TABLE V

COMPARISON OF BOND LENGTHS AND ANGLES

Compd	Ref	N–N,[a] A	N–C, A	C–C, A	∠N–M–N, deg	∠M–N–C, deg	∠N–C–C, deg
$Ni(en)_3(NO_3)_2$	*b*	2.790 (25)	1.500 (25)	1.498 (28)	82.3 (10)	109.7 (12)	111.1 (23)
$Cu(en)_2(NO_3)_2$	*c*	2.772	1.487 (25)	1.545 (27)	86.2	109.1	109.6
			1.476 (25)			108.5	110.6
$Cu(en)_2(SCN)_2$	*d*	2.70 (3)	1.46 (3)	1.56 (4)	84.8	110.5	109.4
			1.49 (3)			108.6	104.7
$Pd(en)_2Cl_2$	*e*	2.713 (10)	1.469 (11)	1.518 (13)	83.6 (3)	108.2 (5)	107.2 (7)
			1.484 (11)			109.6 (5)	107.1 (7)

[a] Within a chelate ring. [b] L. N. Swink and M. Atoji, *Acta Cryst.*, **13,** 639 (1960). [c] Y. Komiyama and E. C. Lingafelter, *ibid.*, **17,** 1145 (1964). [d] B. W. Brown and E. C. Lingafelter, *ibid.*, **17,** 254 (1964). [e] This investigation.

TABLE VI

PERTINENT DATA INVOLVED IN THE HYDROGEN-BONDING SCHEME[a]

Distances of the Hydrogen Atoms from the Line Joining the Chloride Ion and the Nitrogen Atoms

Atoms defining line	Distance of hydrogen from the line, A
N(1)–Cl(III)	0.16
N(2)′–Cl(III)	0.36
N(I)–Cl(III)	0.35
N(II)–Cl(III)	0.03

Angles Involved in the Hydrogen-Bonding Geometry

N(1)–Cl(III)–N(2)′	54.6°
N(1)–Cl(III)–N(I)	100.9°
N(2)′–Cl(III)–N(I)	87.6°
N(I)–Cl(III)–N(II)	153.4°
N(2)′–Cl(III)–N(II)	76.1°
N(1)–Cl(III)–N(II)	86.8°

[a] The lettering refers to the atoms surrounding Cl(III) in Figure 2.

Clellan[19] list N···Cl hydrogen-bonded distances ranging from 2.91 to 3.41 A. These distances in the present structure fall quite nicely within this range. Table VI gives the distances of the hydrogen atoms from the lines joining the chloride ion and the nitrogen atoms.

It can thus be seen that the positions of the hydrogen atoms indicate that there is hydrogen bonding taking place between the chloride ions and the nitrogen atoms. Some pertinent angles concerning the geometry of the nitrogen atoms surrounding the chloride ion are also given in Table VI.

Acknowledgments.—The authors wish to thank the National Science Foundation for partial support of this work under grant No. GP-1601 and also the University of Washington Computer Center for a grant of computer time.

(19) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco and London, 1960, p 290.

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Crystal Structures and Multiple Bonding in *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ and *trans*-$Pt[P(C_2H_5)_3]_2Br_2$

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The crystal structures of the isomorphous pair *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ and *trans*-$Pt[P(C_2H_5)_3]_2Br_2$ have been determined from counter data by two- and three-dimensional single-crystal X-ray techniques, respectively. The structures consist of discrete molecules with the platinum, phosphorus, and halogen atoms in essentially a square-planar arrangement. Only van der Waals interactions exist between molecules. The Pt–P bond lengths were found to be 2.300 ± 0.019 and 2.315 ± 0.004 A in the chloride and bromide, respectively. A Pt–P distance of 2.41 A would be expected from the sum of the single-bond covalent radii. The Pt–Cl and Pt–Br distances were found to be normal single bonds at 2.294 ± 0.09 and 2.428 ± 0.002 A, respectively. Within experimental error, the P–C distances were observed to be normal single bonds, and the Pt–P–C angles tetrahedral.

Introduction

The influence of π bonding on *cis–trans* isomerization and the *trans*-directing effect has been discussed for some time.[3–7] In Pt(II) complexes the usually nonbonding $5d_{xz}$, $5d_{yz}$ filled metal orbitals can interact with π orbitals of appropriate symmetry. With trialkylphosphine ligands these are the empty phosphorus

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(1) In partial fulfillment for the Ph.D. requirements, University of Pittsburgh, 1966.

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(3) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273, 4300 (1952); 70 (1953); 525 (1956).

(4) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *ibid.*, 4456, 4461 (1955).

(5) J. V. Quagliano and L. Schubert, *Chem. Rev.*, **50,** 201 (1952).

(6) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4,** 381 (1962).

(7) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 172, 249.

3d orbitals, whereas with chlorine or bromine ligands these are 3p–3d and 4p–4d hybrid orbitals, respectively. This type of π bonding is generally referred to as dπ–dπ bonding.

Chatt and Wilkens[3] have collected considerable thermodynamic data on *cis–trans* equilibria in benzene solutions of $Pt(MR_3)_2X_2$, where M = P, As, or Sb; R = methyl, . . . , or *n*-pentyl; X = Cl^- or I^-. Their results show that the *cis* isomer is more stable than the *trans*, and the *cis* isomer has a total bond energy approximately 10 kcal/mole greater than the *trans* isomer. This difference in bond energy was attributed to the difference in Pt–P dπ–dπ bonding in the two isomers. We undertook careful three-dimensional X-ray single-crystal structure analyses in order to ascertain whether this difference in bond energy is reflected in the Pt–P bond lengths in the two isomers. There have been reports of Pt–P bond lengths as much as 0.15 A[8,9] shorter than the sum of the appropriate covalent radii. With a few notable exceptions,[9] much of the previous X-ray structure research has been from two-dimensional diffraction data[8,10,11] limited in accuracy and frequently overinterpreted. We report here the results for the *trans* $Pt[P(C_2H_5)_3]_2Cl_2$ and $Pt[P(C_2H_5)_3]_2Br_2$ isomers; the results for the appropriate *cis* isomers will follow.

