Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE CRYSTAL AND MOLECULAR STRUCTURE OF DICARBONYLBIS(DIPHENYLETHYLPHOSPHINE)PLATINUM(0) $Pt(CO)_2[P(C_6H_5)_2(C_2H_5)]_2$

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(Received August 2nd, 1971)

SUMMARY

The complex dicarbonylbis(diphenylethylphosphine)platinum, $Pt(CO)_2[P(C_6H_5)_2(C_2H_5)]_2$, crystallizes in either of the enantiomorphous space groups $P3_121$ (No. 152) and $P3_221$ (No. 154) with cell dimensions $a = 10.64(1)$, $c = 22.06(1)$ Å, $U = 2163$ Å^3; $\rho_c = 1.564$ g/cm^3 for $Z = 3$, $\rho_m = 1.55(3)$ g/cm^3. The intensities of 1177 independent reflections have been determined by counter methods with Mo-$K\alpha$ monochromatized radiation. The structure has been solved by the heavy atom method. The refinement, carried out by full-matrix least squares down to a final R factor of 0.042, has enabled the absolute configuration of the crystal sample (space group $P3_121$) to be ascertained. The molecule is roughly tetrahedral, and has the metal atom lying on a two-fold axis of the cell. Bond parameters are: Pt–C = 1.92(2) Å, Pt–P = 2.360(4) Å, C–Pt–C = 117(1)° and P–Pt–P = 97.9(2)°. The PtC_2 and PtP_2 moieties make a dihedral angle of 86.0(3)°. The overall C_2 symmetry of the molecule is probably only a statistically averaged situation, a disorder in the Pt–CO interactions being apparent from the orientations of the thermal ellipsoids of the C and O atoms.

INTRODUCTION

The determination of the crystal and molecular structure of dicarbonylbis(diphenylethylphosphine)platinum(0), $Pt(CO)_2[P(C_6H_5)_2(C_2H_5)]_2$, whose synthesis has been recently described[1], is part of our program of investigation on mononuclear carbonyl and nitrosyl complexes of the Group VIII metals. We have already reported the structures of two polymorphs of $Pt(CO)[P(C_6H_5)_3]_3$[2,3]; the structure of the complex $Ir(NO)[P(C_6H_5)_3]_3$ has been reported elsewhere[4].

In the series of the carbonylphosphine derivatives of platinum(0) of the $Pt(CO)_n(PR_3)_{4-n}$ type, the present complex seems to represent the limit of stability; the complex $Pt(CO)_4$ is a short-lived species[5] and the stability of $Pt(CO)_3PR_3$, which has never been described, might well be similar. In this connection, the metal–ligand interactions in the present compound appear to be of particular interest.

In describing the structure of $Pt(CO)[P(C_6H_5)_3]_3$[2,3] we have stressed the fact that the Pt–P distances in carbonyl-complexes of Pt^0 and Pt^{II} are something like 0.1 Å longer than the corresponding interactions in non-carbonylated species. This fact was explained in terms of a lower Pt–P bond order, due to the stronger ability of the carbonyl group as a π-acceptor. The present investigation provides an opportunity of checking as to whether a further elongation in the Pt–P bond length is observed in passing from the mono- to the di-carbonylated species.

EXPERIMENTAL SECTION

Crystal data

$Pt(CO)_2[P(C_6H_5)_2(C_2H_5)]_2$, M=679.3, yellow, crystallizes in trigonal bipyramids. All the samples examined had small red inclusions, probably of cluster impurities. The unit cell constants, as determined from precession photographs and refined by the "ω-lag" method[6] on the Pailred diffractometer with Mo-$K\alpha$ radiation (λ=0.70930), are: $a=b=10.64(1)$, $c=22.06(1)$ Å, $U=2163$ Å^3. The experimental specific gravity of the crystal of 1.55(3) g/cm^3, measured by flotation in iodomercurate solutions, agrees with the calculated value of 1.564 g/cm^3 for $Z=3$. The systematic absences observed in precession photographs ($00l$ reflections lacking for $l \neq 3n$) indicate the presence of a 3_1 or 3_2 screw axis. The Laue group being $\bar{3}m$, and the mirror planes of the diffraction pattern being perpendicular to the real cell axes a and b, either of the two enantiomorphous space groups $P3_121$ (D_3^4, No. 152) and $P3_221$ (D_3^6, No. 154) is possible.

