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Structure of Hydridochlorobis(diphenylethylphosphine)platinum[1]

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The crystal and molecular structure of hydridochlorobis(diphenylethylphosphine)platinum, $PtHCl[P(C_6H_5)_2C_2H_5]_2$, has been determined from three-dimensional X-ray data. The material crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions $a = 11.80$, $b = 16.93$, $c = 14.31$ Å., $\beta = 108.4°$. The individual monomeric molecules are well separated, the closest Pt–Pt distance being greater than 9 Å. The phosphorus atoms are *trans* to one another and with the chlorine lie at three of the four corners of an approximate square, with the platinum in the center. In agreement with results reported previously for a similar bromo compound, the Pt–P distances are shorter and the Pt–halogen distance longer than are calculated from the usual radii-sum rules. The Pt–halogen lengthening is consistent with the high lability of the halogen *trans* to a hydrogen. The platinum, phosphorus, and chlorine atoms deviate slightly, but significantly, from coplanarity.

Introduction

The nature of the metal–hydrogen bond in transition metal hydrides has received renewed attention and re-interpretation in the past few years, primarily as the result of the discovery of new classes of stable transition metal hydrides[3] and because diffraction studies[4-9] have shown that in such compounds the hydrogen exerts an important influence on the stereochemistry. This influence was not apparent in earlier chemical[10,11] and spectroscopic studies.[12-14] Of paramount importance in this re-interpretation of the metal–hydrogen bond was the determination by Owston, Partridge, and Rowe[4] of the structure of hydridobromobis(triethylphosphine)platinum. They showed that the *trans* P and Br atoms are at three of the four corners of a square, with the Pt at the center. They found the Pt–P distances to be shorter and the Pt–Br distance to be longer than those predicted from radii-sum rules. Although they obtained no direct evidence for the hydrogen atom location, it seems clear that hydrogen is occupying the fourth corner of the square, for otherwise there would be no reason for the other atoms to be situated at three of the four corners of a square. Their determination of the structure was hampered considerably by the X-ray sensitivity of the crystals, and accordingly it was based on minimal zonal data. Because of this, the limits of error are very high, being ±0.07 Å. for Pt–P and ±0.04 Å. for Pt–Br. The light atoms were not located with any accuracy.

Because of the central role played by this structure determination in the revision of ideas concerning the stereochemical influence of hydrogen in transition metal hydrides, a determination to much higher accuracy on a similar compound seems worthwhile. In addition it is important to establish the bond distances with higher accuracy for use in an eventual description of the bonding and there is the possibility, though faint, that the hydride hydrogen might be located directly. In this report on the structure of hydridochlorobis(diphenylethylphosphine)platinum we indeed do define the geometrical arrangement with much higher accuracy, but we fail to provide direct evidence concerning the hydrogen position.

Collection and Reduction of the X-Ray Data

The white crystals of $PtHCl[P(C_6H_5)_2C_2H_5]_2$ were prepared by H. B. Gray using the method described

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(3) See, for example, J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

(4) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

(5) P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

(6) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

(7) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, in press.

(8) S. J. La Placa, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964).

(9) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

(10) W. Hieber, *Die Chemie*, **55**, 24 (1942).

(11) W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 339 (1958).

(12) W. E. Wilson, *ibid.*, **13b**, 349 (1958).

(13) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

(14) E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *ibid.*, 2484 (1959).

by Chatt, Duncanson, and Shaw.[15] The crystals are air stable; of more importance, we observed none of the signs of decomposition in the X-ray beam found by Owston, *et al.*,[4] for the related Br compound. On the basis of an optical examination and of precession and Weissenberg photographs the crystals were found to belong to the monoclinic system. The cell has the dimensions $a = 11.80 \pm 0.02$, $b = 16.93 \pm 0.03$, $c = 14.31 \pm 0.02$ Å., $\beta = 108.4 \pm 0.3°$, $V = 2713$ Å.^{3}. An experimental density of 1.60 g./cm.^{3}, obtained by flotation in zinc bromide solution, is in good agreement with a density of 1.616 g./cm.^{3} calculated for four molecules in the unit cell. The systematic extinctions $0k0$ for k odd and $h0l$ for l odd strongly favor the space group C_{2h}^5-$P2_1/c$. Thus all atoms are in general positions and no symmetry need be imposed on the molecule.

Intensity data were collected at room temperature by the equi-inclination Weissenberg technique, using Zr-filtered Mo Kα radiation. The crystal was mounted with b as the rotation axis, and the layers $h0l$ to $h14l$ were recorded. The intensities of 1711 independent reflections accessible within the angular range $\theta_{\text{Mo}} \leq 20°$ were estimated visually. After the usual Lorentz-polarization factor had been applied, the resultant F_o^2 values (where F_o is the observed structure amplitude) were corrected for absorption. For this purpose the six faces of the crystal were identified by a combination of Weissenberg photography and optical goniometry and were carefully measured. Even though the calculated volume of the crystal is only 0.00715 mm.^{3} and the calculated weight 11.6 μg., the resultant transmission coefficients for a linear absorption coefficient of 56.95 cm.$^{-1}$ range from about 0.17 to 0.59.[16] Thus the obvious fact is re-emphasized that absorption corrections are essential if one is going to achieve high accuracy in problems of this sort. The F_o values were subsequently brought to an approximate common scale through a modification of Wilson's procedure.

Solution and Refinement of the Structure

The position of the Pt atom was readily determined from a three-dimensional Patterson function. Although the positions of the Cl and P atoms undoubtedly could have been determined from the same function, it was deemed more economical in time to phase a difference Fourier with the Pt contributions. In this difference Fourier the positions of the P and Cl atoms were readily apparent. The positions of all of the carbon atoms were located in a second difference Fourier based on phases obtained from the refined positions of the heavy atoms.

