oxidation potential of the $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ couple with acidity. This increase causes a corresponding decrease in the standard free energy changes for the reactions, thereby lowering their rates.

By and large the results satisfy the Marcus relation reasonably well. If additional studies show that eq. 1 is indeed satisfied by a large variety of systems then any departure from eq. 1, as has been found, for example, in the case of the reactions involving cobalt(III), may well be taken as evidence of a more complex mechanism. Further studies are necessary to determine whether this complexity arises from an inner-sphere mechanism, electronic factors, or some other complicating feature.

Contribution from the Department of Chemistry, Massachusetts
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The Crystal and Molecular Structure of Tris(phenyldiethylphosphine)nonachlorotrirhenium(III)[1a]

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The compound of empirical formula $ReCl_3[(C_6H_5)(C_2H_5)_2P]$ has been shown to be a trimer having essentially the same structure as the $[Re_3Cl_{12}]^{3-}$ ion except that the three in-plane, nonbridging positions are filled by $(C_6H_5)(C_2H_5)_2P$, instead of by Cl^-. The Re_3Cl_9 portions of the two molecules are essentially identical in all their dimensions. The Re–P bonds are considerably longer than would be expected for normal single bonds, an effect which could be caused by crowding of the Cl atoms projecting above and below the Re_3 plane. The earlier suggestion that some compounds of empirical formula ReX_3L might have structures with clusters of three rhenium atoms, like that in the $[Re_3Cl_{12}]^{3-}$ ion, has thus been confirmed. The similar electronic spectra of the $[Re_3Cl_{12}]^{3-}$ and $[Re_3Cl_9(PR_3)_3]$ species are also reported.

Introduction

The recent discovery[2,3] of the existence of a cluster of three rhenium atoms strongly bonded to one another[4] in the compound of empirical formula $CsReCl_4$ has led to investigations of other complexes of trivalent rhenium.[5] Among the several studies completed or in progress in this laboratory is a single-crystal X-ray study of the structure of the compound with the empirical formula $ReCl_3[(C_6H_5)(C_2H_5)_2P]$. This is only one of several compounds of the stoichiometric type ReX_3L, where X = Cl, L = $(C_6H_5)_3P$[6,7]; X = Cl, L = C_5H_5N[6]; X = Cl, L = $P(C_6H_5)(C_2H_5)_2$[7]; and X = Br, L = $P(C_6H_5)(C_2H_5)_2$.[8] It was earlier suggested[3a] that some of these ReX_3L compounds might have trimeric formulas, $Re_3X_9L_3$, with structures derived from that of the $[Re_3Cl_{12}]^{3-}$ ion by replacement of the three in-plane, nonbridging Cl^- ions with the neutral ligands, L. The structural study reported here was carried out to test this suggestion and, as will be seen, shows it to be correct.

Experimental

The compound was prepared by the method of Chatt and Rowe.[7] Small, dark red crystals were obtained directly from the solution of $(C_2H_5)_2(C_6H_5)P$ and $ReCl_3$ in dimethylformamide by allowing the hot solution to cool slowly in a dewar vessel filled with hot water. *Anal.* Calcd.: C, 26.48; H, 3.38. Found: C, 26.2; H, 3.30. The density, determined by flotation in 1,2-dibromoethane, was 2.17 g. cm.$^{-3}$. The linear absorption coefficient for Cu Kα radiation is 224 cm.$^{-1}$.

Using precession and Weissenberg photographs, it was established that the crystals are cubic with $a = 20.53 \pm 0.02$ Å. The following systematic absences were observed: $hk0$, $h \neq 2n$; $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$. These unequivocally establish that the space group is Pa3 (No. 205).[9a] Using the measured density and unit cell dimension, the number of $(C_2H_5)_2(C_6H_5)PReCl_3$ moieties per cell was calculated as 24.7, indicating, therefore, that the rhenium atoms lie on the 24 general positions for this space group, which in turn, means that they fall into eight groups of three, those in each group being related by a threefold axis.

The crystal used for collecting intensity data had the form of a rectangular plate with dimensions 0.10 × 0.15 × 0.15 mm. Intensity data were recorded photographically by the equi-inclination Weissenberg method using Cu Kα radiation. Approximately 1000 reflections were recorded using the $hk0$–$hk5$ layers. The relative intensities were estimated visually by comparison with an intensity wedge prepared from the same crystal. Absorption corrections were made using a general absorption correction program, GNABS, written for the IBM 7094 computer by Dr. C. Burnham and supplied through the courtesy of Professor M. J. Buerger of this Institute. Lorentz and polarization corrections were made in the usual way. Anomalous dispersion corrections have been neglected throughout.

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[1] (a) Supported by the U. S. Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation; (c) National Science Foundation Predoctoral Fellow.

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[5] J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

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[7] J. Chatt and G. A. Rowe, *ibid.*, 4019 (1962).

[8] S. J. Lippard, Massachusetts Institute of Technology, to be published.

[9] "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1952: (a) Vol. I; (b) Vol. III.

TABLE I

FINAL POSITIONAL AND THERMAL VIBRATION PARAMETERS[a]

Atom	x/a	σ_x	y/b	σ_y	z/c	σ_z	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Re	0.1358	0.0001	0.2182	0.0001	0.2247	0.0001	9	1	11	1	11	1	1	1	2	1	0	1
P	0.0294	0.0009	0.2685	0.0009	0.2834	0.0009	9	5	12	6	17	6	−3	5	−1	5	1	6
Cl_1	0.1827	0.0008	0.2891	0.0008	0.2980	0.0008	19	5	8	5	10	5	1	5	−7	5	−1	4
Cl_2	0.0547	0.0008	0.1621	0.0007	0.1692	0.0008	20	5	6	5	10	5	−1	5	−1	5	3	4
Cl_3	0.1459	0.0008	0.1318	0.0008	0.3025	0.0008	18	6	15	5	9	5	−3	5	14	5	10	4
C_1	0.0203	0.0038	0.2394	0.0039	0.3639	0.0039	27	...	27	...	27	...	0	...	0	...	0	...
C_2	−0.0237	0.0032	0.1697	0.0033	0.3702	0.0032	16	...	16	...	16	...	0	...	0	...	0	...
C_3	−0.0279	0.0039	0.1460	0.0040	0.4322	0.0040	30	...	30	...	30	...	0	...	0	...	0	...
C_4	0.0018	0.0032	0.1774	0.0031	0.4861	0.0030	11	...	11	...	11	...	0	...	0	...	0	...
C_5	0.0324	0.0030	0.2299	0.0031	0.4809	0.0030	13	...	13	...	13	...	0	...	0	...	0	...
C_6	0.0481	0.0034	0.2598	0.0034	0.4225	0.0035	20	...	20	...	20	...	0	...	0	...	0	...
C_7	−0.0444	0.0031	0.2492	0.0034	0.2365	0.0032	18	...	18	...	18	...	0	...	0	...	0	...
C_8	−0.0531	0.0030	0.2948	0.0029	0.1745	0.0031	13	...	13	...	13	...	0	...	0	...	0	...
C_9	0.0399	0.0030	0.3589	0.0031	0.2941	0.0030	13	...	13	...	13	...	0	...	0	...	0	...
C_{10}	−0.0289	0.0029	0.3838	0.0029	0.3308	0.0029	11	...	11	...	11	...	0	...	0	...	0	...

