049	1103
7	-4	691	663
8	4	705	679
8	-4	622	701
10	-4	1130	1159
11	-4	819	778
13	-4	771	762
0	5	1463	1446
1	5	1484	1514
1	-5	1265	1224
2	5	1763	1760
3	5	2231	2274
3	-5	926	968
4	5	511	544
4	-5	1825	1873
5	5	1295	1309
5	-5	2772	2973
6	5	2150	2201
7	5	799	795
7	-5	1661	1776
8	5	1770	1755
8	-5	498	559
9	-5	964	1002
10	-5	2571	2552
11	5	821	801
12	-5	1489	1452
13	-5	927	920
0	6	1589	1559
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1	6	1247	1227
2	6	1448	1385
3	-6	954	900
4	-6	885	840
6	-6	1242	1172
7	6	1161	1236
7	-6	764	771
9	-6	745	739
0	7	1064	1036
1	-7	595	608
2	7	1512	1506
3	7	822	780
3	-7	1059	1010
5	-7	998	928
6	-7	1082	1006
7	7	1130	1137
8	7	884	926
0	8	944	962
1	8	671	683
1	-8	1137	1194
2	8	1047	1021
3	8	657	657
3	-8	843	810
4	8	771	850
5	-8	803	792
6	8	681	706
7	-8	935	899
8	-8	642	569
0	5	849	869
1	5	771	732
2	-5	654	658
3	5	1105	1112
4	-5	828	782
5	-5	1058	1066
1	10	804	787
2	-10	658	664
3	10	1059	1019
4	-10	984	1016
5	-10	748	719
8	-10	616	587
0	11	750	672
1	11	995	994
3	11	928	900
4	11	747	745
4	-11	1372	1407
5	-11	806	822
2	12	759	715
2	-12	855	855
4	-12	1303	1145
1	13	776	761
3	-13	1058	1060
4	-13	957	1002
K = 11**			
2	0	770	781
3	0	844	795
6	0	659	543
7	0	744	781
8	0	659	693
0	1	711	699
1	1	1154	1111
1	-1	1935	1876
2	1	835	825
3	1	1201	1232
4	1	716	684
4	-1	1885	1872
5	1	917	904
5	-1	910	949
6	1	1282	1269
6	-1	2859	2846
7	1	1324	1321
7	-1	782	713
9	1	622	598
0	2	967	970
1	-2	623	542
2	2	1017	1027
2	-2	1134	1154
3	2	994	964
4	2	916	903
6	-2	692	700
7	-2	656	668
8	2	976	922
0	3	2622	2617
1	-3	1838	1874
2	3	2102	2099
3	-3	1240	1220
4	-3	820	795
5	3	836	798
5	-3	2538	2537
6	3	790	745
6	-3	1965	1944
7	3	1459	1469
9	3	809	856
0	4	550	514
1	4	648	594
1	-4	682	697
2	-4	665	612
3	4	588	582
4	4	867	986
5	4	669	719
5	-4	857	911
9	-4	758	723
0	5	2258	2334
1	5	2265	2312
2	5	1609	1580
3	5	1285	1309
3	-5	982	977
4	5	831	756
4	-5	908	904
5	5	661	643
5	-5	2003	1909
6	5	1520	1627
7	5	606	531
7	-5	1166	1115
8	5	1328	1419
0	6	680	673
1	6	670	653
2	6	718	723
3	-6	816	793
4	6	947	976
4	-6	738	736
6	6	649	689
9	-6	638	622
1	7	2058	2076
1	-7	943	962
2	-7	697	655
3	7	1176	1141
4	-7	1112	1128
5	-7	740	680
6	7	1242	1287
6	-7	1059	1004
7	7	661	643
9	-7	1146	1154
3	-8	759	753
0	9	892	901
1	9	920	895
1	-9	686	663
2	9	1462	1482
3	-9	1358	1305
4	-9	1233	1219
6	-9	1163	1148
8	-9	862	812
1	10	662	658
3	-10	738	721
2	11	1391	1410
3	11	924	927
3	-11	1833	1874
5	-11	966	908
K = 12**			
0	0	1884	1911
1	0	658	736
2	0	974	1035
5	0	1927	1933
7	0	777	734
8	0	1217	1206
2	1	886	916
3	-1	970	952
4	1	907	960
5	-1	861	820
7	1	953	905
7	-1	675	608
9	1	790	847
0	2	1364	1382
1	2	1968	1998
2	-2	671	708
4	-2	1545	1479
5	2	699	676
5	-2	2092	2061
6	2	1302	1397
6	-2	918	890
7	2	633	544
7	-2	1378	1407
8	2	890	884
8	-2	777	786
1	-3	1024	1056
3	3	853	901