The structure was refined by the least-squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weights w were assigned in the following way: $F \leqslant 30$ e, $w = (F/30)^2$; $30 < F < 80$ e, $w = 1$; $F \geqslant 80$ e, $w = (80/F)^2$. The atomic scattering factors for the neutral atoms tabulated by Ibers[17] were used. The anomalous parts of the Pt, P, and Cl scattering factors were obtained from Templeton's tabulation[18] and were included in the calculated structure factors.[19] Contributions of the hydrogen atoms to the structure factors were ignored. Initially the refinement was carried out with the phenyl rings constrained to their normal geometry (D_{6h} symmetry, C–C = 1.392 Å.), using the group-refinement procedure described previously.[6,7] Each ring was assigned a single, variable isotropic thermal parameter and six variable positional parameters. These are the fractional coordinates x_c, y_c, z_c of the ring center and three angles δ, ϵ, and η which are successive counterclockwise rotations about the internal axes $\mathbf{a}_2'$, $\mathbf{a}_1'$, and $\mathbf{a}_3'$ which bring about the alignment (except for translation) of this orthogonal internal coordinate system $\mathbf{a}'$ with an external orthogonal coordinate system $\mathbf{A}$. The origin of the internal system is taken at the ring center, with $\mathbf{a}_3'$ normal to the ring and $\mathbf{a}_1'$ intersecting a vertex. The external coordinate system has $\mathbf{A}_2$ parallel to $\mathbf{a}_2$, $\mathbf{A}_1$ parallel to $\mathbf{a}_2 \times \mathbf{a}_3$, and $\mathbf{A}_3$ parallel to $\mathbf{A}_1 \times \mathbf{A}_2$, where $\mathbf{a}$ is the original monoclinic coordinate system. This initial refinement of the rings together with the other atoms, each of which was assigned a variable isotropic thermal parameter, converged rapidly to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.11 for the 60 positional and thermal parameters. A difference Fourier based on this refinement provided evidence for anisotropic thermal motion of the heavy atoms. After correction of several indexing errors, a further group refinement was carried out in which the Pt, P, and Cl atoms were assigned anisotropic thermal parameters, but the ethyl carbon atoms were assigned isotropic thermal parameters. This refinement of 80 positional and thermal parameters converged to an R factor of 0.077 and to a weighted R factor R' [$R' = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$] of 0.098.

The obvious advantages of the group refinement are rapid convergence and minimization of computer time through the reduction of the number of variables. We have contended[7] that an additional important advantage is that physically reasonable information can be included in the refinement, and we believe this to be preferable to imposing, for example, no constraints on the phenyl ring geometries, especially since elucidation of an unknown aspect of the structure may suffer less from correlation with errors of assumption than it would from correlation with experimental errors of measurement for the alternative full determination. In previous problems,[7,20,21] because of their size, it has not been possible to compare the unrestricted and group refinements. In the present case, however, the un-

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[15] J. Chatt, L. A. Duncanson, and B. L. Shaw, *Proc. Chem. Soc.*, 343 (1957).

[16] Programs for the IBM 7090 used in this work were local modifications of Burnham's GNABS absorption program, Zalkin's FORDAP Fourier program, and the Busing–Levy ORFLS least-squares program, together with various local programs.

[17] J. A. Ibers, "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. 3, Table 3.3.1.

[18] D. H. Templeton, *ibid.*, Table 3.3.2C.

[19] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

[20] J. A. Ibers and S. J. La Placa, *Science*, **145**, 920 (1964).

[21] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $PtHCl[P(C_6H_5)_2C_2H_5]_2$

Atom	x	y	z	β_{11}[a] or B (Å.^{2})	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.17910 (9)[b]	0.41664 (7)	0.28903 (8)	0.00423 (8)	0.00262 (5)	0.00544 (6)	−0.00045 (6)	0.00164 (6)	−0.00007 (6)
Cl	0.2588 (7)	0.4506 (6)	0.4619 (5)	0.0094 (7)	0.0067 (5)	0.0052 (5)	−0.0030 (5)	0.0019 (5)	−0.0010 (4)
P_1	−0.0015 (6)	0.3837 (5)	0.3022 (5)	0.0059 (6)	0.0026 (4)	0.0049 (4)	−0.0003 (4)	0.0010 (4)	−0.0002 (3)
P_2	0.3438 (5)	0.4567 (5)	0.2526 (5)	0.0040 (6)	0.0025 (4)	0.0059 (4)	0.0000 (3)	0.0014 (4)	0.0000 (3)
P_1EC_1[c]	−0.010 (2)	0.362 (2)	0.427 (2)	3.9 (6)					
P_1EC_2	0.060 (3)	0.281 (3)	0.459 (3)	7.0 (9)					
P_2EC_1	0.485 (2)	0.467 (2)	0.354 (2)	3.5 (5)					
P_2EC_2	0.527 (3)	0.389 (2)	0.406 (2)	6.3 (8)					

Group	x_c[d]	y_c	z_c	δ	ϵ	η	B (Å.^{2})
P_1R_1[e]	−0.1251 (12)	0.2284 (10)	0.1840 (9)	4.32 (1)	6.09 (1)	3.48 (1)	4.5 (3)
P_1R_2	−0.1870 (12)	0.5261 (9)	0.2273 (10)	4.39 (7)	4.87 (1)	5.28 (7)	4.8 (3)
P_2R_1	0.4306 (11)	0.3515 (10)	0.0985 (9)	2.45 (1)	0.31 (1)	5.34 (1)	4.6 (3)
P_2R_2	0.3063 (14)	0.6263 (11)	0.1468 (11)	1.90 (1)	5.93 (1)	3.62 (1)	5.8 (4)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [c] P_1EC_1 refers to ethyl carbon number one on P_1, etc. [d] x_c, y_c, z_c are fractional coordinates of the ring centers. The angles δ, ϵ, η (in radians) are defined in the text. [e] P_1R_1 is ring 1 on P_1, etc.

restricted refinement is feasible and for the sake of comparison it was carried out. In this calculation no geometrical restrictions were placed on the phenyl rings, and each carbon of a phenyl ring was assigned an individual, variable thermal parameter. (Again the Pt, P, and Cl atoms were assigned anisotropic thermal parameters.) This refinement of 148 positional and thermal parameters converged to an R value of 0.076 and an R' value of 0.094. It is not possible to assess directly the significance of this improvement in the usual way,[22] for both the positional and thermal constraints have been removed. However, several remarks of some interest can be made from the detailed comparisons of the results of the two refinements. First, and most important, no significant shifts occurred in the parameters of the nongroup atoms; in fact, the largest shift is less than a standard deviation. Second, as expected, the distribution of the unrestricted C–C distances in the phenyl rings follows essentially a normal error curve, with C–C distances ranging from 1.30 to 1.49 Å. and averaging 1.41 ± 0.01 Å. Clearly this wide distribution, which shows no discernible trend with position in the rings, results from errors in the intensity data, rather than from forces in the crystal, and reinforces our view that if one knows geometries better than he can determine them, then this information should be put into the refinement. Third, the group refinement requires 11 min. of IBM 7094 time per cycle; the unrestricted refinement requires 24 min. per cycle.