Experimental Section

Samples of *trans*-$Pt[P(C_2H_5)_3]_2X_2$, X = Cl, Br, were kindly supplied by Dr. J. Chatt and were recrystallized from methanol solution. Cell constants were obtained with the Picker diffractometer equipped with a GE single-crystal orienter. Owing to the fact that different X-ray tubes were aligned on the diffractometer at different times, the cell parameters of the chloride isomer were measured with Cu Kα (1.5418 A), and the bromide, with Mo Kα (0.7107 A). These cell constants were checked with calibrated Mo Kα precession photographs, and they agreed within the stated error. The crystals were found to be isomorphous and monoclinic, $P2_1/n$ with $a = 11.00 \pm 0.02$ A, $b = 11.52 \pm 0.02$ A, $c = 7.49 \pm 0.01$ A, $\beta = 93° 0' \pm 15'$ for the chloride and $a = 11.28 \pm 0.02$ A, $b = 11.58 \pm 0.02$ A, $c = 7.63 \pm 0.01$ A, $\beta = 91° 55' \pm 15'$ for the bromide. With two formula units per cell, the X-ray density is 1.69 and 1.94 g cm^{-3} for the chloride and bromide, respectively (within 0.02 g cm^{-3} of the density measured by flotation in carbon tetrachloride–bromoform mixtures).

Structure Determinations

***trans*-$Pt[P(C_2H_5)_3]_2Cl_2$.**—Preliminary photographic data were obtained on the Weissenberg and precession cameras for the three principal zones with Mo Kα radiation. These photographs showed strong thermal diffuse scattering, probably due to motions of the ethyl groups. This diffuse scattering increased the background and would complicate the location of the light atoms. Hence, this structure was determined using only two-dimensional data solely to indicate that the results were consistent with those of *trans*-$Pt[P(C_2H_5)_3]_2Br_2$, but more limited in accuracy.

With a crystal 0.20 × 0.23 × 0.50 mm, 250 independent reflections for the three principal zones (*h*0*l*, 0*kl*, *hk*0) were measured by a scanning technique on the Picker diffractometer with a GE single-crystal orienter using Cu Kα radiation. For details, see data collection for Br isomer. No corrections were made for absorption or extinction. The linear absorption coefficient for this crystal with Cu Kα radiation is 177 cm^{-1}.

In space group $P2_1/n$ with two molecules per unit cell, the Pt atoms must be on centers of symmetry. The sets of centers of symmetry positions in $P2_1/n$ differ only in choice of origin; we chose the set 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. This confirms the *trans* configuration for this compound and further requires the Pt and its four nearest neighbors to be coplanar. The phosphorus and chlorine atoms were readily located by Patterson projections in the general positions of $P2_1/n$; $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z)$. Carbon atoms were located from electron density and difference electron density projections.[12] The structure was refined by least squares,[13] including anisotropic temperature factors for Pt, Cl, P, but only a single isotropic temperature factor for C. Scattering factors for neutral platinum, chlorine, phosphorus, and carbon were from the compilation of Ibers.[14] A real dispersion correction was made to the platinum, chlorine, and phosphorus scattering factors from the values given by Cromer.[15] The imaginary dispersion term was neglected. The effect of real and imaginary dispersion terms on atomic coordinates was carefully examined for the Br isomer (see below) and justifies this procedure. The function minimized was $\Sigma w(F_o - F_c)^2$ using equal weights. The final values of the disagreement index *R*, the weighted *R*, and the standard error of an observation[16] are: 0.032, 0.034, 1.12 with $NO = 84$, $NV = 31$; 0.125, 0.115, 2.58 with $NO = 82$, $NV = 19$; 0.073, 0.080, 2.14 with $NO = 139$, $NV = 29$, for *h*0*l*, 0*kl*, and *hk*0, respectively. The agreement is generally poorer in the 0*kl* zone owing to the fact that the Pt and Cl atoms are overlapping in this projection, and the appropriate variables had to be held constant. The final coordinate shifts of phosphorus and chlorine were less than $^1/_{10}\sigma$, whereas final carbon shifts were less than $^1/_3\sigma$. The location of the light carbon atoms in the presence of Pt is of some concern,[17,18] and we have used several criteria to judge the validity of these positions for the structure: (1) peaks of the appropriate peak height appearing on the electron density and difference electron density projections; (2) convergence of the isotropic light-atom temperature factors in the refinement; (3) "reasonable" interatomic dis-

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

[9] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

[10] P. G. Owston and J. M. Rowe, *Acta Cryst.*, **13**, 253 (1960).

[11] S. S. Batsanov, *Russ. J. Inorg. Chem.*, **4**, 773 (1959). (A summary, see detailed references therein.)

[12] Patterson and Fourier calculations made with Sly, Shoemaker, Van den Hende, E.R.F.R.2 on the IBM 7090.

[13] Least-squares calculations were performed with the Busing and Levy ORFLS program. Calculations performed on IBM 7090 or 7094.

[14] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol III, The Kynoch Press, Birmingham, England, 1961, pp 202, 212.

[15] D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

[16] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; standard error = $[\Sigma w(F_o - F_c)^2/(NO - NV)]^{1/2}$.

[17] N. C. Baenziger, R. C. Medrud, and J. R. Doyle, *Acta Cryst.*, **18**, 237 (1965).

[18] A. C. Hazell and M. R. Truter, *Proc. Roy. Soc.* (London), **A254**, 218 (1960).

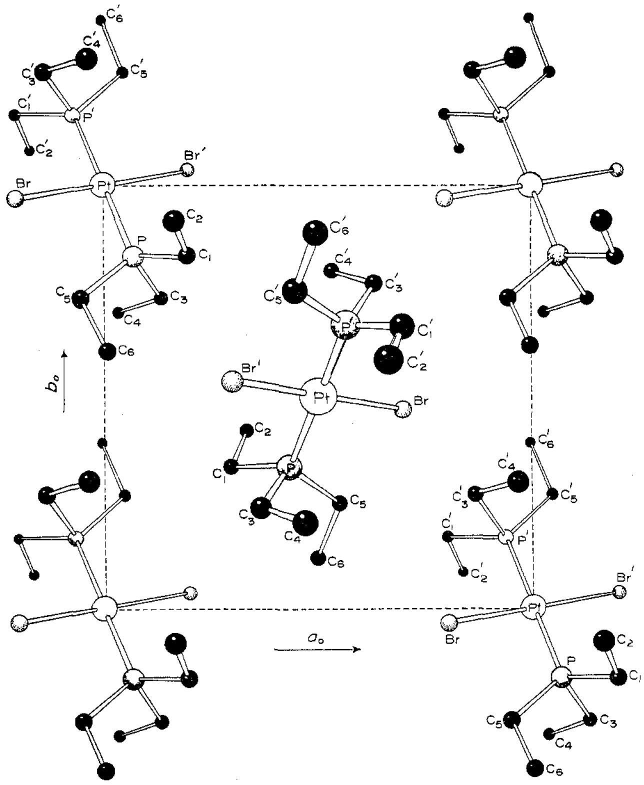

Figure 1.—Perspective view of *trans*-Pt[P(C_2H_5)$_3$]$_2$Br$_2$(Cl$_2$) down the *c* axis. Dotted lines indicate unit cell.