3	-3	1134	1183
8	3	821	878
1	4	2495	2538
1	-4	1091	1137
2	4	1504	1543
2	-4	705	672
3	-4	918	873
4	-4	1751	1768
6	4	1399	1462
6	-4	1932	1964
7	4	1303	1324
7	-4	712	684
9	-4	602	480
0	5	620	606
1	5	827	812
2	-5	1027	1100
3	5	785	819
4	-5	820	884
8	-5	620	672
0	6	1544	1618
1	6	959	969
2	6	2100	2185
3	6	708	737
3	-6	1070	1084
4	-6	984	1012
5	-6	840	832
6	-6	1145	1198
7	6	1671	1753
0	7	600	549
1	-7	961	1025
4	-7	757	730
0	8	1342	1297
2	8	1199	1162
3	8	1058	1133
3	-8	909	928
5	-8	1334	1319
1	-9	675	703
4	9	786	802
6	-9	637	624
0	10	768	849
1	10	873	880
2	-10	1103	1127
3	10	1204	1230
4	-10	1451	1475
5	-10	1357	1334
0	11	595	534
4	-11	643	563
K = 13**			
1	0	991	1019
3	0	630	661
6	0	1407	1428
0	1	729	716
1	1	610	557
1	-1	1054	1023
2	1	761	770
2	-1	737	725
4	1	654	653
5	-1	847	839
6	-1	1412	1469
7	1	918	900
7	-1	1127	1075
0	2	946	949
1	2	608	584
1	-2	806	843
2	2	774	693
3	2	661	688
4	-2	1168	1129
5	2	798	868
5	-2	811	784
6	-2	1242	1238
7	2	836	856
0	3	1461	1476
1	3	733	657
1	-3	1128	1158
2	3	1029	1110
2	-3	870	908
4	3	816	926
5	3	740	752
5	-3	1420	1415
6	-3	1210	1242
7	3	699	694
0	4	1724	1723
1	4	722	687
2	4	1164	1170
3	-4	1045	1014
5	4	648	635
5	-4	1403	1420
6	4	731	750
7	4	648	674
0	5	1367	1376
1	5	1200	1164
1	-5	881	884
2	-5	680	663
3	5	1040	1066
4	5	759	788
4	-5	685	696
5	5	1019	984
5	-5	1345	1329
6	5	908	932
0	6	756	773
1	6	1599	1602
1	-6	865	948
3	6	924	959
3	-6	679	601
4	-6	760	674
5	-6	986	953
6	6	1038	1067
6	-6	705	701
0	7	620	690
1	7	1168	1213
4	7	775	815
4	-7	906	950
6	-7	705	663
0	8	880	966
1	8	765	792
2	-8	708	677
3	8	921	898
4	-8	810	817
6	-8	971	993
1	9	978	1014
2	9	774	781
3	-9	1283	1346
4	-9	899	872
0	10	643	661
3	-10	1048	1016
K = 14**			
4	0	1012	1120
0	1	1495	1530
1	1	1055	1059
2	1	742	773
2	-1	681	717
5	1	997	952
5	-1	1163	1213
6	1	985	994
7	-1	981	1029
1	2	935	938
3	-2	1016	1111
1	3	1838	1916
1	-3	875	954
3	3	847	900
4	-3	1197	1214
5	-3	678	696
6	3	1370	1376
6	-3	1004	1050
7	-3	856	935
2	4	816	849
2	-4	1086	1130
3	4	714	702
3	-4	747	765
0	5	1122	1148
1	5	1229	1254
1	-5	895	920
2	5	1353	1388
4	-5	1302	1362
6	-5	1388	1412
2	-6	767	775
3	6	684	703
6	-6	640	576
0	7	1119	1158
2	7	1518	1577
3	7	607	552
3	-7	1139	1146
4	-7	631	603
5	-7	1175	1187
1	-8	728	808
0	9	641	650
2	-9	611	647
K = 15**			
1	0	1118	1087
4	0	711	744
2	-1	662	623
3	1	793	800
4	-1	723	804
5	1	688	651
0	2	1421	1458
1	-2	1178	1138
2	2	1123	1106
4	2	830	768
5	2	700	683
5	-2	889	973
2	-3	809	812
0	4	1472	1515
1	4	782	771
2	4	902	900
3	4	615	559
5	-4	1440	1491
1	-5	768	803
3	-5	603	570
0	6	937	1004
1	6	1235	1262
4	-6	908	918
0	7	680	673
1	-7	784	847
K = 16**			
0	0	1252	1297
2	0	609	663
0	1	891	945
1	1	1073	1135
3	-1	611	546
0	2	766	813
1	2	745	776
1	-2	702	747
3	-2	650	700
1	3	1132	1189
2	3	643	699
2	-3	660	687
3	-3	627	632
1	4	1036	1073
1	-4	914	939