TABLE II

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a]

Group atom			
$P_1R_1C_1$	−0.073 (2)	0.298 (1)	0.230 (1)
$P_1R_1C_2$	−0.001 (1)	0.236 (1)	0.216 (1)
$P_1R_1C_3$	−0.054 (2)	0.167 (1)	0.171 (1)
$P_1R_1C_4$	−0.178 (2)	0.159 (1)	0.138 (1)
$P_1R_1C_5$	−0.249 (1)	0.221 (1)	0.152 (1)
$P_1R_1C_6$	−0.196 (2)	0.290 (1)	0.197 (1)
$P_1R_2C_1$	−0.111 (2)	0.462 (1)	0.260 (1)
$P_1R_2C_2$	−0.132 (2)	0.491 (1)	0.165 (1)
$P_1R_2C_3$	−0.209 (2)	0.554 (1)	0.132 (1)
$P_1R_2C_4$	−0.263 (2)	0.590 (1)	0.194 (1)
$P_1R_2C_5$	−0.242 (2)	0.562 (1)	0.290 (1)
$P_1R_2C_6$	−0.165 (2)	0.498 (1)	0.323 (1)
$P_2R_1C_1$	0.393 (2)	0.398 (1)	0.164 (1)
$P_2R_1C_2$	0.347 (2)	0.322 (1)	0.140 (1)
$P_2R_1C_3$	0.384 (2)	0.276 (1)	0.075 (1)
$P_2R_1C_4$	0.468 (2)	0.305 (1)	0.033 (1)
$P_2R_1C_5$	0.514 (2)	0.381 (1)	0.057 (1)
$P_2R_1C_6$	0.477 (2)	0.427 (1)	0.123 (1)
$P_2R_2C_1$	0.324 (2)	0.553 (1)	0.194 (2)
$P_2R_2C_2$	0.220 (2)	0.568 (1)	0.116 (2)
$P_2R_2C_3$	0.202 (2)	0.641 (1)	0.070 (1)
$P_2R_2C_4$	0.289 (2)	0.699 (1)	0.100 (2)
$P_2R_2C_5$	0.393 (2)	0.685 (1)	0.177 (2)
$P_2R_2C_6$	9.411 (2)	0.612 (1)	0.224 (1)

[a] C_1 is attached to P; other C atoms are numbered in succession so that C_4 is *para* to C_1.

Because of our feeling that the results of the group refinement are to be preferred on physical grounds, we give in Table I the parameter values obtained from it, together with the standard deviations of the parameters as estimated from the inverse matrix. In Table II the carbon atom positions of the phenyl rings are listed. These were derived from the data of Table I. The standard deviations in Table II are meant to be used in error analyses of functions not involved in the same ring; obviously the intra-ring distances, for example, are fixed. In Table III the values of $10F_o$ and $10|F_c|$ (in electrons) are listed for the 1711 reflections used in the refinement. None of the unobserved reflections accessible on the films has a calculated intensity which exceeds our estimate of the minimum observable, and hence these reflections are omitted from Table III.

The anisotropic thermal parameters can be interpreted in terms of real amplitudes of vibration, since they are essentially uncorrelated with the scale factors. (Note that in the partial anisotropic refinement the 28 carbon atoms, a reasonable fraction of the scattering power, were restricted to isotropic vibration.) In Table IV the principal values of the root-mean-square amplitudes of vibration are listed. The orientations of the thermal ellipsoids, which may be derived from

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(22) W. C. Hamilton, *Acta Cryst.*, in press.

TABLE III: OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 10) FOR $PtHCl[P(C_6H_5)_2C_2H_5]_2$