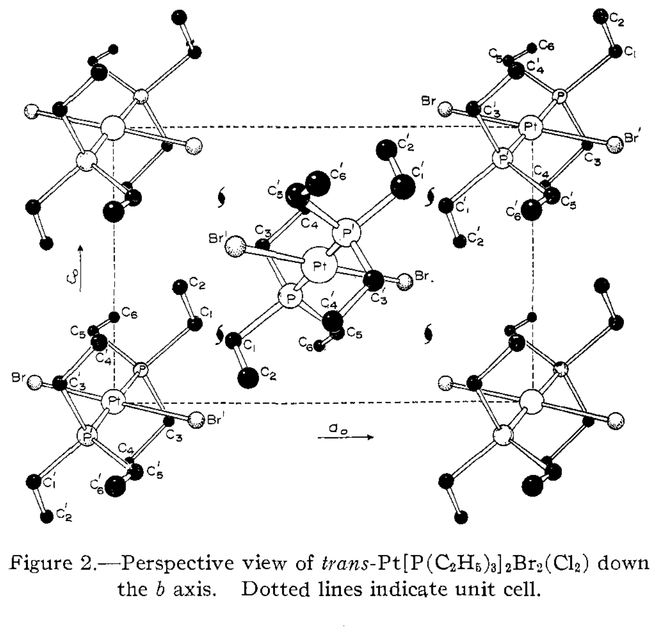

Figure 2.—Perspective view of *trans*-Pt[P(C_2H_5)$_3$]$_2$Br$_2$(Cl$_2$) down the *b* axis. Dotted lines indicate unit cell.

tances, both intramolecular and intermolecular; (4) comparison with the corresponding carbon atom coordinates in the bromine isomer. Within the relatively large errors (to be expected with the limited data), these criteria are satisfied for the carbon atoms of the chlorine isomer. Because of the use of only projection data and the neglect of absorption, no physical interpretation should be made of the anisotropic temperature factors.

The structure is essentially that of *trans*-Pt[P(C_2H_5)$_3$]$_2$Br$_2$ shown in Figures 1 and 2. (See more detailed description below.) Final observed and calculated structure factors are indicated in Table I. Table II contains the atom parameters and errors, and Table III, bond distances, angles, and errors.[18] No physical significance should be attributed to the P–C and C–C bond length differences.

TABLE I

CALCULATED AND OBSERVED STRUCTURE FACTORS[a] FOR *trans*-Pt[P(C_2H_5)$_3$]$_2$Cl$_2$

0kℓ	F(O)	F(C)
0K1		
2	250	187
3	456	518
4	173	-107
5	509	487
6	61	50
7	415	391
8	109	87
9	180	205
10	62	-47
11	233	217
13	150	130
14	25	34
0K2		
1	32	-4
2	393	452
3	23	-25
4	541	510
5	20	-39
6	347	342
7	165	139
8	244	280
9	16	31
10	198	189
11	41	-36
12	149	132
13	51	85
0K3		
1	457	467
2	134	96
3	514	485
4	48	-48
5	358	355
6	77	57
7	230	257
8	52	62
9	244	255
11	134	122
12	12	57
13	107	100
0K4		
1	25	27
2	386	377
3	55	61
4	367	365
5	40	25
6	142	153
7	28	19
8	224	233
9	25	28
10	142	154
11	28	55
12	91	83
13	15	32
0K5		
1	233	212
2	32	-47
3	254	230
4	96	71
5	165	163
6	34	21
7	156	135
8	12	-18
9	126	160
10	35	70
11	95	93
12	7	28
0K6		
1	24	-28
2	141	130
4	116	126
5	42	22
6	131	117
8	81	114
9	8	15
10	71	72
0K7		
1	92	99
3	65	74
5	79	85
6	15	7
7	67	76
9	43	38
0K8		
1	20	-18
2	40	26
3	2	-0
4	42	37
6	41	55
0K9		
1	24	24
h0ℓ	F(O)	F(C)
H01		
3	351	359
-3	337	384
5	435	447
-5	490	498
7	233	230
-7	171	171
9	340	350
-9	219	224
11	347	358
-11	183	179
13	181	195
-13	147	144
H02		
0	512	517
2	265	272
-2	205	207
4	130	139
-4	558	569
6	415	418
-6	386	380
8	290	277
-8	237	229
10	396	405
-10	235	229
12	247	240
-12	88	87
H03		
1	399	407
-1	326	319
3	139	134
-3	424	402
5	420	416
-5	520	514
7	337	342
-7	293	290
9	300	302
-9	294	297
11	306	289
-11	127	130
-13	97	102
H04		
0	325	329
2	309	309
-2	183	183
4	292	282
-4	353	339
6	376	371
-6	258	268
8	245	246
-8	241	225
10	220	214
-10	183	188
12	111	116
-12	80	81
H05		
1	279	277
-1	156	147
3	246	254
-3	170	151
5	285	268
-5	163	152
7	236	232
-7	140	144
9	132	128
-9	167	158
11	125	124
-11	95	96
H06		
0	173	167
2	214	230
-2	111	97
4	157	170
-4	113	134
6	176	177
-6	72	82
8	105	107
-8	100	109
10	92	94
-10	85	97
H07		
1	126	137
3	103	112
5	99	96
7	80	78
-7	50	66
-9	58	68
H08		
0	65	73
2	71	80
4	51	56
6	52	46
hk0	F(C)	F(C)
0K0		
4	441	456
6	430	426
8	254	261
10	135	132
12	203	246
14	97	104
1K0		
2	71	44
3	419	452
4	188	-175
5	450	462
6	145	-143
7	377	371
9	153	164
10	58	-58
11	238	263
12	17	8
13	182	185
14	28	30
2K0		
1	235	231
2	222	243
3	82	-61
4	356	369
5	179	-161
6	412	419
7	31	13
8	323	337
9	28	-33
10	268	273
11	45	-50
12	245	272
13	41	40
14	125	134
3K0		
1	215	239
2	153	184
3	407	398
4	5	16
5	426	439
6	64	65
8	118	92
9	300	310
10	63	-66
11	270	270
12	10	7
13	189	194
14	8	19
4K0		
0	447	471
1	87	100
2	461	499
3	150	143
4	430	403
5	14	12
6	369	394
7	216	134
8	315	306
9	22	-16
10	243	230
11	29	-27
12	159	163
13	18	18
5K0		
1	488	515
2	87	74
3	554	555
4	113	-87
5	406	369
6	26	22
7	267	262
8	41	33
9	260	240
10	46	-39
11	142	132
13	122	130
6K0		
0	376	392
2	470	464
3	73	-62
4	451	404
5	221	-205
6	256	225
8	342	305
9	67	-55
10	227	214
11	14	-5
12	117	117
7K0		
1	202	200
2	30	-37
3	451	416
4	82	-95
5	298	246
6	65	-68
7	283	252
8	33	-27
9	342	324
10	3	-6
11	191	198
12	7	3
8K0		
0	137	143
1	30	-34
2	322	306
3	56	33
4	348	305
5	93	71
6	233	196
7	6	17
8	330	308
10	251	267
11	18	27
9K0		
1	294	306
2	25	-12
3	396	374
4	154	154
5	279	244
6	70	77
7	220	208
9	219	232
10	37	39
10K0		
0	336	366
1	72	-71
2	389	408
4	283	267
5	64	75
6	234	234
7	57	-50
8	170	167
9	14	-8
11K0		
1	287	313
2	97	-97
3	250	245
5	237	242
6	72	-40
7	160	178
8	67	-59
12K0		
0	189	187
1	60	-70
2	172	173
3	31	-36
4	153	157
5	13	-31
13K0		
1	163	153
3	106	114
4	42	53