elsewhere. Propionato hydrogen atoms were not resolvable. A further attempt, using the same procedure as before through two cycles of full-matrix refinement, was made to account for the peak of 0.9 $e^-/Å^3$ through the use of a disordered model. The results were similar to those obtained in the earlier attempt, in that the occupancy factor for the preferred C(6) rapidly attained a value of ~ 1 while the other one dwindled to ~0.3.

A weighting scheme analysis revealed that there was no serious dependence of $w[|F_o| - |F_c|]^2$ on either F_o or $(\sin \theta)/\lambda$. The final standard deviation of an observation of unit weight was 0.61, indicating that a lower value for p, the "uncertainty factor," should probably have been used.

Table I lists the observed and calculated structure amplitudes, $10|F_o|$ and $10|F_c|$, respectively, each in electrons. Final atomic fractional coordinates and isotropic temperature factors are given in Table II for atoms except those of the phenyl groups. Anisotropic temperature factors for Re, Cl, and P are given in Table III. The rigid-body coordinates for the phenyl groups are given in Table IV while Table V lists the derived positional coordinates and the isotropic thermal parameters for individual carbon atoms.[14]

Results

The molecular structure is depicted in Figures 1 and 2, which also show the numbering scheme used in the tables. The intramolecular dimensions are presented

TABLE II

FINAL ATOMIC COORDINATES FOR $Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$

Atom	x	y	z	B,[b] Å^2
Re(1)	0.11121 (5)	0.08100 (4)	0.20286 (4)	
Re(2)	0.27829 (5)	0.09159 (4)	0.16942 (4)	
Cl(b)	0.13934 (28)	0.13300 (22)	0.08173 (23)	
Cl(1)	−0.05449 (26)	0.08987 (26)	0.15510 (24)	
Cl(2)	0.37411 (29)	0.14509 (22)	0.08364 (24)	
P(1)	0.06992 (29)	0.04370 (22)	0.32872 (26)	
P(2)	0.42739 (30)	0.04163 (23)	0.23351 (25)	
O(B)	0.2337 (7)	0.0526 (5)	0.2595 (5)	3.1 (2)
O(1)	0.1289 (7)	0.1920 (5)	0.2492 (5)	3.7 (2)
O(2)	0.2804 (7)	0.1992 (5)	0.2247 (6)	3.6 (2)
O(3)	0.1096 (7)	−0.0276 (5)	0.1505 (6)	3.6 (2)
O(4)	0.2569 (7)	−0.0154 (5)	0.1140 (5)	3.5 (2)
C(1)	0.2093 (12)	0.2256 (9)	0.2469 (9)	3.6 (4)
C(2)	0.2234 (14)	0.3107 (11)	0.2800 (12)	7.0 (5)
C(3)	0.1757 (17)	0.3202 (14)	0.3470 (14)	10.6 (7)
C(4)	0.1763 (12)	−0.0496 (9)	0.1141 (9)	3.7 (4)
C(5)	0.1705 (13)	−0.1246 (10)	0.0682 (10)	6.0 (5)
C(6)	0.0768 (18)	−0.1628 (14)	0.0772 (14)	11.4 (8)

[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 III.