Intensity measurement

The sample used in the data collection was a bipyramid measuring 0.57 mm along the c axis and 0.27 × 0.25 mm in a plane perpendicular to it. The crystal was mounted along the trigonal axis on a Pailred linear equi-inclination diffractometer; the radiation of an Mo tube operated at 48 kV and 16 mA was monochromatized by reflection on a silicon crystal cut normally to {111}; the radiation incident on the sample was the Mo-$K\alpha$ doublet, free from sub-harmonics. The counter was an NaI/Tl crystal coupled with a photomultiplier; the discriminator was assigned with a window so as to detect 95% of the incident radiation. The data were collected at room temperature.

Each reflection was measured by an ω-scan, the counter being fixed at the appropriate 2ϑ value with a receiving aperture of 1.5°. The range of the ω-scan was varied with the equi-inclination angle: $\Delta\omega$ was 0.8° at $\mu=0°$ and 1.6° at the maximum μ. The times spent on peak and background measurements were kept roughly equal. A total of 2793 reflections were measured on 23 different reciprocal lattice levels from $hk0$ to $hk22$, in the 0.08–0.58 range of $\sin\vartheta/\lambda$. The stability of the crystal sample was controlled, during the collection of the data, by measuring periodically a small number of standard reflections. As no decay whatever took place, all the reciprocal lattice layers were assigned with a single scale factor.

Corrections for systematic effects were applied to the 2051 net intensities having a relative counting statistical error, $\sigma(I)/I$, less than 0.25 [$\sigma(I)$, the *esd.* of the net intensity I, is equal to $(I_{\text{peak}}-t^2\cdot I_{\text{background}})^{\frac{1}{2}}$, t being the ratio between the times spent on peak and background measurements]. The transmission factors ($\mu=52.4$ cm^{-1}) were evaluated by the Busing and Levy method[7]; the X-ray path inside the crystal was sampled in 8^3 (512) points and the resulting transmission factors were in the range 0.32–0.38. The bond polarisation correction[8], allowing for the partial polarisation of the incident beam, was adopted.

After averaging the equivalent F_o's, the final experimental set consisted of 1177 independent observations*.

Solution and refinement of the structure

A three-dimensional Patterson map allowed the special positions *a* or *b* of either of the two enantiomorphous space groups to be assigned to the platinum atoms. These positions correspond to independent sets of binary axes perpendicular to the screw axis; the choice of either set is arbitrary and corresponds to an origin shift of *c*/2. The assignment of such positions to the platinum atom implies a molecular symmetry C_2. A Fourier difference phased with the contribution of the heavy atom has disclosed the position of all the non-hydrogen atoms. A structure factor computation at this point gave an *R* factor of 0.17.

The structure refinement was effected by full-matrix least squares, the function minimized being $\Sigma w(F_o-|F_c|)^2$. The variance of F_o was defined as $(1/w=2.4+4\times10^{-2}F_o+6\times10^{-4}F_o^2)$. The coefficients of this polynomial were chosen by trial and error, so as to obtain an approximately constant mean value of $w\Delta F^2$ over the entire range of $\sin\vartheta/\lambda$ and F_o. The following parameters were refined: one positional and four thermal anisotropic parameters for the platinum atom, six positional and one overall thermal isotropic parameter for each of the two independent phenyl rings, which were treated as rigid groups (D_{6h} symmetry, C–C bond length of 1.392 Å), and, finally, nine positional and thermal anisotropic parameters for each of the five independent non-group atoms (one P, one O and three C atoms). This makes a total of 65 parameters, including one overall scale factor, to be refined. In the last few cycles the hydrogen atom contribution to F_c was included. Each hydrogen was placed at 1.08 Å from the carbon atom to which it is bonded; C–C–H angles of 120° were assumed for phenylic hydrogens, and for the atoms belonging to the C_2H_5 group, a staggered configuration and tetrahedral angles were imposed. The hydrogen atoms were assigned isotropic temperature factors equal to those of the corresponding carbon atoms. The atomic scattering factors for least squares and structure factor computations were evaluated according to Cromer and Mann for Pt, P, O and C[9]; for hydrogen atoms the scattering factor given by Forsyth and Wells[10] was adopted. The real and imaginary part of the anomalous scattering of Pt and P (*ref.* 11) have been included in the computations.