H	L	OBS	CAL
******K= 0******			
0	0		11663
0	4	1241	1423
0	8	834	917
0	10	826	675
0	12	1038	988
1	4	753	811
1	6	1948	2131
1	8	1445	1424
1	10	1494	1511
1	12	605	612
1	-4	2581	2840
1	-6	2205	2001
1	-8	313	227
1	-12	286	314
2	2	3088	3365
2	4	2740	2575
2	6	1750	1439
2	8	760	785
2	12	446	368
2	-4	1613	1418
2	-6	1615	1594
2	-8	1302	1217
2	-10	1063	995
2	-12	891	790
3	0	2265	2145
3	2	486	555
3	6	724	692
3	8	469	398
3	10	1018	860
3	-2	1940	2216
3	-4	858	822
3	-6	719	697
3	-8	384	437
3	-10	588	554
3	-12	941	970
4	0	915	617
4	4	1323	1331
4	6	1187	1029
4	8	914	830
4	10	451	486
4	-2	1970	2157
4	-4	2531	2538
4	-6	1777	1714
4	-8	2127	1871
4	-10	844	881
4	-12	563	571
5	0	2266	2193
5	2	1952	2071
5	4	1441	1516
5	6	517	580
5	8	318	284
5	-2	1882	1773
5	-4	318	270
5	-6	787	834
5	-8	2058	2279
5	-10	1537	1626
5	-12	1002	927
6	0	2363	2227
6	2	1583	1601
6	8	935	773
6	-2	2300	2540
6	-4	1615	1694
6	-6	922	1024
6	-10	272	401
6	-12	906	722
7	0	347	210
7	2	833	749
7	4	1162	1343
7	6	1295	1236
7	-2	838	749
7	-4	1611	1869
7	-6	1192	1241
7	-8	997	1071
7	-10	285	336
8	0	881	903
8	2	1385	1389
8	4	817	835
8	6	404	531
8	-2	974	928
8	-4	334	336
8	-6	427	396
8	-8	660	627
8	-10	1268	1210
8	-12	709	640
9	0	871	876
9	-2	931	987
9	-4	1306	1198
9	-6	672	611
9	-8	453	413
10	0	382	336
10	2	833	821
10	-4	1073	1110
10	-6	1358	1394
10	-8	1410	1355
10	-10	1210	1180
11	-2	797	822
11	-4	608	736
******K= 1******			
0	3	998	1091
0	4	446	619
0	5	2088	2298
0	6	1208	1263
0	7	1696	1789
0	8	932	940
0	9	877	883
0	10	236	302
0	11	502	473
1	3	1905	2129
1	4	648	737
1	5	2320	2340
1	6	684	700
1	7	672	734
1	11	519	524
1	12	475	405
1	-4	1419	1296
1	-6	556	506
1	-7	1220	1205
1	-8	474	430
1	-9	729	660
1	-10	399	416
1	-11	939	802
1	-12	449	445
1	-13	388	390
2	2	371	308
2	3	512	509
2	4	343	391
2	5	767	812
2	6	611	602
2	7	1042	1028
2	8	642	629
2	9	1118	1116
2	10	777	743
2	11	1124	1138
2	12	404	383
2	-3	526	533
2	-4	818	780
2	-5	1486	1671
2	-6	733	757
2	-7	588	663
2	-9	301	333
2	-11	241	309
2	-12	361	343
2	-13	859	741
3	0	242	237
3	1	570	459
3	2	1231	981
3	3	1308	1266
3	4	1052	1211
3	5	1812	1926
3	6	580	519
3	7	876	881
3	8	491	479
3	9	724	729
3	-2	495	524
3	-3	1900	1900
3	-4	314	287
3	-5	1173	1100
3	-6	624	593
3	-7	1513	1466
3	-8	801	891
3	-9	1004	978
3	-10	507	565
3	-11	629	592
3	-12	359	383
4	0	1045	962
4	1	1246	1242
4	2	816	768
4	3	1159	1197
4	4	866	789
4	5	236	291
4	9	277	284
4	10	289	251
4	-1	2170	2147
4	-2	1351	1381
4	-3	1253	1216
4	-5	664	631
4	-7	279	358
4	-8	294	350
4	-9	1252	1246
4	-10	844	740
4	-11	1116	974
4	-12	570	504
4	-13	946	885
5	0	1079	850
5	1	1244	1029
5	2	553	381
5	3	265	252
5	4	454	455
5	5	822	787
5	6	541	523
5	7	755	736
5	8	576	477
5	9	837	852
5	-1	2095	1762
5	-2	1392	1390
5	-3	2396	2679
5	-4	896	892
5	-5	1933	2152
5	-6	1135	1158
5	-7	1627	1824
5	-8	514	524
5	-13	607	567
6	0	299	348
6	1	1389	1208
6	2	749	696
6	3	1826	1926
6	4	803	874
6	5	1248	1339
6	6	707	736
6	7	950	920
6	8	444	458
6	-1	945	779
6	-3	943	855
6	-4	791	773
6	-5	1174	1186
6	-6	572	564
6	-7	1173	1357
6	-8	735	810
6	-9	1095	1316
6	-10	349	352
6	-11	362	345
7	0	997	762
7	1	2024	1865
7	2	969	989
7	3	1232	1280
7	4	573	536
7	5	329	355
7	-1	1686	1529
7	-2	454	636
7	-3	1507	1572
7	-4	463	416
7	-5	507	448
7	-9	659	594
7	-10	258	298
7	-11	850	749
7	-12	390	378
8	3	511	533
8	5	515	575
8	-1	458	441
8	-2	477	487
8	-3	1313	1135
8	-4	674	601
8	-5	1311	1135
8	-6	617	608
8	-7	702	623
8	-8	267	299
8	-9	269	342
9	1	928	913
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5	8	607	697
5	-1	1512	1222
5	-2	495	472
5	-3	2158	1860
5	-4	1018	861
5	-5	1367	1241
5	-6	684	695
5	-7	860	900
5	-9	216	234
5	-12	349	365
6	0	464	432
6	1	617	503
6	2	637	639
6	3	1076	1084
6	4	474	526
6	5	878	920
6	6	396	465
6	7	678	738
6	-1	271	363
6	-2	361	400
6	-4	438	441
6	-5	829	757
6	-6	882	857
6	-7	1031	1026
6	-8	563	637
6	-9	1144	1074
6	-10	470	454
6	-11	576	526
7	0	632	563
7	1	1246	1223
7	2	522	469
7	3	981	913
7	4	304	395
7	5	304	360
7	-1	1478	1275
7	-2	407	373
7	-3	1109	1076
7	-4	248	273
7	-5	532	519
7	-7	232	73
7	-8	332	344
7	-9	566	676
7	-10	348	376
7	-11	735	827
8	0	590	568
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8	-2	716	714
8	-3	854	907
8	-4	393	448
8	-5	1034	1032
8	-6	659	672
8	-7	845	818
8	-8	357	353
8	-9	255	323
8	-10	367	395
9	0	726	743
9	1	627	678