TABLE III

ANISOTROPIC THERMAL PARAMETERS (×10^5)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	354 (5)	226 (3)	307 (4)	17 (4)	38 (3)	12 (3)
Re(2)	374 (5)	226 (3)	271 (4)	4 (4)	54 (3)	−1 (3)
Cl(B)	486 (28)	333 (17)	325 (20)	−6 (18)	14 (19)	88 (16)
Cl(1)	355 (25)	488 (20)	454 (22)	21 (22)	−11 (18)	76 (20)
Cl(2)	532 (29)	339 (18)	366 (21)	−14 (19)	164 (20)	25 (16)
P(1)	341 (27)	228 (16)	327 (22)	−6 (18)	61 (19)	−6 (16)
P(2)	360 (29)	272 (17)	294 (21)	18 (19)	53 (19)	−17 (16)

TABLE IV

RIGID-BODY COORDINATES FOR PHENYL GROUPS[a]

				Radians		
Body	x	y	z	D	E	F
C(11)–C(61)	−0.1481 (5)	0.0756 (4)	0.3495 (3)	6.041 (6)	0.353 (7)	6.063 (7)
C(12)–C(62)	0.4295 (5)	−0.1300 (4)	0.3112 (3)	3.512 (6)	3.177 (6)	4.730 (7)
C(13)–C(63)	0.1016 (4)	−0.1337 (4)	0.3710 (4)	3.173 (6)	2.102 (6)	4.952 (6)
C(14)–C(64)	0.5122 (4)	0.1505 (4)	0.3859 (4)	1.152 (6)	1.928 (6)	5.615 (7)
C(15)–C(65)	0.1809 (5)	0.1398 (4)	0.4725 (4)	0.990 (6)	0.292 (11)	4.461 (11)
C(16)–C(66)	0.5918 (5)	0.0202 (4)	0.1374 (4)	3.891 (7)	0.666 (9)	3.336 (10)

[a] For the sets of H atoms H(2*i*)–H(6*i*), x, y, z, D, and E are identical with those for the corresponding sets of C atoms, C(1*i*)–C(6*i*). The angle F for an H atom set is equal to that for the corresponding C atom set plus $2\pi/6$ radians, since there is no H atom on atom C(1*i*) and the H atom set begins with H(2*i*).

TABLE V

DERIVED POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR PHENYL CARBON ATOMS

Atom	x	y	z	B, Å^2
C(11)	−0.0542 (7)	0.0586 (7)	0.3381 (4)	3.1 (4)
C(21)	−0.0903 (8)	0.1327 (6)	0.3248 (5)	4.8 (4)
C(31)	−0.1842 (8)	0.1497 (5)	0.3362 (6)	5.7 (5)
C(41)	−0.2420 (7)	0.0925 (7)	0.3609 (4)	4.7 (4)
C(51)	−0.2058 (8)	0.0184 (6)	0.3742 (5)	5.7 (5)
C(61)	−0.1120 (8)	0.0015 (5)	0.3628 (6)	4.3 (4)
C(12)	0.4264 (9)	−0.0555 (4)	0.2821 (6)	3.5 (4)
C(22)	0.3410 (6)	−0.0939 (6)	0.2888 (5)	4.1 (4)
C(32)	0.3440 (6)	−0.1684 (6)	0.3179 (4)	4.4 (4)
C(42)	0.4325 (9)	−0.2045 (4)	0.3403 (6)	4.6 (4)
C(52)	0.5180 (6)	−0.1661 (6)	0.3335 (5)	4.8 (4)
C(62)	0.5149 (6)	−0.0916 (6)	0.3044 (4)	4.7 (4)
C(13)	0.0922 (8)	−0.0561 (4)	0.3523 (6)	3.3 (4)
C(23)	0.0535 (7)	−0.1113 (6)	0.2989 (4)	4.4 (4)
C(33)	0.0630 (7)	−0.1889 (5)	0.3176 (5)	4.8 (4)
C(43)	0.1111 (8)	−0.2113 (4)	0.3897 (6)	5.1 (4)
C(53)	0.1498 (7)	−0.1561 (6)	0.4431 (4)	5.7 (5)
C(63)	0.1403 (7)	−0.0784 (5)	0.4245 (5)	4.2 (4)
C(14)	0.4758 (7)	0.1016 (6)	0.3256 (5)	3.5 (4)
C(24)	0.4849 (7)	0.1798 (6)	0.3118 (5)	4.0 (4)
C(34)	0.5213 (8)	0.2287 (4)	0.3722 (7)	5.7 (5)
C(44)	0.5486 (7)	0.1994 (6)	0.4463 (5)	5.4 (5)
C(54)	0.5396 (7)	0.1213 (6)	0.4601 (5)	5.3 (4)
C(64)	0.5031 (8)	0.0723 (4)	0.3997 (7)	4.7 (4)
C(15)	0.1334 (11)	0.0973 (5)	0.4107 (5)	3.2 (3)
C(25)	0.2327 (12)	0.1901 (6)	0.4179 (8)	4.9 (4)
C(35)	0.2801 (8)	0.1516 (6)	0.4797 (8)	5.4 (5)
C(45)	0.2283 (11)	0.1823 (5)	0.5343 (5)	4.6 (4)
C(55)	0.1290 (12)	0.1705 (6)	0.5271 (8)	4.5 (4)
C(65)	0.0816 (8)	0.1280 (6)	0.4653 (8)	4.1 (4)
C(16)	0.5224 (13)	0.0315 (7)	0.1853 (7)	3.5 (4)
C(26)	0.6062 (11)	0.0756 (6)	0.1953 (8)	5.2 (4)
C(36)	0.6757 (10)	0.0643 (6)	0.1474 (6)	6.8 (5)
C(46)	0.6612 (13)	0.0089 (7)	0.0894 (7)	7.1 (5)
C(56)	0.5773 (11)	−0.0352 (6)	0.0794 (8)	6.7 (5)
C(66)	0.5079 (10)	−0.0239 (6)	0.1273 (6)	5.6 (5)