[a] $F(C) = 10F(\text{calcd})$; $F(\text{calcd})_{\text{absolute}} = F(\text{calcd})/\text{scale factor}$.

trans-**Pt[P(C_2H_5)$_3$]$_2$Br$_2$.**—A single crystal 0.2 × 0.2 × 0.5 mm was mounted about the needle axis ([001] direction) on the GE single-crystal orienter and used to collect intensity data with the Picker diffractometer using Zr-filtered Mo Kα radiation. Backgrounds were estimated by stationary count for 40 sec at ±1.67°, 2θ of the peak maxima. The peak was then scanned for 100 sec by a 2θ scan. The net peak intensity was then computed by scaling the background to 50 sec

TABLE II

DATA FOR *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$

Positional and Temperature Parameters and Errors; $\sigma' = \sigma \times 10^5$

Atom	x/a	$\sigma'(x/a)$	y/b	$\sigma'(y/b)$	z/c	$\sigma'(z/c)$
Pt	0.5000	. . .[a]	0.5000	. . .[a]	0.5000	. . .[a]
Cl	0.6980	82	0.4549	120	0.4604	168
P	0.4295	88	0.3314	157	0.3676	292
C_1	0.3024	482	0.3623	958	0.1814	1322
C_2	0.3581	660	0.4299	1306	0.0675	1731
C_3	0.3848	948	0.2393	907	0.6155	1647
C_4	0.4460	1717	0.1930	1597	0.5425	621
C_5	0.5391	415	0.2797	893	0.2040	919
C_6	0.5076	679	0.1158	793	0.1829	1215

Thermal Parameters and Standard Deviations; Anisotropic Temperature Factors of the Form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; $\sigma' = \sigma \times 10^5$

Atom	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Pt	0.0023	18	0.0049	42	0.0202	91	0.0001	15	−0.0018	15	0.0009	63
Cl	0.0011	65	0.0049	102	0.0286	363	−0.0004	69	−0.0011	94	−0.0047	. . .
P	0.0020	68	0.0022	112	0.0283	456	−0.0007	73	0.0031	79	−0.0012	219

Isotropic Carbon Temperature Factors

Atom	B, A^2	σ	Atom	B, A^2	σ	Atom	B, A^2	σ
C_1	4.8	1.6	C_3	8.9	5.5	C_5	3.8	1.4
C_2	6.7	3.3	C_4	8.0	3.4	C_6	4.2	3.2

Scale Factors

Zone	Scale factor
$h0l$	0.3829 ± 0.0039
$0kl$	0.3380 ± 0.0083
$hk0$	0.3599 ± 0.0050

[a] Parameter fixed by symmetry.

TABLE III

INTERATOMIC DISTANCES, ANGLES, AND ERRORS FOR *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$

Intramolecular, A

Pt–Cl	2.294 ± 0.009	C_1–C_2	1.33 ± 0.12
Pt–P	2.298 ± 0.018	C_3–C_4	1.74 ± 0.11
		C_5–C_6	1.69 ± 0.10
P–C_1	1.89 ± 0.05		
P–C_3	1.63 ± 0.11	X–Pt–X angles	
P–C_5	1.77 ± 0.05	P–Pt–Cl	87.3 ± 0.14°
		Pt–Pt–Cl	92.7 ± 0.14°

each and subtracting them from the peak scan. A total of 1953 independent *hkl* values was measured by this means. The linear absorption coefficient for this crystal with Mo Kα radiation is 124 cm^{-1}. No corrections were made for absorption. The maximum difference in crystal dimension is only a factor of 2.5; and with linear absorption coefficients of the same magnitude, others have neglected absorption corrections.[19–22] Further, it is generally accepted that neglect of absorption corrections does not affect atomic positional parameters but only thermal parameters.[20,22–25] The least-squares esd involves the assumption that all errors are random. Absorption is a systematic error and our bond length estimates of error should be viewed as lower limits. However, an independent structure determination from equiinclination Weissenberg photographic data[25b] gave Pt–X bond lengths not significantly different from those reported below (Table VI) but with esd's two to four times larger than the present results. The geometries of the counter and Weissenberg techniques are sufficiently different, so that, if absorption errors significantly affected atomic positions, they would produce significant Pt–X bond length changes. Further, our thermal parameters compare favorably with those in similar compounds in which absorption corrections have been calculated (see below). An estimate of the magnitude of the absorption correction might be obtained from the variation in the transmission factor for $PtH[P(C_6H_5)_2C_2H_5]Cl$[9] of 0.17–0.59 with μ = 57 cm^{-1}.

The coordinates of platinum, phosphorus, and halogen were taken from the results of the chloride isomer. Bearing in mind the criteria for the location of light atoms cited above, the carbon atoms were located independently by Fourier and difference Fourier techniques.[12] The structure was refined with complete matrix least squares including anisotropic temperature factors for all atoms by minimizing the function

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(25) (a) Nevertheless, we feel that the effect of absorption on thermal parameters should be carefully examined, and we will make this the subject of a short communication elsewhere. (b) G. G. Messmer and E. L. Amma, unpublished results [Pt–P, 2.328 ± 14 A; Pt–Br, 2.433 ± 5 A]. NOTE ADDED IN PROOF.—A careful analysis of absorption effects with μ = 191 cm^{-1} has recently been published [R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966)], and their conclusions justify our neglect of absorption errors for the determination of positional parameters.