The refinement was performed on both the enantiomorphous space groups $P3_121$ and $P3_221$ and was terminated when all shifts were less than one third of the corresponding *esd*'s.

The final reliability indices were: for space group $P3_121$ $R=\Sigma|F_o-|F_c||/\Sigma F_o=0.042$ and $R_w=(\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}}=0.055$; for space group $P3_221$ $R=0.046$ and $R_w=0.059$.

On the basis of the Hamilton test[12], the hypothesis of the crystal belonging to space group $P3_221$ can be rejected at a confidence level higher than 99.5%.

A final difference Fourier map revealed a peak of ca. 0.4 electrons/Å^3 associated with the position of the heavy atom, and no significant features.

The results of the refinement are summarized in Tables 1–3. Table 1 lists the computed and observed structure factor moduli in electrons; Table 2 gives the posi-

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* In presence of anomalous scatterers, the final set contains a number of Friedel pairs. For many of them, significantly different amplitudes have been noticed (see Table 1).

TABLE 1

OBSERVED AND COMPUTED STRUCTURE FACTORS MODULI IN ELECTRONS FOR $Pt(CO)_2[P(C_6H_5)_2C_2H_5]_2$

H	L	FO	/FC/
	K = -0		
2	1	91	86
2	2	103	95
2	3	150	142
2	4	120	116
2	5	154	146
2	6	80	78
2	7	53	43
2	8	141	135
2	9	18	20
2	11	131	131
2	12	11	10
2	13	36	35
2	14	102	104
2	16	33	32
2	17	60	62
2	18	31	27
2	19	19	15
2	20	49	46
2	21	14	14
3	1	24	24
3	2	67	64
3	3	134	126
3	4	50	49
3	5	80	83
3	6	127	123
3	7	69	64
3	8	62	63
3	9	74	74
3	10	15	19
3	11	38	39
3	12	88	83
3	14	41	41
3	15	80	78
3	16	26	22
3	17	31	33
3	18	58	56
3	20	20	19
3	21	35	33
4	1	124	124
4	2	55	45
4	3	75	77
4	4	116	110
4	5	69	70
4	6	62	67
4	7	108	111
4	8	28	24
4	9	51	49
4	10	49	49
4	11	12	12
4	12	35	37
4	13	48	44
4	15	47	46
4	16	59	58
4	17	25	25
4	18	25	27
4	19	41	43
4	21	20	17
4	22	19	18
5	1	104	102
1	20	19	18
1	21	33	40
1	22	15	14
2	1	182	184
2	2	45	40
2	3	50	51
2	4	158	151
2	5	64	64
2	6	66	71
2	7	154	144
2	8	45	45
2	9	45	51
2	10	86	89
2	11	28	27
2	12	35	36
2	13	85	88
2	14	13	14
2	15	36	36
2	16	66	69
2	17	35	31
2	18	28	30
2	19	55	53
2	22	32	32
3	1	50	92
3	2	128	124
3	3	65	65
3	4	90	86
3	5	123	118
3	6	61	63
3	7	46	45
3	8	81	81
3	9	36	37
3	10	36	42
3	11	75	73
3	12	26	25
3	13	47	47
3	14	65	67
3	16	45	34
3	17	50	50
3	18	22	23
3	19	24	23
3	20	35	36
4	1	29	36
4	2	67	66
4	3	58	56
4	4	45	47
4	5	61	62
4	6	57	54
4	7	51	50
4	8	46	55
4	9	42	41
4	10	23	35
4	11	22	32
4	12	19	41
4	13	15	13
4	14	19	42
4	15	50	49
4	17	17	28
4	18	36	36
4	20	14	31
4	21	21	20
5	1	64	71
-1	5	51	51
1	6	61	61
-1	6	168	163
1	7	82	79
-1	7	95	91
1	8	143	144
-1	8	47	43
1	9	49	51
-1	9	119	123