in Table VI. 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 phenyl 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, *e.g.*, carbon atoms C(11), C(13), and C(15) are attached to P(1). In Figure 2 only one carbon atom of each ring has been labeled; the other labels may be determined using this label and the foregoing rule.

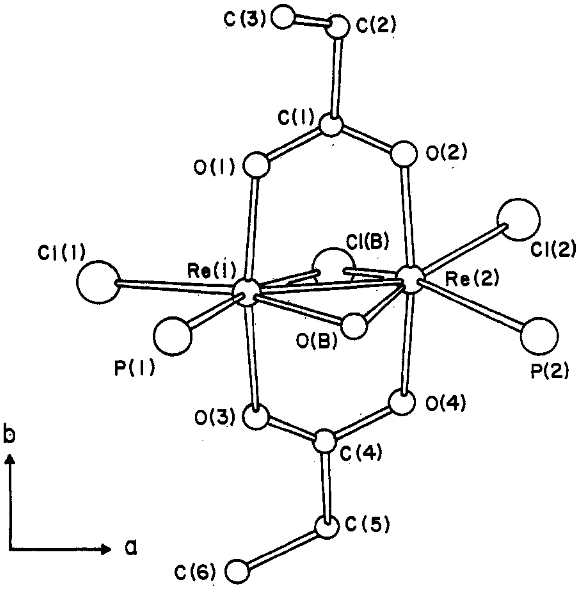

Figure 1.—Inner coordination sphere of $Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$ as seen in projection down the crystallographic *c** axis.

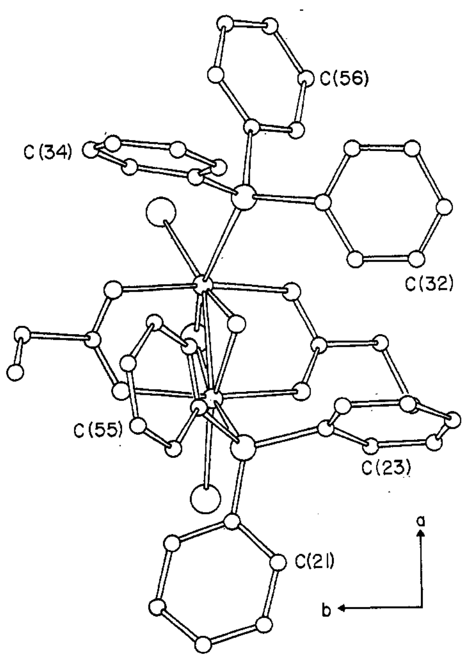

Figure 2.—The molecular structure of $Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$ as seen in projection down the crystallographic *c** axis.