[a] All β values and their σ values are 10^{-4} times the figures listed.

Solution of the Structure

A three-dimensional Patterson synthesis was computed[10] for one octant of the unit cell. A large peak on each of the Harker lines ($^1/_2 - 2x$, $^1/_2$, 0), (0, $^1/_2 - 2y$, $^1/_2$), and ($^1/_2$, 0, $^1/_2 - 2z$) provided coordinates (x, y, z) for the general position of the rhenium atoms. The Re–Re distances in the groups of three rhenium atoms anticipated were found to be $\sim$2.5 Å., in good agreement with the Re–Re distances in $Cs_3Re_3Cl_{12}$.[2,3]

Structure factors were then calculated using only the rhenium atoms. Here and subsequently, atomic scattering factors were taken from the tables of ref. 9b (Table 3.3.1A for Cl^0, P^0, C^0; Table 3.3.1B for Re^0). Using the phases thus obtained, a three-dimensional Fourier synthesis was computed[10] from which the parameters of the three independent chlorine atoms and the phosphorus atom were determined. Scale factors for each zone and positional parameters for the five heavy atoms were refined by several cycles of least squares[11]; then two more cycles were run, in which isotropic temperature factors for the five heavy atoms were also varied. The conventional residual, $R = [\Sigma(|F_o - F_c|)]/\Sigma|F_o|$, was 0.18 at this stage.

A difference Fourier synthesis was now computed and the coordinates of the ten carbon atoms were determined therefrom. Four cycles of refinement were now run on all fifteen atoms in which the scale factors, atom coordinates, and isotropic temperature factors were varied, dropping the residual to 0.14. The correlation matrix showed considerable interaction between the scale factors and the temperature factors. Since the former were by this time practically constant, they were fixed and the refinement was continued with a changeover to anisotropic temperature factors. Also at this point, a new weighting routine of the form $w = 140/[|F_o| + (4900/|F_o|)]$, using unscaled F_o values, was included to give more weight to those values of F_o which corresponded to the middle range of the series of standard intensities, as these were considered to be the most accurate. The first cycle indicated that several of the carbon atoms had negative diagonal temperature factors. A further cycle of refinement failed to make them positive, so the refinement was continued varying anisotropic temperature factors for the heavy atoms only. A final cycle of refinement brought the residual down to 0.126.

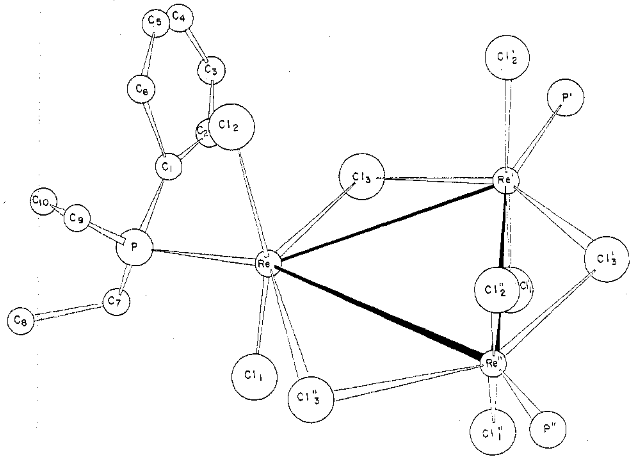

Fig. 1.—A perspective view of the $Re_3Cl_9(P(C_2H_5)_2C_6H_5)_3$ molecule. The organic parts of two of the $P(C_2H_5)_2C_6H_5$ groups are omitted for clarity.

The final positional parameters and temperature factors are recorded in Table I, along with their standard deviations. Table II gives the final calculated structure factors (F_c) together with the square roots of the observed intensities, corrected for Lorentz and polarization factors (F_o).

Discussion of the Structure

Figure 1 shows a perspective drawing of the molecule (two of the phenyldiethylphosphine groups have the organic portions omitted for clarity). The trinuclear unit has crystallographic C_3 symmetry; thus all three of the component $(C_2H_5)_2(C_6H_5)PReCl_3$ groups constituting it are equivalent. The $Re_3Cl_9P_3$ portion of the trinuclear molecule has D_{3h} symmetry to within the experimental uncertainties, as did the $[Re_3Cl_{12}]^{3-}$ unit

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[10] Using W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende's ERFR-2, IBM 709-7090 Fourier Program, 1962.

[11] Using C. T. Prewitt's program for the IBM 7090 computer, which furnishes, on request, the correlation matrix.[12]

[12] S. Geller, *Acta Cryst.*, **14**, 1026 (1961).