1	10	18	23
-1	10	47	48
1	11	116	119
1	12	31	30
-1	12	134	135
1	13	22	22
-1	13	13	9
1	14	78	79
1	15	13	12
-1	15	93	93
1	16	23	25
1	17	51	54
-1	17	24	24
1	18	22	23
-1	18	63	64
1	19	23	27
-1	19	18	14
1	20	43	43
-1	20	16	14
1	21	20	17
-1	21	34	34
1	22	19	15
-1	22	16	13
2	0	130	131
2	1	39	45
2	2	80	74
2	3	125	120
2	4	34	36
2	5	49	49
2	6	117	114
2	7	54	60
2	8	56	58
2	9	78	81
2	10	71	69
2	11	37	38
2	12	79	78
2	13	29	29
2	14	40	40
2	15	62	62
2	16	16	15
2	17	33	33
2	18	47	48
2	19	15	18
2	20	21	23
2	21	33	33
3	1	106	104
3	2	51	51
3	3	73	74
3	4	104	101
3	5	49	47
3	6	56	57
3	7	84	85
3	8	41	39
0	2	94	93
0	3	165	165
0	4	44	48
0	5	81	83
0	6	111	111
0	7	39	37
0	8	79	75
0	9	97	98
0	10	62	57
0	11	15	15
0	12	106	109
0	13	26	28
0	15	54	60
0	17	28	27
0	18	46	46
0	19	24	22
0	20	26	26
0	21	35	39
0	22	19	17
1	0	57	55
-1	0	80	79
1	1	101	97
-1	1	57	55
1	2	23	24
-1	2	114	111
1	3	58	58
-1	3	44	43
1	4	92	92
-1	4	46	45
1	5	64	60
-1	5	124	126
1	6	67	69
-1	6	68	67
1	7	126	122
-1	7	86	84
1	8	54	56
-1	8	145	143
1	9	53	54
-1	9	52	53
1	10	96	97
-1	10	26	28
1	11	52	51
-1	11	119	119
1	12	28	28
-1	12	33	30
1	13	62	64
-1	13	20	18
1	14	28	28
-1	14	81	80
1	15	18	22
1	16	37	40
-1	16	20	23
1	17	25	24
-1	17	55	56
1	18	32	31
-1	18	26	25
1	19	39	40
-1	19	26	29
1	20	17	18
-1	20	43	44
1	21	25	22
-1	21	20	17
4	7	31	25
4	8	33	34
4	9	46	47
4	10	27	26
4	11	32	31
4	12	38	35
4	13	24	25
4	14	23	24
4	15	26	26
4	16	18	18
5	1	44	44
5	2	22	21
5	3	34	37
5	4	32	35
5	6	33	33
5	7	33	33
5	8	19	16
5	9	22	15
5	10	43	41
5	12	18	18
5	13	30	25
6	1	17	18
6	2	26	26
6	4	21	25
6	5	30	26
6	7	21	21
6	8	30	35
6	11	25	24
7	3	27	24
7	6	23	23
	K = 4		
0	0	95	95
0	1	28	32
0	2	74	75
0	3	78	77
0	4	62	61
0	5	97	95
0	6	63	61
0	7	97	91
0	8	111	111
0	9	36	38
0	10	27	26
0	11	74	76
0	12	34	35
0	14	36	38
0	15	33	32
0	16	30	30
0	17	34	35
0	18	26	24
0	19	30	32
0	20	34	35
0	21	17	16
0	22	17	14
1	0	67	65
-1	0	45	43
1	1	79	77
-1	1	89	84
1	2	54	54
-1	2	19	21
1	3	67	65
2	16	21	21
-2	16	21	20
2	17	26	25
-2	17	33	31
2	18	19	19
-2	18	51	50
2	19	20	20
-2	19	18	18
-2	20	27	26
-2	21	35	35
-2	22	15	16
3	0	61	60
3	1	48	44
-3	1	88	89
3	2	40	38
-3	2	169	166
3	3	58	63
-3	3	67	65
3	4	38	40
-3	4	40	46
3	5	37	39
-3	5	130	126
3	6	41	40
-3	6	61	66
3	7	32	33
-3	7	47	46
3	8	24	29
-3	8	86	86
3	9	30	28
-3	9	34	35
3	10	36	35
-3	10	35	40
3	11	24	23
-3	11	69	69
3	12	37	36
-3	12	23	20
3	13	30	32
-3	13	44	45
3	14	14	20
-3	14	65	65
3	15	32	32
3	16	22	22
-3	16	42	39
-3	17	54	52
3	18	20	19
-3	18	22	25
3	19	17	14
-3	19	22	24
-3	20	37	37
-3	21	16	17
-3	22	18	16
4	0	23	25
4	2	30	32
4	3	17	17
4	4	45	44
4	5	27	27
4	6	19	19
4	7	33	31
4	8	41	41
4	9	19	20
4	11	31	33
4	12	17	17
-1	15	21	22
1	16	32	26
-1	16	34	30
1	17	18	16
-1	17	31	29