Root-mean-square vibrational amplitudes and their direction cosines are presented in Table VII. Table VIII gives the equations for three important planes in the inner coordination sphere and the distances of the atoms from these planes.

Discussion

Description of the Structure. The crystal structure, which is defined by the unit cell dimensions, the positional parameters of Tables II and V, and the space

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(14) With respect to scattering factors and corrections for anomalous scattering, the following references are pertinent: Re atom: D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965). Nonhydrogen atoms: J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202. Hydrogen atoms: R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1966, p 57. Dispersion corrections: C. T. Prewitt, Ph.D. Thesis, Massachusetts Institute of Technology, 1962, p 163; D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

group symmetry operations, consists of normally packed, discrete dinuclear molecules. Figure 1 shows the inner coordination about the rhenium atoms, and the complete molecular structure is displayed in Figure 2. 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 many triphenylphosphine–metal complexes, the crystal packing is mainly dependent upon the intermolecular interactions of the bulky phenyl groups. As in the structure of $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$,[2] effects of different packing environments for the chemically related "halves" of the molecule may be seen in the discrepancies between related pairs of Re–P–C, C–P–C, and P–C–C_{para} angles. These discrepancies are small, however.

The molecular structure of $Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$ is quite similar to that of $Re_2OCl_5(C_2HCO_2)[P(C_6H_5)_3]_2$. Thus, while the molecular structure as a whole possesses only C_1 symmetry, the inner coordination sphere (Figure 1) has virtual symmetry C_{2v} if the β-carbon atoms of the propionato groups are ignored. The dinuclear molecular unit consists of coordination octahedra which share an edge and have two sets of vertices bridged by carboxyl groups. The Re–Re bond is quadruply bridged by a chlorine atom, an oxygen atom, and two propionato groups. For a thorough discussion of the bond lengths and comparison with other structures the reader is referred to the paper[2] on the structure of $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$. The bond lengths and geometry are compared below to that structure.

Calculations of weighted least-squares best planes (Table VIII) show that only *one* of the three sets of atoms involved in the bridging forms a planar group (*i.e.*, Re(1), Re(2), O(B), Cl(B)) without serious deviations. The carboxylate groups are considerably distorted, as evidenced by these calculations and by observation of differences in angles such as P–Re–O and Cl–Re–O and nonbonded contacts such as rhenium–carboxylate oxygen (see Table VI). The rhenium to

Table VI

Principal Intramolecular Distances and Angles

(a) Bond Distances, Å

Re(1)–Re(2)	2.514 (1)	C(1)–O(1)	1.28 (2)
Re(1)–Cl(1)	2.357 (4)	C(1)–O(2)	1.22 (2)
Re(2)–Cl(2)	2.362 (4)	C(4)–O(3)	1.24 (2)
Re(1)–P(1)	2.457 (4)	C(4)–O(4)	1.29 (2)
Re(2)–P(2)	2.453 (4)	C(1)–C(2)	1.60 (2)
Re(1)–Cl(B)	2.400 (4)	C(2)–C(3)	1.45 (3)
Re(2)–Cl(B)	2.406 (4)	C(4)–C(5)	1.56 (2)
Re(1)–O(B)	1.918 (9)	C(5)–C(6)	1.50 (3)
Re(2)–O(B)	1.913 (9)	P(1)–C(11)	1.797 (10)
Re(1)–O(1)	2.103 (10)	P(1)–C(13)	1.809 (9)
Re(2)–O(2)	2.115 (10)	P(1)–C(15)	1.831 (11)
Re(1)–O(3)	2.107 (9)	P(2)–C(12)	1.828 (9)
Re(2)–O(4)	2.109 (9)	P(2)–C(14)	1.826 (11)
		P(2)–C(16)	1.810 (17)

(b) Intramolecular Nonbonded Contacts, Å

Re(1)–O(2)	3.129	Re(2)–C(1)	2.946
Re(1)–O(4)	3.232	Re(2)–C(4)	2.930
Re(2)–O(1)	3.217	Cl(B)–Cl(1)	3.275
Re(2)–O(3)	3.136	Cl(B)–Cl(2)	3.303
Re(1)–C(1)	2.925	P(1)–Cl(1)	3.372
Re(1)–C(4)	2.955	P(2)–Cl(2)	3.326