9	2	323	393
9	-5	657	619
9	-7	801	822
9	-8	474	487
9	-9	873	907
10	-2	718	664
10	-3	662	640
10	-4	337	481
10	-5	456	530
10	-6	440	461
******K= 8******			
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0	5	255	216
0	6	363	133
0	7	453	408
0	8	382	225
0	9	830	871
0	10	218	139
0	11	815	770
1	2	252	287
1	3	256	279
1	4	287	304
1	5	854	926
1	6	650	654
1	7	963	1027
1	8	282	336
1	9	994	933
1	10	319	351
1	-3	1543	1926
1	-4	575	646
1	-5	1326	1335
1	-6	1262	1103
1	-7	834	911
1	-8	437	424
1	-9	663	722
1	-10	212	271
2	0	1596	1523
2	1	1273	1288
2	2	1185	1219
2	3	1587	1731
2	4	1112	1064
2	5	1225	1156
2	6	620	653
2	7	878	886
2	-1	216	196
2	-2	161	131
2	-3	170	232
2	-4	263	244
2	-5	1077	1025
2	-6	525	460
2	-7	884	944
2	-8	714	761
2	-9	1031	1010
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2	-11	737	650
3	0	951	883
3	1	1850	1726
3	2	714	674
3	3	752	743
3	4	434	417
3	5	557	514
3	6	203	237
3	9	530	514
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3	-2	1048	991
3	-3	1633	1518
3	-4	370	405
3	-5	817	851
3	-6	163	232
3	-7	246	324
3	-8	457	511
3	-10	494	525
3	-11	620	642
4	0	496	338
4	3	1156	1112
4	4	467	434
4	5	1162	1160
4	6	386	353
4	7	1108	1113
4	8	542	599
4	-1	491	424
4	-2	1404	1082
4	-3	1074	919
4	-4	1184	1071
4	-5	1289	1335
4	-6	741	814
4	-7	896	887
4	-8	471	455
4	-9	642	719
5	1	1823	1690
5	2	539	492
5	3	1235	1284
5	4	408	479
5	5	798	782
5	6	245	325
5	7	253	285
5	-1	1225	1090
5	-3	275	296
5	-4	321	349
5	-5	434	511
5	-6	374	402
5	-7	783	774
5	-8	513	516
5	-9	849	899
5	-10	218	388
5	-11	761	778
6	0	363	361
6	1	881	833
6	2	273	349
6	5	265	256
6	-1	1399	1346
6	-2	1022	942
6	-3	1289	1263
6	-4	672	593
6	-5	997	904
6	-6	457	464
6	-8	367	398
6	-9	219	272
6	-11	639	625
7	0	469	399
7	1	480	450
7	2	681	675
7	3	590	586
7	4	583	607
7	5	819	821
7	-1	605	474
7	-3	982	1038
7	-4	741	731
7	-5	1167	1140
7	-6	629	610
7	-7	1070	1116
7	-8	534	588
7	-9	668	698
7	-10	238	223
8	0	725	726
8	1	1204	1194
8	2	952	830
8	3	770	784
8	-1	993	1014
8	-2	410	431
8	-3	400	456
8	-6	350	376
8	-7	575	588
8	-8	488	443
8	-9	551	596
9	0	590	538
9	1	521	500
9	-1	1230	1174
9	-2	422	604
9	-3	1208	1167
9	-4	659	627
9	-5	1116	1097
9	-7	629	635
******K= 9******			
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0	4	1263	1425
0	5	223	12
0	6	1224	1235
0	8	1051	1085
0	9	309	125
0	10	583	492
1	2	1652	1780
1	4	1218	1283
1	6	367	381
1	7	198	346
1	10	241	297
1	-5	381	421
1	-6	437	469
1	-8	740	814
1	-10	1074	1052
2	0	1655	1621
2	2	569	622
2	5	530	522
2	6	397	453
2	7	366	414
2	8	810	852
2	9	239	240
2	-2	1811	2177
2	-4	1716	1790
2	-6	988	1053
2	-8	560	439
3	0	420	315
3	2	1319	1235
3	4	1495	1443
3	5	588	549
3	6	1203	1188
3	8	708	788
3	-3	439	439
3	-4	1058	1063
3	-6	1482	1357
3	-7	322	296
3	-8	1264	1231
3	-9	211	51
3	-10	727	735
4	0	2003	1785
4	2	1805	1677
4	4	1021	995
4	6	532	533
4	-1	311	245
4	-2	1351	1159
4	-3	791	725
4	-4	827	777
4	-5	251	211
4	-7	194	178
4	-8	409	433
4	-9	215	263
4	-10	668	706
5	0	1024	866
5	1	458	421
5	3	500	455
5	4	603	608
5	6	747	746
5	-1	259	177
5	-2	1471	1261
5	-3	207	202
5	-4	1487	1400
5	-5	277	299
5	-6	916	887
5	-8	478	493
6	0	470	479
6	2	876	849
6	4	951	918
6	6	821	881
6	-2	259	20
6	-3	477	370
6	-4	682	772
6	-5	379	305
6	-6	1097	1129
6	-7	442	361
6	-8	1117	1135
6	-10	873	917
7	0	1387	1307
7	1	415	369
7	2	900	879
7	4	438	511
7	-2	949	845
7	-3	269	264
7	-4	637	603
7	-8	484	459
7	-10	747	725
8	0	600	582
8	-2	1187	1187
8	-4	1189	1233
8	-6	1002	1099
8	-8	636	688
9	-1	312	363
9	-5	300	289
9	-6	609	768
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0	7	203	27
0	8	488	492
0	9	405	301
0	10	592	594
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1	3	414	431
1	4	328	411
1	5	642	709
1	6	572	592
1	7	821	805
1	8	643	660
1	9	707	707
1	-3	948	1196
1	-4	978	1135
1	-5	1178	1309
1	-6	577	653
1	-7	990	1012
1	-8	599	589
1	-9	541	500
2	1	1037	1153
2	2	903	917
2	3	1194	1185
2	4	458	462
2	5	970	1006
2	6	527	528
2	7	454	429
2	8	241	240
2	9	256	181
2	-1	796	848
2	-3	137	197
2	-4	439	460
2	-5	681	673
2	-6	640	658
2	-7	1051	1098
2	-8	541	579
2	-9	1099	1080
2	-10	536	552
3	0	1126	966
3	1	1383	1302
3	2	598	610
3	3	863	805
3	4	210	239
3	5	220	227
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3	-1	1651	1613
3	-2	950	947
3	-3	1469	1438
3	-4	1224	1176
3	-5	899	847
3	-6	374	394
3	-9	391	481