1	18	19	19
-1	18	31	33
-1	19	19	18
-1	20	20	20
-1	21	26	30
-1	22	17	15
2	0	40	40
-2	0	45	43
2	1	63	67
-2	1	56	57
2	2	42	42
-2	2	61	61
2	3	27	28
-2	3	78	82
2	4	54	56
-2	4	35	41
2	5	26	27
-2	5	62	65
2	6	23	25
-2	6	66	67
2	7	35	35
-2	7	52	42
2	8	26	25
-2	8	56	55
2	9	27	30
-2	9	47	48
2	10	44	44
-2	10	41	42
2	11	31	33
-2	11	65	64
2	12	20	20
-2	12	41	39
2	13	35	37
-2	13	34	38
2	14	26	25
-2	14	33	35
-2	15	36	35
2	16	26	27
-2	16	34	33
2	17	19	18
-2	17	31	38
-2	18	23	23
-2	19	23	23
-2	20	35	35
-2	21	17	15
3	0	27	26
3	1	23	23
-3	1	105	102
3	2	55	54
-3	2	57	57
3	3	28	30
-3	3	65	67
3	4	20	19
-3	4	106	103
3	5	42	40
-3	5	54	53
3	6	34	32
0	13	41	39
0	14	25	29
0	16	30	29
0	19	19	17
1	0	45	44
-1	0	76	74
-1	1	45	51
1	2	54	51
-1	2	34	42
1	3	46	45
-1	3	73	79
1	4	21	21
-1	4	47	50
1	5	54	56
-1	5	43	43
1	6	17	18
-1	6	46	45
1	7	17	16
-1	7	32	33
1	8	47	49
-1	8	44	46
-1	9	41	37
1	10	29	32
-1	10	31	24
1	11	36	37
-1	11	40	41
1	12	29	28
-1	12	48	49
-1	13	29	30
1	14	30	29
1	15	27	27
-1	15	44	43
-1	16	32	27
-1	17	21	23
-1	18	21	20
1	20	23	15
2	0	46	46
-2	0	38	38
2	1	27	30
-2	1	37	33
2	2	25	26
-2	2	63	61
2	3	46	49
-2	3	48	48
2	4	31	29
-2	4	45	51
2	5	53	54
2	6	37	37
-2	6	38	38
2	7	25	22
-2	7	54	54
2	8	42	43
2	9	33	32
-2	9	43	43
2	10	17	18
-2	10	46	46
-2	11	54	51
2	12	29	31
-2	12	34	38
2	13	20	18
-2	13	27	28
-2	14	47	39
-5	18	19	17
-5	19	21	22
-5	21	19	17
	K = 7		
0	0	52	54
0	3	54	56
0	4	36	34
0	5	23	23
0	9	44	37
0	12	30	32
0	13	21	21
0	15	26	25
0	16	24	23
0	18	25	18
-1	0	42	44
1	1	35	36
-1	1	17	14
1	2	27	25
-1	2	58	57
-1	3	45	46
1	4	43	44
-1	4	23	21
1	5	20	25
-1	5	53	54
-1	6	19	20
1	7	38	40
-1	7	17	16
-1	8	44	45
1	10	33	30
-1	10	28	29
-1	11	38	38
-1	12	24	26
-1	14	32	32
-1	15	29	27
-1	17	24	23
-1	18	20	14
2	0	17	16
-2	0	37	38
2	1	68	69
2	2	39	30
-2	2	41	40
2	3	21	21
-2	3	29	31
-2	4	58	60
2	5	32	34
-2	5	32	32
2	6	18	16
-2	6	27	28
-2	7	35	35
2	8	28	28
-2	8	27	28
-2	9	24	29
-2	10	43	42
2	11	22	23
-2	11	31	32
-2	13	37	38
-2	14	26	25
-2	16	32	31
-2	17	20	18
-2	19	19	16
0	5	31	34
0	8	32	30
0	11	25	21
1	0	29	30
1	1	17	14
-1	1	40	40
-1	2	30	24
1	3	26	24
-1	4	45	42
-1	5	26	25
1	6	23	23
-1	7	35	35
1	9	28	25
-1	10	32	30
2	1	19	17
-2	1	29	30
-2	2	26	25
-2	3	48	51
2	4	22	23
-2	4	25	30
-2	6	15	13
-2	9	33	30
-2	12	30	32
-3	0	29	30
-3	1	27	21
-3	2	60	60
-3	3	27	26
-3	4	14	20
-3	5	42	41
-3	6	29	25
-3	8	26	27
-3	9	33	32
-3	11	33	26
-3	12	21	22
-4	1	50	46
-4	2	10	36
-4	3	19	17
-4	4	46	45
-4	5	26	26
-4	6	24	25
-4	7	31	25
-4	8	39	35
-4	9	14	21
-4	10	19	23
-4	11	35	34
-4	13	25	26
-5	1	42	45
-5	2	19	20
-5	3	39	36
-5	4	29	31
-5	6	30	31
-5	7	32	35
-5	8	19	17
-5	9	19	21
-5	10	45	43
-5	13	27	25
-6	1	31	33
-6	2	23	22
-6	3	39	41
-6	6	33	36
-6	8	23	21
-6	9	40	41