Table II

Observed and Calculated Structure Factors for $[(C_6H_5)(C_2H_5)_2P]_3Re_3Cl_9$

h	k	l	F_o	F_c
4	0	0	137.64	113.57
6	0	0	61.06	37.90
8	0	0	72.03	62.61
10	0	0	56.14	-42.23
12	0	0	157.88	-156.34
14	0	0	145.84	148.72
16	0	0	94.86	-84.37
18	0	0	36.94	36.40
20	0	0	67.98	-81.94
2	1	0	149.38	-212.54
4	1	0	107.01	103.11
8	1	0	20.63	-4.93
10	1	0	149.86	-153.89
12	1	0	144.56	147.89
14	1	0	34.80	-36.57
18	1	0	25.64	-19.67
20	1	0	24.50	18.90
2	2	0	83.80	90.51
4	2	0	19.77	-25.01
8	2	0	69.15	-58.73
10	2	0	32.68	21.39
12	2	0	147.86	134.51
14	2	0	97.33	-95.97
16	2	0	33.38	31.47
20	2	0	32.06	26.81
2	3	0	82.00	89.88
4	3	0	20.02	-16.32
8	3	0	28.23	14.02
10	3	0	92.15	86.41
14	3	0	51.74	-43.14
16	3	0	67.67	70.50
18	3	0	0.	-1.79
20	3	0	24.26	-21.03
2	4	0	15.03	4.43
4	4	0	53.36	-40.69
6	4	0	40.02	35.01
8	4	0	53.61	35.23
12	4	0	67.55	-56.50
14	4	0	36.70	35.68
18	4	0	36.80	-35.78
2	5	0	55.49	-48.76
4	5	0	22.87	21.06
6	5	0	33.70	31.20
8	5	0	60.41	-46.11
12	5	0	77.67	-59.35
14	5	0	66.49	61.88
16	5	0	63.17	-65.43
6	6	0	24.54	12.12
8	6	0	43.75	-32.12
10	6	0	27.00	18.51
12	6	0	27.39	18.35
2	7	0	51.01	39.74
4	7	0	63.28	-62.63
6	7	0	87.74	89.34
8	7	0	79.46	-85.52
10	7	0	100.07	96.11
12	7	0	30.29	-24.38
16	7	0	32.46	34.29
2	8	0	50.28	-41.29
4	8	0	102.89	99.78
6	8	0	61.24	-55.82
8	8	0	39.28	32.45
12	8	0	44.35	-31.67
16	8	0	56.83	-60.19
18	8	0	30.85	30.14
20	8	0	30.25	-35.26
2	9	0	32.23	-22.59
4	9	0	47.75	39.61
6	9	0	100.66	-100.53
8	9	0	75.71	72.88
10	9	0	65.61	-61.58
12	9	0	65.91	65.56
14	9	0	62.58	-60.40
16	9	0	36.56	42.35
2	10	0	27.32	18.68
4	10	0	85.66	-73.56
6	10	0	46.60	28.91
8	10	0	47.67	33.65
12	10	0	29.16	-23.37
16	10	0	37.04	38.36
18	10	0	36.32	-40.85
2	11	0	47.49	-45.06
4	11	0	44.30	33.71
6	11	0	68.87	58.79
10	11	0	33.69	-20.42
14	11	0	30.98	33.32
16	11	0	28.40	-27.72
18	11	0	27.16	-30.65
2	12	0	113.23	119.04
8	12	0	53.04	-53.75
12	12	0	63.07	62.80
14	12	0	71.93	-79.17
16	12	0	28.32	29.19
2	13	0	88.42	96.68
4	13	0	92.80	-89.63
6	13	0	27.62	12.00
8	13	0	55.17	-45.53
10	13	0	104.29	110.94
12	13	0	78.10	-72.26
2	14	0	89.01	-102.72
8	14	0	60.55	59.62
12	14	0	69.00	-61.39
14	14	0	71.34	69.27
2	15	0	72.51	-76.96
4	15	0	44.26	38.19
8	15	0	31.19	21.75
10	15	0	71.57	-74.46
12	15	0	52.08	50.03
16	15	0	27.28	-26.61
2	16	0	27.84	27.92
4	16	0	25.80	22.73
6	16	0	0.	-2.58
8	16	0	27.41	-23.97
12	16	0	44.78	47.04
14	16	0	42.88	-37.65
2	17	0	44.20	46.26
8	17	0	29.10	26.76
12	17	0	0.	-6.27
14	17	0	38.54	-43.19
4	18	0	40.40	-44.09
6	18	0	30.92	36.22
2	19	0	47.58	-55.47
4	19	0	36.03	39.49
10	19	0	25.96	-27.51
2	20	0	38.60	49.41
8	20	0	23.03	-27.11
10	20	0	0.	4.98
2	1	1	35.24	-34.84
3	1	1	13.62	-24.16
4	1	1	62.53	59.96
5	1	1	21.96	13.11
6	1	1	25.29	-17.62
7	1	1	38.32	-27.67
8	1	1	29.90	25.26
10	1	1	54.78	-46.23
11	1	1	24.31	-17.96
12	1	1	74.34	78.79
13	1	1	11.46	16.18
14	1	1	39.96	-43.96
15	1	1	24.75	-20.63
16	1	1	32.02	36.73
1	2	1	35.24	-34.84
2	2	1	122.94	147.62
3	2	1	20.37	20.43
4	2	1	38.21	-45.69
5	2	1	30.22	-20.88
6	2	1	31.96	24.91
7	2	1	58.81	-41.22
8	2	1	41.27	-30.70
9	2	1	29.43	21.69
12	2	1	67.96	54.82
14	2	1	85.66	-90.58
16	2	1	52.72	50.39
17	2	1	28.07	25.64
18	2	1	40.41	-39.23
20	2	1	32.03	35.18
1	3	1	13.62	-24.16
2	3	1	109.18	123.82
3	3	1	61.26	51.56
4	3	1	56.52	-56.06
5	3	1	15.57	-20.20
6	3	1	52.89	47.22
7	3	1	57.34	45.82
8	3	1	82.41	-77.35
9	3	1	30.29	-29.69
10	3	1	154.94	144.98
11	3	1	64.28	51.10
12	3	1	155.98	-151.98
13	3	1	38.82	-34.25
14	3	1	47.21	43.19
15	3	1	25.31	22.31
16	3	1	0.	5.17
1	4	1	62.53	59.96
2	4	1	67.10	-61.83
3	4	1	28.96	-27.49
5	4	1	38.55	33.49
6	4	1	19.03	-16.84
7	4	1	25.07	17.81
8	4	1	56.36	53.48
10	4	1	35.34	-27.43
12	4	1	67.85	-58.11
13	4	1	30.70	-24.88
14	4	1	77.43	68.43
15	4	1	30.91	22.26
16	4	1	0.	-4.26
17	4	1	25.80	-18.57
1	5	1	21.96	13.11
2	5	1	36.97	-32.98
3	5	1	76.03	-79.83
5	5	1	44.33	40.83
6	5	1	54.22	52.06
7	5	1	53.42	-39.92
8	5	1	0.	0.73
9	5	1	36.17	26.90
10	5	1	50.81	-42.56
11	5	1	53.74	-37.99
12	5	1	67.89	59.67
13	5	1	29.09	22.59
14	5	1	41.58	39.55
15	5	1	0.	-4.12
16	5	1	45.06	-42.25
1	6	1	25.29	-17.62
2	6	1	53.95	-42.15
4	6	1	84.84	90.03
5	6	1	25.72	18.55
6	6	1	49.69	-45.46
7	6	1	26.06	-18.19
8	6	1	51.22	-41.30
11	6	1	0.	5.25
12	6	1	47.30	41.15
14	6	1	56.76	-47.07
18	6	1	40.58	45.87
1	7	1	38.32	-27.67
2	7	1	82.00	80.32
3	7	1	75.39	69.45
4	7	1	44.15	-38.99