(c) Interbond Angles, Deg

P(1)–Re(1)–Cl(1)	88.9 (1)	Re(1)–Cl(B)–Re(2)	63.1 (1)
P(2)–Re(2)–Cl(2)	87.4 (1)	Re(1)–P(1)–C(11)	114.2 (4)
P(1)–Re(1)–O(1)	85.8 (3)	Re(1)–P(1)–C(13)	113.9 (4)
P(2)–Re(2)–O(2)	97.0 (3)	Re(1)–P(1)–C(15)	114.6 (5)
P(1)–Re(1)–O(3)	99.5 (3)	Re(2)–P(2)–C(12)	118.2 (4)
P(2)–Re(2)–O(4)	88.8 (3)	Re(2)–P(2)–C(14)	113.5 (4)
Cl(B)–Re(1)–O(1)	88.1 (3)	Re(2)–P(2)–C(16)	112.3 (4)
Cl(B)–Re(2)–O(2)	88.8 (3)	C(11)–P(1)–C(13)	104.8 (5)
Cl(B)–Re(1)–O(3)	87.0 (3)	C(13)–P(1)–C(15)	105.5 (6)
Cl(B)–Re(2)–O(4)	85.8 (3)	C(15)–P(1)–C(11)	102.6 (5)
Cl(1)–Re(1)–O(1)	97.4 (3)	C(12)–P(2)–C(14)	105.3 (5)
Cl(2)–Re(2)–O(2)	88.4 (3)	C(14)–P(2)–C(16)	106.4 (7)
Cl(1)–Re(1)–O(3)	87.7 (3)	C(16)–P(2)–C(12)	99.6 (7)
Cl(2)–Re(2)–O(4)	96.4 (3)	C(1)–C(2)–C(3)	110.7 (16)
Re(2)–Re(1)–O(1)	87.9 (3)	C(4)–C(5)–C(6)	106.8 (15)
Re(1)–Re(2)–O(2)	84.6 (3)	P(1)–C(11)–C(41)	175.1 (5)
Re(2)–Re(1)–O(3)	85.0 (3)	P(1)–C(13)–C(43)	175.5 (6)
Re(1)–Re(2)–O(4)	88.3 (3)	P(1)–C(15)–C(45)	178.6 (8)
O(1)–Re(1)–O(3)	172.7 (4)	P(2)–C(12)–C(42)	177.8 (6)
P(2)–Re(2)–O(4)	172.6 (4)	P(2)–C(14)–C(44)	177.2 (6)
Re(1)–O(B)–Re(2)	82.0 (3)	P(2)–C(16)–C(46)	176.2 (10)

Table VII

Root-Mean-Square Amplitudes of Vibration and Their Direction Cosines[a]

Atom	Minor axis	Medium axis	Major axis
Re(1)	0.180	0.192	0.218
	(0.696, −0.685, 0.213)	(0.694, 0.718, 0.045)	(−0.184, 0.117, 0.976)
Re(2)	0.186	0.191	0.203
	(−0.321, 0.946, 0.036)	(0.945, 0.323, −0.044)	(0.053, −0.020, 0.998)
Cl(B)	0.191	0.218	0.257
	(0.206, −0.632, 0.747)	(0.917, 0.392, 0.079)	(−0.342, 0.669, 0.660)
Cl(1)	0.182	0.252	0.292
	(0.932, −0.112, 0.344)	(−0.330, −0.655, 0.680)	(−0.149, 0.747, 0.647)
Cl(2)	0.196	0.231	0.254
	(0.762, 0.287, −0.580)	(−0.319, 0.946, 0.049)	(0.563, 0.148, 0.813)
P(1)	0.181	0.188	0.223
	(0.965, 0.259, 0.024)	(−0.261, 0.963, 0.058)	(−0.008, −0.062, 0.998)
P(2)	0.184	0.203	0.216
	(0.942, −0.331, −0.046)	(0.296, 0.764, 0.573)	(−0.154, −0.554, 0.818)

[a] Direction cosines are referred to the orthogonal axis system *a*, *b*, *c**.