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS[a] FOR *trans*-$Pt[P(C_2H_5)_3]_2Br_2$

	F(O)	F(C)
H00		
2	151	129
4	220	222
6	143	138
8	25	22
10	132	125
12	22	23
14	63	65
16	32	30
20	14	17
H10		
1	182	256
2	85	65
3	12	26
4	46	51
5	247	244
6	14	-14
7	18	17
8	6	5
9	112	110
10	11	-19
11	73	69
13	31	33
15	56	56
17	12	10
H20		
0	202	220
1	18	-24
2	23	20
3	64	71
4	193	193
5	12	10
6	158	155
8	68	71
9	2	10
10	128	126
11	34	-37
12	23	24
13	6	7
14	48	49
16	21	24
H30		
1	187	173
2	46	-55
3	96	102
4	73	72
5	212	219
6	51	-55
7	94	94
8	38	41
9	119	118
11	62	60
15	38	38
H40		
0	208	204
1	116	-118
2	101	105
3	35	38
4	136	144
5	36	-39
6	118	122
7	33	-29
8	78	76
9	56	58
10	84	85
11	20	-22
12	33	31
13	26	24
14	37	38
H50		
1	169	161
2	78	-74
3	125	127
4	45	46
5	119	122
6	94	-93
7	63	64
8	42	46
9	70	72
11	55	57
13	40	42
15	35	34
H60		
0	139	138
1	86	-86
2	135	135
3	52	52
4	102	105
6	66	65
7	20	-22
8	57	56
9	32	31
10	53	54
11	30	-33
12	48	50
13	19	16
14	37	37
16	29	24
H70		
1	123	120
2	12	-13
3	120	118
4	81	81
5	64	67
6	28	-28
7	82	80
8	22	21
9	51	51
10	16	-18
11	43	44
12	8	-13
13	35	38
15	17	21
H80		
0	60	52
1	33	-28
2	115	110
3	46	46
4	74	77
6	73	82
8	87	83
10	36	34
12	50	41
14	18	17
H90		
1	42	41
2	18	-19
3	93	95
4	10	11
5	47	49
6	27	-26
7	93	89
8	9	12
9	42	43
11	35	34
13	28	27
15	13	9
H100		
0	28	33
1	22	-25
2	96	92
3	7	-10
4	53	53
6	51	51
8	61	59
10	24	22
12	39	36
14	15	14
H110		
1	67	65
2	14	-10
3	78	72
5	20	21
7	50	50
9	26	23
10	8	3
11	27	25
13	23	26
15	7	11
H120		
0	43	42
1	9	6
2	69	67
4	34	34
6	28	28
8	34	32
10	13	14
12	30	27
14	18	13
H130		
1	38	35
3	46	48
4	5	2
5	25	24
6	7	7
7	38	35
8	10	-4
9	21	19
11	23	19
13	17	16
H140		
0	17	17
1	4	6
2	32	33
4	26	26
6	28	28
8	30	28
10	16	15
12	18	14
14	12	7
H150		
1	22	20
3	25	24
5	22	20
7	25	26
9	17	16
H160		
0	16	18
2	20	21
4	15	18
6	13	16
8	16	14
H01		
-1	222	233
1	230	293
-3	119	109
3	60	43
-5	219	205
5	217	205
-7	5	-6
7	44	39
-9	116	110
9	105	101
-11	33	34
11	97	95
-13	40	42
13	30	31
-15	55	54
15	58	55
17	3	11
-17	15	11
19	15	15
H11		
0	298	330
-1	68	74
1	64	47
-2	105	91
2	106	97
-3	68	-69
3	62	62
-4	253	256
4	151	151
5	30	29
-6	102	95
6	158	152
-7	15	-19
7	42	-42
-8	66	65
8	32	32
-9	16	-12
-10	112	108
10	131	128
-11	20	21
-12	14	15
12	35	36
-14	65	63
14	47	48
H21		
0	99	88
-1	115	113
1	205	218
2	64	-58
-3	132	135
3	54	58
-4	89	-88
4	83	83
-5	218	224
5	226	228
-6	17	18
6	47	-44
-7	48	51
7	71	66
-8	49	-48
8	13	-12
-9	146	146
9	82	83
-10	18	22
-11	56	52
11	76	73
-12	4	7
-13	37	38
-15	40	40
15	46	47
-17	2	7
H31		
0	218	213
-1	149	136
1	90	-85
2	130	134
-3	65	-68
-4	160	174
4	151	157
-5	31	38
-6	94	93
6	185	187
7	33	-33
-8	96	98
8	61	60
-9	19	-18
9	43	42
-10	111	108
10	93	94
-11	32	30
11	20	-20
-12	24	27
12	27	25
-13	21	-19
-14	49	47
14	30	33
H41		
-1	120	112
1	222	217
-2	14	17
2	133	-126
-3	80	87
3	100	99
-4	35	-40
4	59	57
-5	133	140
5	169	174
-6	91	91
6	49	-51
-7	60	64
7	96	99
-8	39	-41
8	39	37
-9	99	100
9	76	79
-10	11	15
10	19	19
-11	48	49
11	63	63
12	13	-13
-13	38	39
13	28	28
14	11	13
-15	35	32
15	31	36
17	20	16
H51		
0	171	163
-1	88	79
1	100	-94
-2	132	133
2	109	109
-3	57	-55
3	12	13
-4	147	148
4	88	89
-5	59	59
5	7	10
-6	90	90
6	88	87
-7	19	15
7	33	-32
-8	64	65
8	57	59
-9	29	-31
9	51	53
-10	59	58
10	67	70
-11	20	21
11	21	-21
-12	39	38
12	47	49
-13	28	-29
13	5	8
-14	38	38
14	36	37
-16	23	22
16	17	24
-18	11	16
H61		
0	45	51
-1	157	157
1	124	123
-2	28	28
2	50	-52
-3	145	150
3	96	103
-4	42	-45
4	73	77
-5	99	101
5	67	66
-6	51	53
6	41	-38
-7	70	72
7	61	64
-8	41	-41
8	15	15
-9	47	47
9	60	61
-10	22	25
-11	42	41
11	54	57
-12	2	0
-13	40	37
13	45	44
-14	10	-6
14	12	15
-15	29	26
15	29	27
-16	13	10
16	10	-8
-17	25	19
17	20	17
-19	15	11
19	12	10
H71		
0	107	99
-1	63	64
1	35	-32
-2	133	127
2	125	119
-3	77	-77
3	22	24
-4	73	75
4	87	84
5	18	22
-6	76	79
6	70	68
-7	14	-14
7	42	-42
-8	66	64
8	79	77
-9	16	-14
9	14	16
-10	37	36
10	45	44
-11	32	30
11	25	-24
-12	42	43
12	45	45
-13	11	-10
13	12	8
-14	26	23
14	28	27
15	14	4
-16	21	20
16	15	18
-18	15	13
18	17	14
H81		
0	40	35
-1	77	72
1	72	68
-2	7	-2
2	15	-15
-3	79	78
3	117	114
-4	32	-30
4	47	48
-5	46	49
5	64	65
-6	23	22
6	28	-30
-7	93	91
7	92	89
-8	31	-29
-9	47	45
9	48	49
-10	16	17
-11	44	44
11	31	30
-12	5	2
12	13	-10
-13	32	30
13	30	31
-15	14	13
15	15	14
-17	16	16
17	11	17
H91		
0	32	31
-1	30	27
1	12	-15
-2	88	89
2	97	94
-3	13	-15
3	7	4
-4	45	46
4	79	85
-5	25	23
-6	68	68
6	65	65
-8	68	68
8	70	69
9	16	17
-10	36	34
10	21	22
-12	46	41
12	34	32
-14	7	12
14	13	17
-16	7	14
16	12	14
18	14	13
H101		
0	2	-4
-1	65	65
1	50	47
2	33	-31
-3	75	74
3	90	90
-4	6	5
4	5	0
-5	33	33
5	34	36
-6	13	18
-7	69	67
7	62	59
-9	27	27
9	33	35
-11	35	34
11	25	24
-13	24	23
-15	16	10
-17	13	14
H111		
0	45	46
-2	87	86
2	71	68
-4	34	36
4	39	40
-6	43	45
6	24	25
-8	37	35
8	49	47
10	21	21
-12	33	29
12	33	30
H121		
-1	63	59
1	40	38
2	9	8
-3	58	58
3	55	54
-5	26	28
5	19	18
-7	44	41
7	38	36
-9	12	12
9	29	27
-11	23	22
11	22	21
-13	15	17
13	28	23
-15	9	10
15	9	9
H131		
0	25	25
1	16	15
-2	52	50
2	41	40
-3	10	0
-4	28	28
4	34	36
-5	12	-7
-6	33	32
6	21	24
-8	27	26
8	32	31
-10	20	15
-12	23	19
12	22	19
-14	4	8
14	13	11
H141		
-1	25	26
1	25	23
-3	29	26
3	14	38
-5	22	20
5	25	25
-7	30	30
7	29	28
-9	20	18
9	24	19
-11	18	17
11	12	11
H151		
0	22	19
-1	6	-5
-2	6	22
2	28	26
-4	15	16
4	24	25
-6	20	22
6	25	21
-8	19	20
8	23	21
-10	13	13
10	12	10
H161		
-1	20	20
1	22	18
-3	16	18
3	16	20
-5	16	16
5	21	16
-7	15	15
7	15	15
-9	9	10
9	11	12
H02		
0	215	203
2	109	108
-4	250	246
4	15	10
-6	67	63
6	164	158
-8	93	88
8	48	46
-10	75	72
10	118	115
-12	7	12
12	54	53
-14	61	59
14	35	34
-16	15	13
16	29	31
-18	22	21
-20	14	11
H12		
-1	100	105
1	274	281
-3	184	177
3	35	28
-4	26	-27
4	32	35
-5	201	189
5	172	164
6	46	-45
-7	34	36
7	96	91
-8	42	-40
8	11	-14
-9	130	123
9	70	66
-11	21	21