5	7	1	78.01	-75.14
6	7	1	63.12	-62.03
7	7	1	55.03	47.44
8	7	1	37.68	31.84
9	7	1	56.15	-49.20
10	7	1	51.44	38.32
11	7	1	41.81	29.99
14	7	1	65.32	-62.72
15	7	1	0.	-4.44
16	7	1	68.33	78.66
1	8	1	29.90	25.26
3	8	1	34.04	-27.58
4	8	1	103.62	-95.92
7	8	1	31.46	-27.68
8	8	1	84.73	79.77
9	8	1	23.89	-10.92
10	8	1	39.92	-32.50
11	8	1	32.34	27.59
12	8	1	44.40	-43.61
13	8	1	46.18	-39.52
14	8	1	66.28	66.55
15	8	1	31.19	24.73
18	8	1	30.82	-32.14
2	9	1	85.77	-92.57
3	9	1	36.47	-27.29
4	9	1	73.38	78.56
5	9	1	60.73	52.73
7	9	1	58.73	-54.71
8	9	1	66.39	62.93
9	9	1	75.37	78.63
10	9	1	115.55	-126.52
11	9	1	60.65	-53.11
12	9	1	86.84	89.78
13	9	1	29.57	20.77
16	9	1	64.35	-71.79
19	9	1	0.	-4.77
1	10	1	54.78	-46.23
2	10	1	132.95	145.76
3	10	1	50.12	44.61
5	10	1	29.50	-26.07
6	10	1	42.57	33.99
7	10	1	29.87	29.59
8	10	1	92.25	-96.25
11	10	1	44.28	-42.02
12	10	1	81.12	88.35
13	10	1	51.75	49.82
14	10	1	113.91	-137.99
15	10	1	32.41	-33.63
16	10	1	53.28	56.34
18	10	1	25.18	-22.94
20	10	1	41.31	48.82
1	11	1	24.31	-17.96
2	11	1	111.92	116.94
3	11	1	38.27	34.31
4	11	1	114.39	-123.87
5	11	1	53.74	-51.34
6	11	1	28.55	24.95
7	11	1	61.16	50.32
8	11	1	78.19	-78.96
9	11	1	69.27	-65.02
10	11	1	124.62	140.99
11	11	1	59.85	53.66
12	11	1	108.91	-131.43
13	11	1	33.37	-35.25
14	11	1	33.95	33.24
19	11	1	0.	-0.01
1	12	1	74.34	78.79
2	12	1	103.88	-109.93
3	12	1	41.97	-40.25
5	12	1	26.78	23.12
6	12	1	27.42	-22.88
7	12	1	0.	-2.00
8	12	1	52.91	50.61
11	12	1	35.89	33.47
12	12	1	57.54	-58.66
13	12	1	44.48	-45.85
14	12	1	82.77	92.28
15	12	1	30.17	30.61
16	12	1	28.30	-30.86
17	12	1	26.04	-18.69
18	12	1	26.40	26.43
1	13	1	11.46	16.18
2	13	1	63.43	-63.71
3	13	1	32.24	-23.88
4	13	1	52.86	47.17
6	13	1	0.	-3.34
7	13	1	31.51	-24.34
8	13	1	46.18	43.08
9	13	1	32.39	30.11
10	13	1	62.21	-61.18
11	13	1	48.17	-45.34
12	13	1	64.04	71.13
13	13	1	31.09	27.71
15	13	1	0.	-4.62
16	13	1	27.82	-20.56
17	13	1	0.	4.83
2	14	1	26.78	7.90
4	14	1	25.49	18.69
5	14	1	0.	-1.90
12	14	1	37.54	37.46
13	14	1	34.10	31.31
14	14	1	33.85	-28.67
1	15	1	24.75	-20.63
3	15	1	27.73	27.78
4	15	1	28.12	24.53
6	15	1	42.40	-40.64
7	15	1	0.	2.85
8	15	1	37.40	31.61
10	15	1	38.85	-36.52
12	15	1	30.17	22.12
14	15	1	38.67	-41.96
1	16	1	32.02	36.73
2	16	1	25.43	18.26
4	16	1	28.27	-29.79
6	16	1	26.53	23.30
8	16	1	30.01	-33.95
3	0	2	121.71	103.44
4	0	2	40.14	5.10
5	0	2	68.07	-56.12
6	0	2	17.85	-9.36
7	0	2	51.19	45.74
8	0	2	50.81	-47.52
9	0	2	37.92	-26.00
10	0	2	32.83	21.50
11	0	2	54.68	-51.86
12	0	2	140.12	137.00
13	0	2	101.08	111.27
14	0	2	114.30	-118.22
15	0	2	84.30	-88.58
16	0	2	35.82	32.13
17	0	2	55.49	53.24
2	1	2	132.42	154.03
3	1	2	119.04	129.20
4	1	2	81.62	-64.51
5	1	2	38.59	-34.41
6	1	2	56.03	-43.98
7	1	2	103.14	83.81
9	1	2	108.65	-96.59
10	1	2	145.47	152.09
11	1	2	124.87	122.02
12	1	2	116.24	-114.70
13	1	2	73.25	-66.48
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2	2	2	27.51	-26.27
3	2	2	87.23	-96.17
4	2	2	72.28	-77.37
5	2	2	9.41	4.80
6	2	2	48.63	38.74
7	2	2	60.63	-52.15
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10	2	2	36.76	-31.10
11	2	2	52.94	50.70
12	2	2	76.55	-83.78
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14	2	2	50.04	49.68
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16	2	2	26.27	18.95
17	2	2	39.98	-41.63
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1	3	2	24.93	21.32
2	3	2	87.23	-96.17
3	3	2	59.44	-64.37
4	3	2	32.95	24.37
5	3	2	21.96	18.22
6	3	2	89.86	93.40
7	3	2	25.29	-22.61
8	3	2	69.35	-64.06
9	3	2	81.48	68.73
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11	3	2	82.04	-71.79
13	3	2	24.12	16.88
14	3	2	42.35	36.50
15	3	2	39.40	35.82
16	3	2	57.91	-55.75
17	3	2	27.74	-31.03
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2	4	2	72.28	-77.37
3	4	2	17.93	18.63
4	4	2	108.85	121.64
5	4	2	43.10	44.65
6	4	2	89.77	-93.98
7	4	2	56.47	49.91
8	4	2	32.86	-23.38
9	4	2	22.49	-10.70
10	4	2	23.92	11.53
11	4	2	25.11	-19.61
12	4	2	30.17	21.52
13	4	2	65.98	61.77
15	4	2	55.65	-46.21
16	4	2	48.08	-45.98
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1	5	2	37.00	-21.79
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3	5	2	73.45	74.35
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5	5	2	47.51	-45.10
6	5	2	100.70	-109.32
7	5	2	20.68	17.99
8	5	2	89.96	93.58
9	5	2	42.42	-36.60
10	5	2	55.02	-49.67
12	5	2	60.31	46.58