TABLE VIII

Best weighted least-squares planes[a]		
Plane	Atoms	Equation
1	Re(1)-Re(2)-O(B)-Cl(B)	$0.0269x + 0.9141y + 0.4047z = 2.7452$
2	Re(1)-Re(2)-O(1)-O(2)-C(1)-C(2)	$0.2407x - 0.3948y + 0.8867z = 2.8068$
3	Re(1)-Re(2)-O(3)-O(4)-C(4)-C(5)	$0.2392x - 0.4485y + 0.8612z = 2.6398$

Distances of atoms from mean plane, Å						Angles between planes, deg	
Atoms	Plane 1	Atoms	Plane 2	Atoms	Plane 3	Planes	Angle
Re(1)	0.001	Re(1)	0.000	Re(1)	0.000	1–2	89.7
Re(2)	0.001	Re(2)	0.000	Re(2)	0.000	1–3	86.9
Cl(B)	0.000	O(1)	−0.022	O(3)	0.097	2–3	176.9
O(B)	−0.013	O(2)	0.080	O(4)	−0.025		
		C(1)	−0.015	C(4)	0.015		
		C(2)	−0.067	C(5)	−0.114		

[a] The method of calculation is outlined in "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 93. The orthogonal axis system is a, b, c^*.

TABLE IX

AVERAGE METAL–LIGAND BOND LENGTHS[a]
(FOR EXPECTED CHEMICALLY EQUIVALENT BONDS)

Bond	$Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$	$Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$
Re–Cl	2.356 (4)	2.360 (3)
Re–Cl(B)	2.411 (3)	2.403 (3)
Re–P	2.490 (3)	2.455 (3)
Re–O	2.095 (8)	2.108 (5)
Re–O(B)	1.889 (8)	1.916 (6)
Re–Re	2.522 (1)	2.514 (1)

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

carboxylate oxygen bonds are longer than in compounds such as $Re_2(O_2CC_6H_5)_4Cl_2$ (~2.02 Å); it has been previously[2] observed that this effect is probably due, at least in part, to the fact that the Re–Re distance exceeds the optimum "bite" of the propionato group.

The Re–Re distance, 2.514 Å, definitely indicates direct metal-to-metal bonding and is nearly identical with the Re–Re distance of 2.522 Å found in $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$. The difference in formal oxidation state for the rhenium atom (*i.e.*, 3.5 for the present and 4.0 for the former compound) has little effect on the molecular geometry and dimensions, and the arguments set forth previously[2] regarding the nature of the metal–metal bond are applicable here. Table IX presents a comparison of other bond lengths in the two molecules; it can be readily seen that there are only slight differences between them.

In view of the increasing tendency toward formation of Re–Re bonds as the oxidation state of the metal decreases and the knowledge that a Re–Re distance indicative of bonding exists[2] in $Re_2OCl_5(O_2CC_2H_5)[P(C_6H_5)_3]_2$, it was, of course, to be expected that for $Re_2OCl_3(O_2CC_2H_5)_2[P(C_6H_5)_3]_2$ a short Re–Re distance would also be found. That the two distances should be identical to within less than 0.01 Å and that the two structures in their entirety should be as nearly identical as their stoichiometric differences permit are more surprising. Since $Re_2OCl_5(O_2CC_2H_5)[P(C_6H_5)_3]_2$ is reported[6] to have no unpaired electrons, while $Re_2OCl_3(O_2CC_2H_5)_2[P(C_6H_5)_3]_2$ appears likely to have one,[6] it would seem that the two compounds must have virtually identical electronic structures, with the extra electron in the latter compound occupying a molecular orbital that is neither strongly bonding nor strongly antibonding. This extra electron does not, therefore, have any distinct effect upon the molecular dimensions.

Finally, we note that while the question of whether compounds of stiochiometry $ReCl_3(O_2CR)_2[P(C_6H_5)_3]_2$ actually exist has perhaps not been definitively answered, it seems quite unlikely that they have, in fact, been prepared. Through the cooperation of Professor Wilkinson and Dr. Rouschias we obtained a sample of one of their original preparations for comparison with our own, but, unfortunately, decomposition had proceeded so far as to preclude any meaningful comparison. However, since the properties of material we have prepared and studied, $Re_2OCl_3(O_2CC_2H_5)_2[P(C_6H_5)_3]_2$, correspond so closely to those reported[6] for the $Re_2Cl_3(O_2CR)_2[P(C_6H_5)_3]_2$ compounds and the preparative conditions were identical insofar as possible, we feel that there is no doubt that the same substances are involved in both studies and that a change is required in the formulas originally proposed.