[illegible]

TABLE 2

POSITIONAL AND THERMAL PARAMETERS OF NONGROUP ATOMS[a-c]

Atom	x/a	y/b	z/c	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Pt	0	2998(1)	6667	250(2)	250(2)	−20(0)	184(1)	−10(0)	22(0)
P	455(4)	4682(4)	5883(1)	201(7)	265(10)	0(3)	229(7)	6(3)	21(1)
C(1)	−1660(27)	1231(20)	6401(8)	424(47)	313(57)	−32(23)	154(25)	11(16)	36(4)
O	−2576(22)	120(17)	6248(8)	440(41)	219(50)	−126(25)	177(24)	−22(18)	68(6)
C(2)	2220(16)	6426(17)	5897(7)	155(23)	154(39)	23(14)	222(25)	22(15)	30(4)
C(3)	3501(20)	6120(28)	5920(10)	183(29)	368(68)	26(19)	490(54)	62(27)	38(6)

[a] All values × 10^4. [b] The β_{ij} are the coefficients of the form: $h^2\cdot\beta_{11}+k^2\cdot\beta_{22}+l^2\cdot\beta_{33}+h\cdot k\cdot\beta_{12}+h\cdot l\cdot\beta_{13}+k\cdot l\cdot\beta_{23}$. [c] The numbers in parentheses here and in the succeeding Tables are the *esd*'s on last significant digits.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS OF GROUP ATOMS[a]

Atom	x/a	y/b	z/c	B(Å^2)
C(4)	−894(11)	5259(13)	5823(6)	8.1(2)
C(5)	−2350(13)	4188(10)	5791(6)	8.1(2)
C(6)	−3418(10)	4573(11)	5740(6)	8.1(2)
C(7)	−3030(11)	6032(13)	5721(6)	8.1(2)
C(8)	−1574(13)	7103(10)	5752(6)	8.1(2)
C(9)	−507(10)	6718(11)	5803(6)	8.1(2)
C(10)	421(13)	4027(12)	5110(4)	7.8(2)
C(11)	694(11)	2891(11)	5024(4)	7.8(2)
C(12)	765(14)	2436(11)	4440(5)	7.8(2)
C(13)	562(13)	3117(12)	3941(4)	7.8(2)
C(14)	289(11)	4255(11)	4028(4)	7.8(2)
C(15)	217(14)	4709(11)	4611(5)	7.8(2)

[a] x/a, y/b, z/c × 10^4.

tional and thermal parameters of non-group atoms and Table 3 the corresponding values for the phenylic carbon atoms, as derived from the refined group parameters.