13	5	2	0.	1.64
14	5	2	53.64	-44.75
15	5	2	28.23	-28.00
16	5	2	44.41	47.23
17	5	2	30.86	30.31
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3	6	2	61.88	-62.65
4	6	2	64.75	-70.72
5	6	2	17.54	-12.11
6	6	2	60.85	62.57
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9	6	2	24.53	-22.16
10	6	2	24.22	-15.45
11	6	2	25.55	21.38
12	6	2	26.86	12.07
13	6	2	32.71	-32.28
15	6	2	31.81	31.12
18	6	2	25.32	-19.99
1	7	2	54.01	-43.01
2	7	2	60.63	-52.15
4	7	2	74.99	73.49
5	7	2	32.56	31.60
6	7	2	51.39	-44.87
7	7	2	51.33	-43.76
8	7	2	51.72	35.33
9	7	2	65.99	63.30
10	7	2	64.36	-49.62
11	7	2	25.95	-17.39
12	7	2	42.94	34.63
13	7	2	30.93	21.11
14	7	2	30.45	-29.12
17	7	2	0.	-4.15
1	8	2	34.67	-32.04
2	8	2	38.32	32.15
3	8	2	76.08	71.83
4	8	2	47.73	-48.23
5	8	2	59.27	-58.11
6	8	2	32.87	25.63
7	8	2	25.86	-23.83
8	8	2	59.11	-50.26
9	8	2	51.78	36.07
10	8	2	27.25	16.92
11	8	2	41.78	-39.73
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13	8	2	28.68	27.80
14	8	2	45.46	-37.60
15	8	2	28.06	-26.35
16	8	2	51.08	53.16
17	8	2	26.18	18.91
1	9	2	24.81	22.63
4	9	2	38.79	-29.53
5	9	2	42.41	-33.10
6	9	2	70.79	73.51
7	9	2	68.79	71.35
8	9	2	68.04	-63.99
9	9	2	50.69	-46.51
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11	9	2	26.95	24.49
12	9	2	48.53	-44.71
13	9	2	45.99	-39.21
14	9	2	51.21	41.35
15	9	2	37.62	29.20
16	9	2	27.44	-20.36
17	9	2	26.27	-19.84
2	10	2	36.76	-31.10
3	10	2	25.85	-27.47
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5	10	2	26.24	23.07
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7	10	2	35.17	25.07
8	10	2	24.87	-10.35
9	10	2	48.41	-37.49
10	10	2	0.	-4.32
13	10	2	29.56	19.42
16	10	2	36.52	-37.71
18	10	2	35.82	44.80
2	11	2	52.94	50.70
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15	11	2	29.61	-27.30
1	12	2	56.51	57.20
2	12	2	76.55	-83.78
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4	12	2	25.05	-21.66
7	12	2	39.12	-42.20
8	12	2	52.17	46.88
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3	13	2	26.42	-22.97
4	13	2	82.82	93.06
5	13	2	26.09	19.48
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9	13	2	54.99	53.10
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12	13	2	73.41	87.44
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2	14	2	50.04	49.68
3	14	2	59.13	64.07
4	14	2	36.12	33.11
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6	14	2	42.61	-15.19
7	14	2	27.80	28.23
8	14	2	54.36	-53.14
9	14	2	0.	3.15
10	14	2	36.36	28.45
11	14	2	44.01	-46.72
12	14	2	37.02	35.50
13	14	2	52.93	60.29
14	14	2	48.12	-51.16
15	14	2	38.11	-41.27
16	14	2	0.	3.12
17	14	2	23.96	17.16
2	15	2	66.65	76.79
4	15	2	30.43	-28.04
7	15	2	27.22	24.41
9	15	2	54.16	-50.93
10	15	2	55.20	56.46
11	15	2	61.40	64.98
12	15	2	39.11	-45.64
13	15	2	29.57	-28.53
1	16	2	42.97	52.58
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12	16	2	27.92	-25.49
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15	16	2	24.46	21.67
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3	1	3	63.15	50.60
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5	1	3	88.75	-78.34
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15	1	3	31.13	27.26
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5	2	3	71.15	69.92
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2	4	3	35.37	22.92
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6	11	3	46.26	36.36
7	11	3	56.47	-44.18
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9	11	3	74.76	73.19
10	11	3	50.46	-44.08
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8	13	3	27.50	18.98
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13	14	3	55.53	-48.78
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6	15	3	58.60	72.34
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9	15	3	0.	-0.89
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14	15	3	39.99	40.85
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1	16	3	0.	5.07
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4	16	3	32.51	34.64
6	16	3	25.41	-20.77
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8	16	3	31.56	35.60
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6	1	4	93.60	90.99
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1	2	4	58.79	-62.48
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7	2	4	84.42	71.18