3	-10	240	256
4	2	529	420
4	3	626	619
4	4	532	521
4	5	823	862
4	6	604	666
4	7	850	916
4	-1	785	691
4	-3	1144	1071
4	-4	416	376
4	-5	1338	1146
4	-6	470	467
4	-7	807	787
4	-8	310	408
4	-9	327	353
4	-10	243	267
5	0	784	682
5	1	1231	978
5	2	934	913
5	3	1097	1039
5	4	535	516
5	5	815	860
5	-1	680	568
5	-2	619	564
5	-3	383	328
5	-4	367	341
5	-5	420	321
5	-6	508	533
5	-7	641	685
5	-8	513	394
5	-9	593	604
5	-10	500	490
6	0	499	480
6	1	735	653
6	-1	1121	970
6	-2	478	403
6	-3	1036	1040
6	-4	340	323
6	-5	701	688
6	-7	237	311
7	3	471	506
7	-2	439	472
7	-3	574	588
7	-4	384	358
7	-5	1115	1114
7	-6	767	685
7	-7	1133	1055
7	-8	518	492
7	-9	769	813
8	0	639	534
8	1	1095	1099
8	-1	897	759
8	-2	326	364
8	-3	319	383
8	-4	427	349
8	-7	482	541
******K=11******			
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0	5	855	867
0	6	494	547
0	7	970	940
0	8	314	287
0	9	757	624
1	2	648	737
1	3	1036	1240
1	4	478	514
1	5	462	486
1	-3	256	327
1	-4	295	324
1	-5	400	433
1	-7	200	277
1	-8	483	420
1	-9	819	750
2	0	642	636
2	1	863	927
2	2	165	167
2	3	248	290
2	6	375	372
2	7	400	458
2	8	425	424
2	-1	1114	1349
2	-2	1050	1201
2	-3	1301	1642
2	-4	986	1076
2	-5	1281	1277
2	-6	542	507
2	-7	813	803
3	0	315	191
3	1	624	621
3	2	454	476
3	3	1054	1101
3	4	727	717
3	5	991	989
3	6	568	633
3	7	1074	997
3	-1	272	236
3	-2	420	417
3	-3	575	598
3	-4	707	694
3	-5	968	998
3	-6	1018	1003
3	-7	878	877
3	-8	656	671
3	-9	829	787
3	-10	244	271
4	0	832	669
4	1	1819	1542
4	2	980	894
4	3	1070	1018
4	4	786	715
4	5	625	668
4	6	259	266
4	-1	1187	1063
4	-2	517	430
4	-3	1075	977
4	-4	189	76
4	-5	274	271
4	-6	285	220
4	-7	424	390
4	-8	446	520
4	-9	407	427
4	-10	350	360
5	0	384	325
5	3	270	304
5	5	391	509
5	-1	900	791
5	-2	586	531
5	-3	917	829
5	-4	373	417
5	-5	898	817
5	-7	389	395
5	-9	243	237
6	1	951	787
6	2	311	329
6	3	731	775
6	4	302	368
6	-2	279	190
6	-3	258	253
6	-5	1120	1032
6	-6	530	541
6	-7	1150	995
6	-8	552	470
6	-9	665	688
7	0	533	477
7	1	705	703
7	2	328	336
7	-1	1000	957
7	-2	443	524
7	-3	503	544
7	-4	389	357
7	-5	375	385
8	-1	892	794
8	-2	466	486
8	-3	1208	1120
8	-4	903	780
8	-5	1101	1136
******K=12******			
0	4	220	299
0	5	175	216
0	8	452	335
1	2	133	31
1	4	599	662
1	6	747	783
1	8	821	837
1	-3	130	284
1	-4	1154	1311
1	-6	1020	1037
1	-8	821	813
2	0	928	939
2	2	1113	1316
2	4	1025	1157
2	6	636	698
2	-1	325	47
2	-2	317	306
2	-3	411	167
2	-4	349	449
2	-6	714	790
2	-7	202	250
2	-8	956	967
3	0	1694	1620
3	2	1378	1307
3	3	294	277
3	4	511	505
3	-2	1428	1529
3	-3	233	244
3	-4	1145	1137
3	-6	387	413
3	-8	220	27
4	0	435	473
4	2	484	428
4	4	818	798
4	6	1042	1045
4	-2	585	549
4	-4	811	840
4	-6	862	840
4	-8	559	516
5	0	1092	928
5	2	1202	1082
5	4	855	839
5	-2	426	400
5	-6	442	480
5	-8	530	542
6	0	934	825
6	1	301	44
6	2	443	370
6	-2	939	850
6	-4	827	775
6	-6	539	419
7	0	310	74
7	-2	631	581
7	-4	888	891
7	-6	1185	1097
******K=13******			
0	3	534	646
0	4	456	595
0	5	851	843
0	6	505	523
0	7	722	674
1	2	445	538
1	3	613	777
1	4	344	403
1	5	310	301
1	6	239	178
1	-3	216	285
1	-4	352	109
1	-7	337	314
1	-8	364	387
2	0	436	479
2	1	938	951
2	2	197	261
2	5	241	182
2	-1	1201	1290
2	-2	448	587
2	-3	1454	1600
2	-4	822	893
2	-5	974	1008
2	-6	547	626
2	-7	530	511
2	-8	255	219
3	0	259	225
3	1	497	482
3	2	576	583
3	3	795	863
3	4	567	469
3	5	883	871
3	-2	397	178
3	-3	464	493
3	-4	481	473
3	-5	1118	1130
3	-6	589	574
3	-7	988	926
3	-8	515	474
4	0	698	617
4	1	1438	1146
4	2	565	477
4	3	1031	946
4	4	287	245
4	-1	835	890
4	-2	545	481
4	-3	322	354
4	-4	551	510
4	-7	252	129
5	0	317	297
5	1	330	246
5	3	319	228
5	-1	645	514
5	-2	287	313
5	-3	663	808
5	-4	572	547
5	-5	825	741
5	-6	366	417
5	-7	267	239
6	0	340	301
6	1	607	526
6	-5	632	554
6	-6	399	358
******K=14******			
0	3	408	536
0	4	191	98
0	5	214	74
0	6	236	18
1	3	263	296
1	4	360	370
1	5	397	401
1	6	353	271
1	-3	537	717
1	-4	552	626
1	-5	800	860
1	-6	457	447
2	0	535	545
2	1	873	978
2	2	580	585
2	3	944	944
2	4	406	392
2	5	710	716
2	-1	439	522
2	-2	232	293
2	-4	192	199
2	-5	420	461
2	-6	544	533
2	-7	721	688
3	0	950	842
3	1	1373	1131
3	2	803	783
3	3	570	617
3	4	265	282
3	-1	1081	1090
3	-2	766	790
3	-3	1075	1094
3	-4	419	449
3	-5	527	485
3	-6	237	30
4	0	301	109
4	1	307	34
4	3	508	501
4	-1	640	567
4	-2	254	249
4	-3	693	657
4	-4	559	504
4	-5	993	871
4	-6	355	340
5	0	465	349
5	1	848	758
5	-1	578	452