11	93	91
-13	46	46
13	22	24
15	38	42
17	17	15
H22		
0	260	243
-1	107	105
-2	57	55
2	156	158
-3	33	-38
3	36	32
-4	212	203
4	125	126
-5	14	21
5	7	11
-6	57	52
6	176	177
-7	26	-29
7	52	-48
-8	92	90
8	32	32
-9	16	-15
9	15	17
-10	94	85
10	83	83
-11	11	18
-12	26	23
12	33	35
-13	8	-8
13	12	8
-14	53	51
14	30	30
-15	13	13
-16	9	9
16	31	33
-18	18	17
18	16	11
-20	17	10
20	8	14
H32		
0	43	45
-1	74	73
1	234	218
2	79	-84
-3	65	67
3	92	89
-4	18	-20
4	45	41
-5	110	114
5	175	180
-6	44	44
6	30	-32
-7	44	45
7	83	84
-8	33	-38
-9	118	117
9	50	52
-10	29	28
-11	45	44
11	58	60
-13	52	47
13	20	20
-15	30	28
15	36	38
17	11	19
H42		
0	174	162
-1	17	26
1	16	-52
-2	62	64
2	133	126
-3	78	-69
3	18	-15
-4	126	133
4	107	103
-5	69	81
5	43	51
-6	71	75
6	123	125
7	20	-23
-8	86	89
8	56	55
9	41	44
-10	70	72
10	69	69
-11	17	19
-12	36	37
12	37	39
-13	23	-26
-14	42	41
14	29	30
-16	17	14
16	25	27
-18	12	15
18	14	13
-20	13	8
20	10	11
H52		
0	33	33
-1	122	121
1	125	121
-2	43	-49
2	64	-69
-3	144	146
3	78	81
4	67	65
-5	109	106
5	83	88
-6	59	55
-7	67	68
7	74	76
-8	35	-36
8	13	13
-9	61	61
9	61	62
-10	32	34
10	18	23
-11	30	31
11	56	60
-12	6	-15
12	17	-21
-13	36	34
13	33	35
-15	23	23
15	25	26
-17	18	16
17	13	16
-19	18	12
H62		
0	102	95
-1	61	57
1	22	-19
-2	153	148
2	102	98
-3	63	-69
3	14	-16
-4	118	116
4	72	74
-5	39	38
5	31	32
-6	80	78
6	67	71
-7	21	-23
7	40	-39
-8	62	61
8	74	72
-9	11	-5
9	21	25
-10	34	32
10	54	58
-11	21	19
-12	31	31
12	47	48
-13	13	-16
-14	23	24
14	27	27
-15	14	13
-16	18	19
16	10	17
-18	16	14
18	10	11
-20	10	7
20	16	7
H72		
0	72	75
-1	98	92
1	76	74
2	40	-35
-3	97	95
3	103	99
-4	16	-13
4	33	35
-5	62	63
5	55	56
-6	17	22
6	35	-30
-7	80	79
7	76	74
-8	40	-38
8	11	-14
-9	43	40
9	57	57
-10	22	22
-11	41	39
11	39	40
12	6	-10
-13	31	28
13	36	34
-15	15	17
15	16	18
-17	20	16
17	21	15
-19	3	7
19	3	9
H82		
0	55	56
-1	47	44
1	6	2
-2	87	86
2	98	95
-3	30	-30
-4	34	37
4	84	87
-5	24	24
-6	66	68
6	53	55
-7	19	-20
7	33	-33
-8	57	57
8	65	64
9	14	11
-10	37	38
10	24	26
-11	6	10
11	7	-5
-12	44	42
12	31	31
13	11	3
-14	15	15
14	23	22
-16	2	16
16	8	15
-18	15	8
18	13	13
-20	11	5
20	9	6
H92		
0	16	14
-1	83	78
1	61	53
2	22	-22
-3	62	59
3	110	107
4	17	18
-5	34	35
5	57	58
-6	10	13
-7	67	66
7	58	56
-8	10	-13
-9	31	31
9	37	36
-10	11	11
-11	47	43
11	21	18
13	26	27
-15	11	12
15	12	13
-17	18	12
17	12	14
19	17	8
H102		
0	43	43
-1	5	-2
1	15	-13
-2	82	80
2	66	65
-4	29	28
4	64	66
-5	18	17
5	16	16
-6	53	53
6	33	32
-8	38	35
8	49	50
9	5	11
-10	24	24
10	16	21
-11	5	1
-12	34	31
12	27	26
14	18	18
-16	21	14
16	11	10
-18	6	6
18	19	10
H112		
-1	65	64
1	30	32
-3	54	53
3	56	57
-5	35	37
5	16	21
-6	5	6
6	8	7
-7	52	49
7	42	39
-9	16	13
9	38	37
-11	23	25
11	23	21
-13	18	14
13	24	24
H122		
0	33	32
-2	65	61
2	38	35
-3	3	3
-4	32	33
4	33	34
-6	46	45
6	21	20
-8	22	23
8	39	39
-10	13	14
10	18	21
-12	19	19
12	15	21
-14	2	7
H132		
-1	40	39
1	20	21
-3	33	33
3	42	40
-5	24	25
5	25	25
-6	8	-9
-7	31	31
7	26	27
-9	19	14
9	20	23
-11	25	19
11	10	13
-13	2	10
13	12	15
H142		
0	24	24
-2	29	28
2	33	31
-4	15	14
4	34	34
-6	24	24
6	13	20
-8	18	18
8	21	21
-10	15	16
10	10	11
-12	15	14
12	8	10
-14	11	6
H152		
-1	22	23
1	23	22
-3	12	14
3	28	28
-5	11	15
5	17	20
-7	19	18
7	17	17
-9	10	12
-11	20	13
11	10	8
-13	6	7
H162		
0	15	18
-2	19	18
2	12	16
-4	14	15
4	14	17
-6	13	15
6	8	13
-8	9	10
8	14	12
-10	17	9
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H13		
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H23		
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H63		
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H24		
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18	12	9
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H64		
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14	16	7
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5	13	12
H164		
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8	12	8
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H05		
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H15		
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H25		
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H35		
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H45		
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H55		
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H65		
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H75		
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H85		
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H95		
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H105		
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13	5	11
H115		
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10	18	14
H125		
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9	17	15
H135		
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H145		
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H155		
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4	2	10
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H165		
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3	7	7
5	15	8
H06		
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12	17	20
H16		
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H26		
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H36		
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H46		
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H56		
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H66		
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9	7	18
H86		
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8	19	17
H96		
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7	14	12
H106		
0	21	23
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2	15	14
-4	11	15
H116		
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-3	13	8
3	16	17