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6	5	4	133.91	162.48
7	5	4	77.08	81.81
8	5	4	118.54	-128.53
9	5	4	49.44	-45.68
10	5	4	72.31	68.61
11	5	4	0.	4.55
12	5	4	63.03	-54.58
13	5	4	0.	-5.25
14	5	4	76.57	74.27
1	6	4	21.47	-17.02
2	6	4	91.90	-91.02
4	6	4	76.10	76.30
5	6	4	59.03	59.62
6	6	4	35.38	-34.57
7	6	4	18.10	-12.14
10	6	4	55.98	46.77
13	6	4	0.	6.12
14	6	4	43.15	32.30
1	7	4	22.83	18.00
2	7	4	63.44	48.35
3	7	4	27.46	23.49
5	7	4	19.16	-16.62
6	7	4	28.62	-23.80
7	7	4	22.81	19.04
8	7	4	26.25	23.92
9	7	4	43.97	-33.10
11	7	4	28.68	18.51
13	7	4	33.91	-27.39
1	8	4	45.92	54.05
2	8	4	22.70	-22.65
3	8	4	68.41	-69.61
4	8	4	9.45	11.69
5	8	4	57.18	49.46
6	8	4	21.15	-12.69
7	8	4	21.89	-15.70
8	8	4	30.09	19.54
9	8	4	24.02	-16.72
10	8	4	39.83	-35.26
2	9	4	21.53	-10.37
3	9	4	24.28	-22.42
4	9	4	53.70	43.55
5	9	4	64.94	63.07
6	9	4	54.59	-42.38
7	9	4	93.46	-90.52
8	9	4	52.93	46.74
9	9	4	52.54	48.22
10	9	4	49.48	-38.35
11	9	4	27.35	-22.77
12	9	4	25.95	21.01
13	9	4	35.17	33.32
1	10	4	28.07	-27.72
2	10	4	20.32	11.17
3	10	4	48.81	46.01
4	10	4	57.09	-46.64
5	10	4	55.05	-45.62
6	10	4	51.04	45.27
8	10	4	27.81	-20.04
9	10	4	37.73	27.69
11	10	4	25.71	19.09
2	11	4	20.79	-18.99
3	11	4	28.51	-28.29
5	11	4	30.26	-27.95
6	11	4	40.26	33.48
7	11	4	41.08	36.11
8	11	4	42.03	-33.77
9	11	4	27.35	22.58
11	11	4	38.08	-32.25
1	12	4	50.41	-58.72
2	12	4	25.68	20.85
3	12	4	26.65	31.44
7	12	4	27.27	26.18
8	12	4	43.77	-38.71
9	12	4	25.95	-23.39
10	12	4	38.33	32.53
11	12	4	27.17	-18.89
13	12	4	36.73	31.60
14	12	4	28.12	-26.89
1	13	4	26.02	-25.15
2	13	4	55.38	59.82
3	13	4	46.66	55.08
4	13	4	29.31	-21.85
5	13	4	24.12	-15.62
7	13	4	0.	-0.65
8	13	4	0.	2.16
9	13	4	55.52	-50.86
10	13	4	47.06	50.92
11	13	4	62.81	66.18
12	13	4	40.28	-40.90
13	13	4	48.42	-52.97
14	13	4	27.99	-20.21
1	14	4	58.86	69.16
3	14	4	30.18	-32.37
4	1	4	44.54	-8.48
7	14	4	28.16	-27.11
8	14	4	54.81	55.17
10	14	4	57.56	-59.70
11	14	4	28.03	19.44
12	14	4	0.	0.48
13	14	4	52.93	-49.30
2	1	5	22.68	-20.52
3	1	5	13.63	-19.85
4	1	5	39.34	32.91
5	1	5	49.86	40.13
6	1	5	29.32	18.23
7	1	5	88.94	-73.85
9	1	5	62.48	51.83
10	1	5	29.75	-25.62
11	1	5	51.39	-50.46
12	1	5	26.57	22.72
1	2	5	27.17	-32.41
3	2	5	21.33	17.17
4	2	5	47.32	42.06
5	2	5	48.29	-42.48
6	2	5	22.02	-11.41
7	2	5	34.48	29.76
8	2	5	64.88	-54.74
9	2	5	45.04	-31.18
10	2	5	25.54	21.73
12	2	5	22.60	13.25
1	3	5	70.27	-78.46
2	3	5	66.57	70.03
3	3	5	77.87	75.46
4	3	5	75.12	-74.03
5	3	5	72.93	-68.82
6	3	5	59.64	-54.61
7	3	5	52.37	40.59
8	3	5	28.40	22.39
9	3	5	60.65	-54.70
10	3	5	44.28	28.60
11	3	5	71.69	63.04
12	3	5	44.07	-35.58
2	4	5	20.50	-6.62
3	4	5	68.62	62.07
4	4	5	95.48	-98.57
5	4	5	43.04	-35.19
6	4	5	54.98	57.98
7	4	5	19.92	-16.16
8	4	5	52.15	48.11
9	4	5	70.21	61.33
10	4	5	54.29	-44.37
11	4	5	31.11	-27.18
12	4	5	22.02	13.68
1	5	5	49.86	40.13
2	5	5	48.29	-42.48
3	5	5	72.93	-68.82
4	5	5	43.04	-35.19
5	5	5	36.91	-36.94
7	5	5	66.78	71.63
6	5	5	127.75	147.67
7	5	5	70.26	71.63
8	5	5	112.04	-118.81
9	5	5	40.69	-29.95
10	5	5	30.17	24.51
1	6	5	56.07	51.17
2	6	5	103.49	-102.98
3	6	5	142.68	-146.98
4	6	5	144.82	158.02
5	6	5	127.75	147.67
6	6	5	65.23	-62.52
7	6	5	50.50	-44.31
8	6	5	38.59	-27.30
9	6	5	71.80	-62.43
10	6	5	46.53	36.34
11	6	5	46.31	35.98
12	6	5	25.66	13.99
1	7	5	41.47	-39.23
2	7	5	21.84	16.95
3	7	5	60.03	47.80
4	7	5	89.04	79.56
5	7	5	70.26	71.63
6	7	5	141.98	-165.48
7	7	5	135.59	-150.81
8	7	5	108.90	116.70
9	7	5	71.00	67.38
10	7	5	26.04	-17.53
11	7	5	29.94	-26.01
1	8	5	24.99	0.72
2	8	5	96.59	88.14
3	8	5	94.12	88.84
4	8	5	122.36	-125.00
5	8	5	112.03	-118.81
6	8	5	61.36	59.49
7	8	5	27.83	20.13
8	8	5	24.31	13.30
9	8	5	48.29	44.59
10	8	5	50.70	-44.45
1	9	5	26.06	26.44
2	9	5	32.33	-34.48
3	9	5	39.87	-33.67
4	9	5	51.09	-44.42
5	9	5	40.69	-29.95
6	9	5	104.03	108.23
7	9	5	71.00	71.95
8	9	5	69.66	-71.65
9	9	5	0.	3.96
10	9	5	25.11	14.75
11	9	5	34.48	-30.57
1	10	5	39.02	-41.82
2	10	5	40.32	-46.78
3	10	5	20.21	-15.16
4	10	5	74.60	66.72
5	10	5	30.17	24.51
6	10	5	23.27	-19.03
7	10	5	21.62	16.13
8	10	5	45.99	-33.07
9	10	5	52.02	-43.21
10	10	5	49.13	44.07
1	11	5	33.68	-37.34
2	11	5	20.01	14.40
3	11	5	29.91	26.09
4	11	5	0.	4.42
6	11	5	56.06	-53.59
9	11	5	37.84	-38.72
11	11	5	60.54	55.94
12	11	5	25.83	-20.39
1	12	5	48.62	58.65
2	12	5	35.59	43.87
4	12	5	45.65	-53.08
7	12	5	0.	-4.24
8	12	5	38.38	37.52
9	12	5	35.76	32.46
10	12	5	36.51	-35.12