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATIONS (IN Å.)

Atom	Minimum	Intermediate	Maximum
Pt	0.157(2)	0.199(2)	0.227(1)
Cl	0.20 (1)	0.23 (1)	0.34 (1)
P_1	0.18 (1)	0.20 (1)	0.23 (1)
P_2	0.16 (1)	0.19 (1)	0.24 (1)

the data of Table I, are not given. A rigid-body analysis has not been attempted, largely because it seems inapplicable. For example, only the Cl atom shows maximum displacement along the direction perpendicular to the Pt, P, Cl plane.

A final difference Fourier, based on the group refinement, shows peaks as high as 2.2 e/Å.^{3} in the vicinity of the Pt atom. Considerable effort was made to locate the hydride H atom, using the method of successively limiting the angular range of terms in the Fourier, a method which worked with success in our study of $RhH(CO)[P(C_6H_5)_3]_3$.[6,7] Although the noise in the vicinity of the Pt diminished considerably as the angular range was reduced, it never decreased sufficiently to enable us to discern with certainty the electron density of the hydrogen. This density is calculated to be about 0.3 to 0.5 e/Å.^{3},[7] some 30% of the noise level on the difference Fourier with terms limited to the angular range $(\lambda^{-1} \sin \theta) \leq 0.35$ Å.$^{-1}$. The reasons for the noise level here are probably related to the white radiation problem always inherent with Mo Kα radiation, to errors in the published values of μ/ρ used in the absorption correction,[23] and to an improper treatment of the platinum scattering. (The Thomas–Fermi–Dirac scattering factor for Pt used in this study differs in the range of interest by only a few tenths of an electron from the new Hartree–Fock values[24] and by some 1 to 2 electrons from the new Hartree–Fock–Slater values[25]; nevertheless, the differences are smooth and should be compensated for in part by changes in the thermal parameters.) The one discernible feature on this difference map is that the phenyl carbon atoms nearest to phosphorus are vibrating less than those further away. This effect is also evident in the unrestricted refinement: the thermal parameters average on C_1 (attached to P), C_2 and C_5 (*ortho*), C_3 and C_6 (*meta*), and C_4 (*para*) 3.6, 4.6, 5.5, and 5.5 Å.,^{2} respectively. Obviously one could improve the group refinement, with consequent increase in computing time, by assigning individual thermal parameters to the group atoms; this does not seem worthwhile, since the differences from the group average can always be derived from a difference Fourier.

Description of the Structure

The structure described by the cell constants, the symmetry operations of the space group, and the atomic parameters consists of the packing of discrete molecules of $PtHCl[P(C_6H_5)_2C_2H_5]_2$. The closest Pt–Pt approach is greater than 9 Å. The P atoms are *trans* to one another and together with the Cl atom lie at three of the four corners of a distorted square. The Pt atom is at the center of the square. This arrangement is shown in perspective in Figure 1. The important intramolecular distances are listed in Table V. The general agreement with the much less precise results of Owston, *et al.*,[4] on the related bromine compound is exceedingly good: they found Pt–P distances of 2.26 ± 0.07 Å., a Pt–Br distance of 2.56 ± 0.04 Å., and Br–Pt–P angles of 94.1 and 93.7° (±2.0°). The Pt–P distances of 2.267 and 2.269 ± 0.008 Å. found here are toward the low end of the range found recently between P and other second or third row transition elements (Rh–P = 2.32 Å. in $RhH(CO)[PC_6H_5)_3]_3$[6,7]; Ir–P = 2.36, 2.37 Å. in $IrO_2Cl(CO)[P(C_6H_5)_3]_2$[20]; Ru–P = 2.37, 2.41, 2.23 Å. in $RuCl_2[P(C_6H_5)_3]_3$).[21] The Pt–Cl distance of 2.422 ± 0.009 Å. is consistent with the Pt–Br distance found by Owston, *et al.*,[4] since the covalent radius of Cl is generally considered to be some 0.12 Å. less than that of Br. The Pt–Cl distance is longer than is predicted from radii-sum rules (2.30 Å.), and this lengthening is consistent with the high chemical lability of the chlorine in this compound. Yet the Ru–Cl distance is 2.39 Å. in $RuCl_2[P(C_6H_5)_3]_3$[21] and the Ir–Cl distance is approximately 2.40 Å. in $IrO_2Cl(CO)[P(C_6H_5)_3]_2$. Owston, *et al.*,[4] discuss the Pt–P shortening and Pt–Br lengthening in terms of possible *trans* influence of the hydrogen atom and/or as a result of d-orbital contributions to Pt–P bonding.

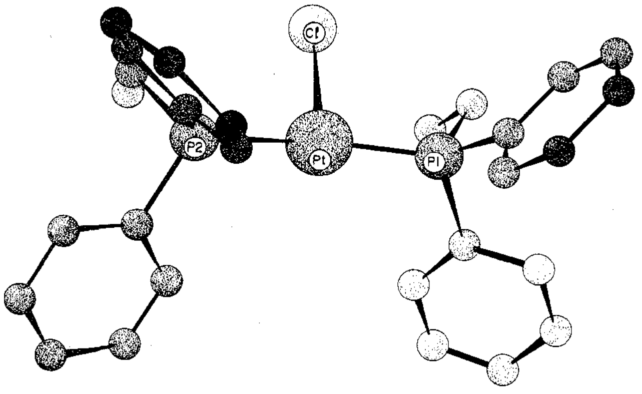

Figure 1.—A perspective drawing of one molecule of $PtHCl[P(C_6H_5)_2C_2H_5]_2$. Positions of the hydrogen atoms were not determined and are not shown.