---

[a] $F(C) = 10F(\text{calcd})$; $F(\text{calcd})_{\text{absolute}} = F(\text{calcd})/\text{scale factor}$.

TABLE V

DATA FOR *trans*-$Pt[P(C_2H_5)_3]_2Br_2$

Atom Positional and Temperature Parameters and Errors;[a] $\sigma' = \sigma \times 10^5$

Atom	x/a	$\sigma'(x/a)$	y/b	$\sigma'(y/b)$	z/c	$\sigma'(z/c)$
Pt	0.5000	. . .[b]	0.5000	. . .[b]	0.5000	. . .[b]
Br	0.7037	15	0.4570	21	0.4304	40
P	0.4303	35	0.3288	38	0.3787	76
C_1	0.3050	222	0.3332	210	0.2193	341
C_2	0.3265	315	0.4113	399	0.0816	741
C_3	0.3682	201	0.2309	178	0.5521	424
C_4	0.4674	335	0.2002	369	0.7160	761
C_5	0.5449	176	0.2423	194	0.2543	354
C_6	0.4962	233	0.1156	247	0.2101	617

Thermal Parameters and Standard Deviations; Anisotropic Temperature Factors of the Form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; $\sigma' = \sigma \times 10^5$

Atom	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Pt	0.0046	5	0.0059	5	0.0307	24	0.0000	4	−0.0008	8	0.0006	10
Br	0.0054	11	0.0108	16	0.0540	73	0.0002	13	0.0024	22	−0.0047	32
P	0.0067	30	0.0070	31	0.0435	145	0.0000	25	−0.0018	52	−0.0020	56
C_1	0.0169	267	0.0109	198	0.0385	645	−0.0009	188	−0.0110	318	0.0042	290
C_2	0.0198	413	0.0283	578	0.1046	1817	0.0075	398	−0.0267	735	−0.0389	924
C_3	0.0124	212	0.0092	178	0.0770	1001	0.0007	156	0.0061	381	0.0134	357
C_4	0.0187	381	0.0210	449	0.1229	1957	−0.0056	342	0.0054	712	0.0294	826
C_5	0.0095	161	0.0115	195	0.0535	718	−0.0002	142	0.0050	280	−0.0155	312
C_6	0.0126	246	0.0123	269	0.1136	1668	0.0008	212	−0.0055	507	0.0124	554

Scale factor = 0.1296 ± 0.0006

[a] With real and imaginary corrections. [b] Parameter fixed by symmetry.

$\Sigma w(F_o - F_c)^2$. The observations were weighted as the inverse of their variance $\sigma^2F^2 = S(1/Lp)^2[N + 2B + (0.04N)^2]$, where N is the net count in a peak, B is the background count, S is the scale factor, and Lp is the Lorentz-polarization correction.[26] Refinement was carried out in three different ways: (a) no dispersion correction,[13] (b) real dispersion correction,[13] and (c) real and imaginary dispersion corrections.[27] The scattering factors for Pt, Br, P, and neutral C were from the compilation of Ibers[14] and the dispersion corrections from the tables of Cromer.[15] Final atomic coordinate shifts were less than 4×10^{-6} and 2×10^{-4} of a cell edge for the heavier atoms and carbon, respectively. The atomic coordinates in all three refinements were found to be equal to within less than one standard deviation. In fact, even the rms displacements of the Pt, Br, and P atoms along the principal axes were found to be within two standard deviations for (a) and (c) and only slightly more different for (b). For refinement (c) the final R factor, weighted R, and standard error were found to be 0.077, 0.114, and 0.557, respectively. Final calculated and observed structure factors are listed in Table IV. Table V contains the final atomic parameters, temperature factors, and errors. Table VI contains the bond distances, angles, and errors.