of $Cs_3Re_3Cl_{12}$. A comparison of the internuclear distances and interbond angles common to the Re_3Cl_9 unit in each of these compounds is given in Table III. There are no significant differences between the Re_3Cl_9 moieties in the two cases.

TABLE III

COMPARISON OF DIMENSIONS OF THE Re_3Cl_9 PORTIONS OF $[Re_3Cl_{12}]^{3-}$ AND $Re_3Cl_9(P(C_2H_5)_2C_6H_5)_3$

Dimension	$[Re_3Cl_{12}]^{3-}$	$[Re_3Cl_9(P(C_2H_5)_2C_6H_5)_3]$
	Interatomic distances, Å.	
Re–Re	2.48 ± 0.01	2.493 ± 0.004
$Re–Cl_a$	2.36 ± 0.03	2.323 ± 0.017 ($Re–Cl_1$)
(out-of-plane)		2.305 ± 0.017 ($Re–Cl_2$)
$Re–Cl_b$	2.39 ± 0.03	2.395 ± 0.017 ($Re–Cl_3$)
(bridging)		2.371 ± 0.017 ($Re'–Cl_3$)
$Cl_a–Cl_a$	3.28 ± 0.05	3.257 ± 0.023 ($Cl_1–Cl_1'$)
		3.226 ± 0.023 ($Cl_2–Cl_2'$)
$Cl_a–Cl_b$	3.37 ± 0.05	3.374 ± 0.023 ($Cl_1–Cl_3$)
		3.318 ± 0.023 ($Cl_2–Cl_3$)
		3.297 ± 0.023 ($Cl_1'–Cl_3$)
		3.305 ± 0.023 ($Cl_2'–Cl_3$)
	Interbond angles, degrees	
$Re–Cl_b–Re$	62.4 ± 1.0	63.06 ± 0.43
$Cl_a–Re–Cl_a$	157.8 ± 1.5	158.89 ± 0.60

It was noted in the $[Re_3Cl_{12}]^{3-}$ structure that while the Re–Cl (out-of-plane) and Re–Cl (bridge) bonds are of about the expected length for normal Re–Cl single bonds, the three remaining Re–Cl bonds are some 0.10–0.15 Å. longer than that. Because of the evident crowding of the out-of-plane Cl atoms, it is not certain whether lengthening of the Re–Cl (in-plane) bonds occurs solely as a means of relieving crowding (which, in any case, it does do), whether it occurs only because the rhenium atoms inherently tend to form weaker bonds in these directions, or whether both of these factors contribute cooperatively to give the observed result.

The present molecule shows the same end result to an even greater degree. The Re–P distance of 2.70 Å. is 0.2–0.4 Å. more than the value which might be expected for a normal single bond. Thus, in $HRh(CO)(P(C_6H_5)_3)_3$, the Rh–P distances[13] are 2.33 ± 0.02 Å., while in *trans*-$ReOCl_3(P(C_2H_5)_2C_6H_5)_2$, they are ~2.46 Å.[14] Using the covalent radii (~1.3 Å.), suggested by Pauling[15] for ions similar to Re^{III}, a single bond distance of ~2.4 Å. would be estimated. We believe that the very long Re–P distance found here supports the view that lengthening of bonds at this position in the Re_3 cluster is the result of steric pressure operating upon a relatively weak bond.

Obviously, with as bulky a ligand as $P(C_2H_5)_2C_6H_5$, the relief of crowding among the out-of-plane chlorine atoms would lead to very severe crowding of the $P(C_2H_5)_2C_6H_5$. Here, as well as in the $[Re_3Cl_{12}]^{3-}$ case, the only way out of this situation is for one or more of the metal–ligand bonds to lengthen. Since, in both cases, such bond lengthening occurs in the same positions, it seems likely that bonds formed at this position are inherently weaker than the others. This conclusion is entirely in harmony with the report by Fergusson, Penfold, and Robinson[5] that the Re_3 cluster survives with one of these positions entirely vacant in $[Re_3Cl_{11}]^{2-}$ and is also in harmony with the approximation of predominantly square, dsp^2 hybridization of the metal atoms in this and several other metal atom clusters which was used to simplify the molecular orbital treatment[4] of the metal-to-metal bonding in those clusters.

Additional dimensions of the $Re_3Cl_9(P(C_2H_5)_2C_6H_5)_3$ are given in Table IV. Within the standard deviations, which are quite large for those involving the carbon atoms, all these dimensions appear to be reasonable.

TABLE IV

ADDITIONAL DIMENSIONS OF THE $[Re_3Cl_9(P(C_2H_5)_2C_6H_5)_3]$ MOLECULE

	Interatomic distances, Å.		
$Cl_1–P$	3.246 ± 0.025	$C_1–C_6$	1.40 ± 0.11
$Cl_2–P$	3.190 ± 0.025	$C_5–C_6$	1.39 ± 0.09
$Cl_3–P$	3.907 ± 0.025	$C_4–C_5$	1.25 ± 0.09
$Cl_3–P'$	3.588 ± 0.025	$C_3–C_4$	1.42 ± 0.11
Re–P	2.700 ± 0.019	$C_2–C_3$	1.37 ± 0.10
$P–C_1$	1.768 ± 0.082	$C_1–C_2$	1.69 ± 0.11
$P–C_7$	1.838 ± 0.069	$C_7–C_8$	1.59 ± 0.09
$P–C_9$	1.883 ± 0.065	$C_9–C_{10}$	1.68 ± 0.09
	Interbond angles, degrees		
$Cl_3–Re–P$	93.2 ± 0.6	$C_1–C_6–C_5$	121.1 ± 6.6
$Cl_3–Re'–P'$	89.8 ± 0.6	$C_6–C_5–C_4$	124.9 ± 6.3
$Re–P–C_1$	112.0 ± 2.7	$C_5–C_4–C_3$	122.7 ± 6.5
$Re–P–C_9$	109.7 ± 2.0	$C_4–C_3–C_2$	122.6 ± 7.0
$Re–P–C_7$	110.5 ± 2.2	$C_3–C_2–C_1$	109.7 ± 6.1
$C_1–P–C_7$	109.2 ± 3.4	$C_2–C_1–C_6$	114.0 ± 6.1
$C_9–P–C_7$	111.6 ± 3.0	$P–C_9–C_{10}$	101.7 ± 3.4
		$P–C_7–C_8$	112.7 ± 4.4

The new compound, $Re_3Br_9(P(C_2H_5)_2C_6H_5)_3$, has been synthesized and shown to be isomorphous with $Re_3Cl_9(P(C_2H_5)_2C_6H_5)_3$, thus establishing for the first time that the Re_3Br_9 cluster is capable of existence. Studies of this and other bromo compounds of Re^{III} will be reported elsewhere.[8]

Spectra of Re_3Cl_9 Clusters

In order to see if there might be electronic absorption bands characteristic of the Re_3Cl_9 cluster in $Re_3Cl_9X_3$ species, which would persist independently of the nature of X (this being a phosphine or Cl^- in the known compounds), the spectra of $[Re_3Cl_{12}]^{3-}$ and $Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$ have been measured.