TABLE V

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

Intramolecular distance, Å.		Angles, deg.	
Pt–Cl	2.422(9)	P_1–Pt–Cl	92.6(4)
Pt–P_1	2.267(8)	P_2–Pt–Cl	94.5(4)
Pt–P_2	2.269(8)	P_1–Pt–P_2	188.8(3)
Cl–P_1	3.39(1)	P_1–P_1EC_1–P_1EC_2	105(2)
Cl–P_2	3.45(1)	P_2–P_2EC_1–P_2EC_2	113(2)
P_1–P_1EC_1	1.86(3)	$P_1R_1C_1$–P_1–P_1EC_1	103(1)
P_2–P_2EC_1	1.84(3)	$P_1R_1C_1$–P_1–$P_1R_2C_1$	104(1)
P_1EC_1–P_1EC_2	1.59(5)	$P_1R_2C_1$–P_1–P_1EC_1	102(1)
P_2EC_1–P_2EC_2	1.52(5)	$P_2R_1C_1$–P_2–P_2EC_1	101(1)
P_1–$P_1R_1C_1$	1.83(2)	$P_2R_1C_1$–P_2–$P_2R_2C_1$	101(1)
P_1–$P_1R_2C_1$	1.82(2)	$P_2R_2C_1$–P_2–P_2EC_1	104(1)
P_2–$P_2R_1C_1$	1.85(2)		
P_2–$P_2R_2C_1$	1.82(2)		

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(24) D. T. Cromer, A. C. Larson, and J. T. Waber, *ibid.*, **17**, 1044 (1964).

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Such d-orbital contributions have recently been put forth[26] as the explanation for the short Pt–As bond lengths of 2.38 Å. in Pt(diarsine)$_2$I$_2$[27] and in Pt(diarsine)$_2$Cl$_2$.[26] Since the covalent radius of As is some 0.10 Å. longer than that of P, the contraction of the Pt–As bonds is similar to that of the Pt–P bonds found here. Nevertheless, there is sufficiently little information on M–P and M–Cl distances (where M is a second or third row transition element) so that very little can be said with certainty about the bonding in this platinum compound. It is not possible to assess the relative importance of the *trans* effect or of d-orbital contributions, or in fact of any other effects that one might fancy. Yet, on the basis of the spreading of the P–Pt–Cl angles from the presumably ideal value of 90° to 92.6 and 94.5° there is the indication of some steric interaction between Cl and P. (A similar deviation of the angles from 90° was observed in the bromo compound.[4]) Hence any factor that tends to shorten the Pt–P bond distance will, through steric effects, lengthen the Pt–Cl distance and *vice versa*.

Of some interest in this regard is that the Pt, P, Cl portion of the molecule is significantly nonplanar. The best least-squares plane[28] through these four atoms has the equation $3.528x - 15.805y + 1.336z = 5.572$ (monoclinic coordinates). The deviations from this plane are Pt, 0.005 ± 0.001; Cl, -0.021 ± 0.010; P$_1$, -0.095 ± 0.008; and P$_2$, -0.096 ± 0.008 Å. A careful examination of the intermolecular distances suggests no explanation for a lack of planarity in terms of packing distortions. (In fact all intermolecular contacts appear to be normal, and hence are not tabulated here.) The only explanation for this lack of planarity that we can suggest involves the intramolecular steric repulsions of P and Cl.

The geometry of the diphenylethylphosphine ligand closely resembles that found previously for the triphenylphosphine ligand.[7,20,21]

Acknowledgment.—We are indebted to H. B. Gray, who kindly supplied the crystals, for his diligent laboratory work.

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A Five-Coordinated d^6 Complex: Structure of Dichlorotris(triphenylphosphine)ruthenium(II)[1]

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A complete X-ray structure determination of dichlorotris(triphenylphosphine)ruthenium(II), RuCl$_2$[P(C$_6$H$_5$)$_3$]$_3$, has been carried out in order to ascertain if in this compound the Ru(II) (d^6) is five-coordinated. The compound crystallizes in space group C$_{2h}^5$-P2$_1$/c of the monoclinic system in a cell of dimensions a = 18.01, b = 20.22, c = 12.36 Å., β = 90.5°. The observed density is 1.43 g./cm.^{3}, and the density calculated for four molecules in the cell is 1.415 g./cm.^{3}. There are no crystallographic symmetry conditions imposed on the molecule. The structure consists of the packing of individual monomeric molecules. In these molecules the Ru lies toward the center of a distorted square pyramid which consists of *trans* Cl atoms and *trans* P atoms in the base and an apical P atom. The apical Ru–P distance of 2.23 Å. is about 0.16 Å. shorter than the basal Ru–P distances. This is the only known example from X-ray structural studies of a five-coordinated d^6 complex, and it probably occurs not because of an inherent tendency toward five-coordination, but rather because the unused octahedral site about the square-pyramidal configuration is effectively blocked by a phenyl ring.

Introduction

Of the two dozen or so five-coordinated transition metal complexes that have been established by X-ray diffraction studies, none is a d^6 complex.[2] This is not surprising, for it has frequently been noted[3] that the spin-paired d^6 configuration is an especially favorable one for the formation of octahedral complexes. Of the relatively few d^6 complexes thought to be five-coordinated that are reported in the literature, the case for five-coordinated Os(II) in dibromotris(triphenylphosphine)osmium(II) seems one of the most convincing. This compound was prepared by Vaska[4] in 90% yield from the reaction of (NH$_4$)$_2$OsBr$_6$ with triphenylphosphine in 2-methoxyethanol at 25°. In a similar manner Vaska[5] has prepared dichlorotris(triphenylphosphine)ruthenium(II). From magnetic, molecular weight, conductivity, and spectroscopic measurements Vaska concludes that these compounds are diamagnetic, monomeric, and are not hydrides. A preliminary X-ray examination by Pollack[6] indicated that the

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. A. Ibers, *Ann. Rev. Phys. Chem.*, in press.

[3] For example, see R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

[4] L. Vaska, *Chem. Ind.* (London), 1402 (1963).

[5] L. Vaska, private communication.

[6] S. S. Pollack, as quoted by Vaska.[5]