Computations

All the computations were carried out on an IBM 7040 computer. For absorption correction a local program was used, in which the directions of primary and diffracted beams are evaluated as recently described[13]. Counter data reduction and statistical analysis for weighting schemes were also based upon Fortran programs written in our laboratory. In addition, local versions of entries No. 7528, 7531, 7532 and 7535 in the "International World List of Crystallographic Programs" were used for Fourier analysis, structure factor and least-squares calculations; Johnson's ORTEP for thermal ellipsoid plotting; and a program by Domenicano and Vaciago for computation of the molecular parameters.

RESULTS AND DISCUSSION

The structure consists of a packing of discrete monomeric molecular units

$Pt(CO)_2[P(C_6H_5)_2(C_2H_5)]_2$ in space group $P3_121$. A survey of all non-bonding molecular contacts reveals no unusual interactions. The absolute configuration of the packing, as shown in Fig. 1, is that of a right-handed helical sequence of molecules, the axis of the helix being the crystal axis *c*. The molecules have their PtC_2 and PtP_2 planar moieties almost orthogonal and, respectively, parallel to this axis. Each mole-

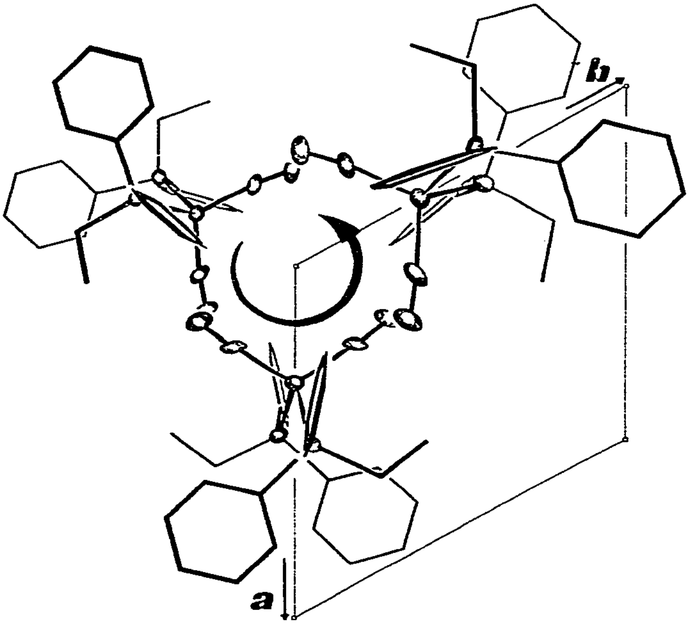

Fig. 1. Right-handed helix formed by $Pt(CO)_2[P(C_6H_5)_2C_2H_5]_2$ molecules around the *c* axis.

TABLE 4

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES IN $Pt(CO)_2[P(C_6H_5)_2C_2H_5]_2$

Distances (Å)			
Pt–P	2.360(4)	C(2)–C(3)	1.55(3)
Pt–C(1)	1.92(2)	P–P′	3.558(5)
C(1)–O	1.14(2)	C(1)–C(1)′	3.28(3)
P–C(4)	1.83(2)	P–C(1)	3.40(2)
P–C(10)	1.84(1)	P–C(1)′	3.62(2)
P–C(2)	1.87(1)		
Angles (°)			
P–Pt–P′	97.9(2)	C(4)–P–C(2)	104(1)
P–Pt–C(1)	105.0(6)	C(10)–P–C(2)	102(1)
P–Pt–C(1)′	115.1(8)	P–C(2)–C(3)	110(1)
C(1)–Pt–C(1)	117(1)	P–C(4)–C(5)	118(1)
Pt–C(1)–O	174(3)	P–C(4)–C(7)	178(1)
Pt–P–C(4)	114.3(4)	P–C(4)–C(9)	122(1)
Pt–P–C(10)	115.8(5)	P–C(10)–C(11)	119(1)
Pt–P–C(2)	117.7(6)	P–C(10)–C(13)	177(1)
C(4)–P–C(10)	101(1)	P–C(10)–C(15)	121(1)