$Cs_3Re_3Cl_{12}$ was dissolved in 12 *M* hydrochloric acid; we assume, tentatively at least, that the major if not the only Re^{III} species present is $[Re_3Cl_{12}]^{3-}$. The spectrum is shown in Fig. 2, and the numerical data are given in Table V. The spectrum of $Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$ was recorded in chloroform; the results for a 1.37×10^{-4} *M* solution for the range 10,000–25,000 cm.$^{-1}$ and for a 3.37×10^{-6} *M* solution for the range 25,000–40,000 cm.$^{-1}$ are shown in Fig. 2. A spectrum essentially identical with that obtained with $Cs_3Re_3Cl_{12}$ is obtained by dissolving $ReCl_3$ in 12 *M* hydrochloric

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[13] S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

[14] H. W. W. Ehrlich and P. G. Owston, *J. Chem. Soc.*, 4368 (1963).

[15] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 248*et. seq.*

Table V

Electronic Absorption Spectra of Some $[Re_3Cl_9X_3]$ Species and Related Data

Compound	Solvent	Concn. of $[Re_3Cl_9X_3]$, M	Energy, cm.$^{-1}$	Molar extinction, ϵ_{max}
$Cs_3[Re_3Cl_{12}]$	12 M aq. HCl	1.39×10^{-4}	12,800	468
			19,200	1,770
			25,000 (sh)	1,020
		1.39×10^{-5}	29,400	6,490
			32,300	7,570
			40,000 (sh)	18,800
$Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$	$CHCl_3$	1.37×10^{-4}	12,300	420
			18,600	1,490
			22,700 (sh)	1,400
		3.37×10^{-6}	30,000	20,100
			36,400	36,900
$(C_2H_5)_2C_6H_5P$	$CHCl_3$	2.5×10^{-3}	26,800	53
			32,500	205
		2.5×10^{-4}	37,400 (sh)	5,420
			38,500	5,870

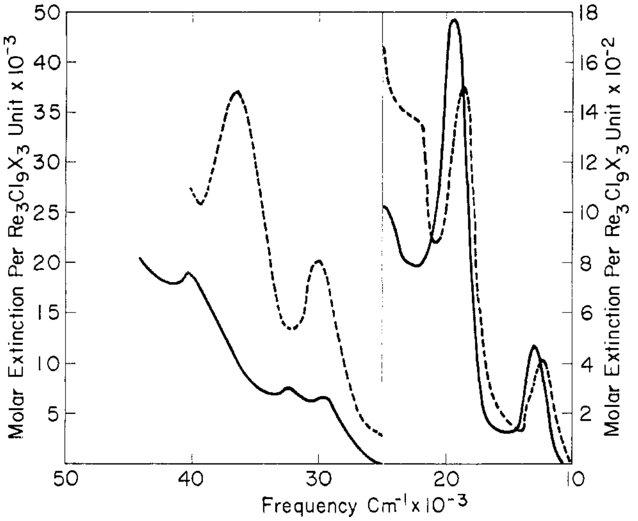

Fig. 2.—Electronic absorption spectra of $[Re_3Cl_{12}]^{3-}$ ($Cs_3Re_3Cl_{12}$ in 12 M HCl) ——— and $[Re_3Cl_9((C_2H_5)_2C_6H_5P)_3]$ in $CHCl_3$ ---------.

acid. Our spectral data agree semiquantitatively with those of Fergusson, Penfold, and Robinson[5] over the range common to both sets of measurements.

In order to estimate how much of the ultraviolet absorption of $Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$ is due to the $(C_2H_5)_2C_6H_5P$ groups, the spectrum of this ligand was recorded in the same solvent. The results are given in Table V. We conclude with some certainty that the following absorption maxima are qualitatively characteristic of the Re_3Cl_9 group: 12,000–14,000 cm.$^{-1}$, $300 < \epsilon < 500$; 18,000–20,000 cm.$^{-1}$, $1500 < \epsilon < 1800$. Because of the possibility of changes in the spectrum of $(C_2H_5)_2C_6H_5P$ when it becomes coordinated (*e.g.*, its strong band at 38,500 cm.$^{-1}$ is shifted to 36,400 cm.$^{-1}$) and because there may be charge-transfer bands involving the ligands X in $Re_3Cl_9X_3$, no further specifications of "characteristic" bands seem certain enough to be included. At present we cannot propose any specific assignments for these bands; the published molecular orbital treatment,[4] which was intended only to deal qualitatively with the metal-to-metal bonding, is, of course, much too crude to be useful for spectral assignments. While the structure of $Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$, of course, precludes measurement of the polarization of the bands, such measurements will be made on $Cs_3Re_3Cl_{12}$. With this additional data and a more refined theory, some reasonably certain assignments may be possible.

It was found that while the spectrum of $Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$ appears to obey Beer's law to within the limits of error in the visible region, there are small but detectable deviations in the ultraviolet. The most distinct effect occurs for the strong ultraviolet band. This is at 275 mμ with an ϵ_{max} of 12,300 per $(C_2H_5)_2C_6H_5P$ unit, for concentrations of $Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$ of 3.37×10^{-6} M or greater, but changes steadily upon dilution until at a concentration of 8.37×10^{-7} M it is at 266 mμ with an ϵ_{max} of 9750 per $(C_2H_5)_2C_6H_5P$. Although unquestionably real, these changes are too small to provide sufficiently accurate numerical differences for a quantitative treatment. Qualitatively, however, we believe they are subject to the following interpretation. $Re_3Cl_9((C_2H_5)_2C_6H_5P)_3$ dissociates into $Re_3Cl_9(C_2H_5C_6H_5P)_{3-n} + n(C_2H_5)_2C_6H_5P$, where n is at least 1, and possibly greater. Thus the ultraviolet band shifts both in position and in intensity toward the values for free $(C_2H_5)_2C_6H_5P$ as dilution occurs.

Since chloroform has little if any significant tendency to serve as an electron-pair donor, we assume that the $Re_3Cl_9((C_2H_5)_2C_6H_5P)_{3-n}$ species simply have vacant positions where the n-$(C_2H_5)_2C_6H_5P$ groups have left. This is, of course, in complete accord with the findings of Fergusson, Penfold, and Robinson[5] regarding the structure of $[Re_3Cl_{11}]^{2-}$. The failure to find any detectable effect of the dissociation in the visible region is in accord with the relative insensitivity of the visible bands to the identity of the groups X in $Re_3Cl_9X_3$, or even to their presence or absence.[5]