TABLE VI

BOND PARAMETERS FOR *trans*-$Pt[P(C_2H_5)_3]_2Br_2$

Intramolecular Distances

Bonding, A		Nonbonding, A	
Pt–P	2.315 (4)	Br–C_1	4.94 (2)
Pt–Br	2.428 (2)	Br–C_2	4.96 (3)
P–C_1	1.84 (2)	Br–C_3	4.73 (2)
P–C_3	1.90 (2)	Br–C_4	4.62 (3)
P–C_5	1.92 (2)	Br–C_5	3.32 (2)
C_1–C_2	1.46 (6)	Br–C_6	4.88 (3)
C_3–C_4	1.64 (5)		
C_5–C_6	1.61 (4)	C_1–C_3	2.88 (3)
		C_1–C_4	4.43 (6)
Bond angles, deg		C_1–C_5	2.91 (3)
P–Pt–Br	92.8 (1)	C_1–C_6	3.34 (3)
P–Pt–Br′	87.2 (1)	C_2–C_3	4.19 (6)
Pt–P–C_1	119.3 (8)	C_2–C_4	5.61 (8)
Pt–P–C_3	111.1 (1.0)	C_2–C_5	3.37 (5)
Pt–P–C_5	114.8 (6)	C_2–C_6	4.01 (5)
P–C_1–C_2	109.2 (1.8)		
P–C_3–C_4	113.4 (1.7)	C_3–C_5	3.11 (3)
P–C_5–C_6	112.0 (1.6)	C_3–C_6	3.41 (4)
C_1–P–C_3	99.9 (1.2)		
C_1–P–C_5	102.6 (1.1)	C_4–C_6	4.10 (8)
C_3–P–C_5	107.6 (1.1)		

Intermolecular Distances, A

Pt–Pt	7.629
Br–C_6	3.94 (3)
Br–C_3	3.69 (3)
All others	>4

Discussion of Structures

The crystal structures of the isomorphous pair, *trans*-$Pt[P(C_2H_5)_3]_2X_2$, X = Cl, Br, are composed of discrete molecules separated by normal van der Waals distances (Figures 1 and 2 and Tables III and VI). The Pt–P–C and C–P–C angles are not significantly different from the expected tetrahedral value, and the P–C, C–C distances are normal single bonds. Carbon–carbon nonbonded distances within a $P(C_2H_5)_3$ group are similar to those found in free trimethylphosphine.[28]

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[26] S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957).

[27] Modification of ORFLS for the C.D.C. 1604, including dispersion corrections. We wish to thank Professor L. Dahl for the use of this program and making the University of Wisconsin C.D.C. 1604 available for this calculation.

[28] H. D. Springall and L. O. Brockway, *J. Am. Chem. Soc.*, **60**, 996 (1938); D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).

The Pt–Pt separation is 7.61 A; there cannot be any significant metal–metal interaction.

Our average rms amplitudes were calculated to be 0.22 and 0.26 A for platinum and phosphorus, respectively, and are to be compared to the 0.19 and 0.21 A for these same atoms found by Eisenberg and Ibers.[9] Our larger values arise from larger β_{33} values which are physically reasonable since this would correspond to a motion normal to the PtP_2Br_2 plane. Further, the terminal carbon atoms (C_2, C_4, C_6) have higher temperature factors than those bonded to phosphorus (C_1, C_3, C_5), as would be expected. The spread in observed carbon–carbon distances and the carbon temperature factors are similar to those found in other Pt(II) complexes where absorption corrections were made.[17]

Referring to Tables III and VI, it is seen that in both *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ and *trans*-$Pt[P(C_2H_5)_3]_2Br_2$ the metal–halogen bond distance is that of a "normal" Pt–X single bond. On the other hand, the Pt–P distances in both these compounds are approximately 0.1 A shorter than the sum of the covalent radii. The difference between these observed Pt–P distances and that calculated from the sum of the covalent radii is certainly real. It might be argued that our platinum radius of 1.31 A is not an appropriate value for a platinum single-bond radius, but the Pt–X bonds in this case give us an internal standard and seem to justify the use of this value. Our Pt–Cl distance is also in good agreement with the 2.32 A average distance observed by Baenziger, Medrud, and Doyle.[17]

Pt–P distances ranging from 2.26[8,9] to 2.16 A[9,10] have been reported. Except for the structure determination of $PtH[P(C_6H_5)_2C_2H_5]_2Cl$[9] by Ibers and Eisenberg, Pt–P bond distances have not been reliable. In most of the Pt–P containing structures that have been reported, the bond length errors are as large as ±0.07 A. Under these circumstances, 2.26 A is not statistically different from 2.41 A—the sum of the single-bond covalent radii. The large errors in the above two structures are to be expected from analysis of only two-dimensional photographic data. Further, experience has shown that estimates of error from two-dimensional data are frequently too small, particularly if only the diagonal approximation is used for least-squares refinement. We have reported the chloride results only to show that the same trend exists as in the bromide, and our estimates of error may also be somewhat optimistic for the chloride. The bond length variation between these isomers and the *cis* isomers will be discussed in a following paper.

The statistically significant distortion of the P–Pt–Br angle from the idealized 90° to the observed value of 92.8 ± 0.1° is probably due to the Br–C_5 nonbonded interaction (see Table VI). It is to be noted from the C_n–C_5 distances that C_5 is rather rigidly constrained by its neighbors and cannot avoid the Br interaction.

It appears that in *trans*-$Pt[P(C_2H_5)_3]_2X_2$, the platinum nonbonding d orbitals interact with the empty phosphorus d orbitals to give a substantial amount of multiple bonding. By this interaction the phosphorus removes the partial positive charge that it would acquire by the donation of its pair of nonbonding electrons to the platinum in the formation of the complex. This has been frequently referred to as back-bonding. The fact that our Pt–P distance of 2.315 ± 0.004 A is significantly different from the 2.268 ± 0.008 A distance found by Eisenberg and Ibers[9] in hydridochlorobis(diphenylphosphine)platinum, where the phosphorus atoms have the same relative configuration, must mean that Pt–P distances are not completely independent of substituents in the *cis* positions. On the other hand, the halogens do not interact with the platinum to form multiple bonds, at least, no more so than in the diatomic halogens themselves.[29]

These results raise serious questions about the reliability of the Pt–Br bond distance of 2.7 A found by Bokii[30] in $PtBr_3NH_3 \cdot H_2O$. In the past, much has been made of Pt–R (R a general ligand) bond lengths and the *trans* effect from, almost without exception, two-dimensional analyses and incomplete refinements.[11,31]

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(29) R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 884 (1955).

(30) G. B. Bokii and G. A. Kukina, *Soviet Phys. Cryst.*, **2**, 395 (1957).

(31) G. B. Bokii, Abstracts of Papers, 7th International Union of Crystallography, Rome, Italy, Sept 9–18, 1963, p A1.