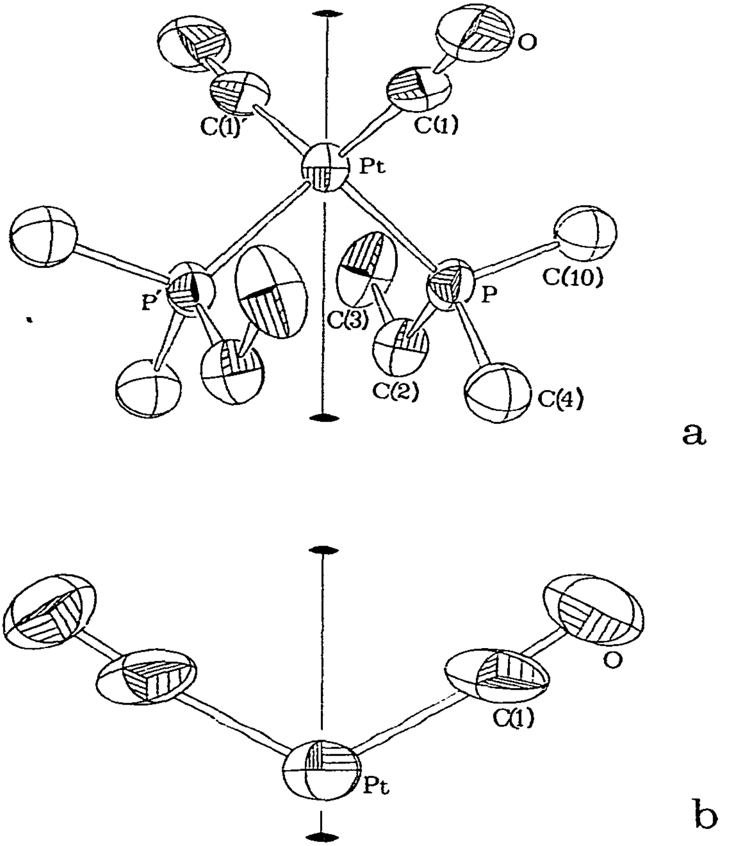

Fig. 2. (a), Inner coordination sphere of $Pt(CO)_2[P(C_6H_5)_2C_2H_5]_2$; (b), the $Pt(CO)_2$ moiety projected on the C–Pt–C plane. In both drawings the 30% probability ellipsoids are shown.

cule points its carbonyl groups toward the inside of the helix.

The metal atom exhibits a distorted tetrahedral coordination (see Fig. 2); the symmetry of the PtC_2P_2 group – which would be expected to be C_{2v} – is actually C_2, the same as that of the whole molecule, the mirror being destroyed by the fact that the dihedron between the planes of PtC_2 and PtP_2 is 86.0(3)°. The lower symmetry in the metal coordination sphere is probably due to non-bonding intra- and inter-molecular interactions. The most important intra-molecular interactions are given in Table 4, where inter-atomic distances and angles are listed together with their *esd*'s.

The nearest terms of comparison with the present molecule are found in the structures of the two polymorphs $Pt(CO)[P(C_6H_5)_3]_3$[2,3] and corresponding interactions in the mono-and dicarbonylated species are therefore compared in Table 5.

As mentioned in the introduction, a substantial lengthening of the Pt–P bonds was observed in these two polymorphs with respect to the same interaction in non-carbonylated Pt^0 and Pt^{II} complexes. On this basis, it was assumed that the variation in Pt–P bond length was due to a different extent of the metal-to-phosphorus (d_π–d_π) back-donation, which becomes lower in the presence of a competing π-acceptor such as a CO group (this assumption implies that the effect of non-bonding repulsions on

TABLE 5

IMPORTANT BOND LENGTHS AND ANGLES FOR $Pt(CO)_nL_{4-n}$ COMPLEXES

	$Pt(CO)_2(PPh_2Et)_2$[a]	$Pt(CO)(PPh_3)_3$[b]	$Pt(CO)(PPh_3)_3$[c]
Bond lengths (Å)			
Pt–P	2.360(4)	2.352(8)	2.36(1)
		2.335(8)	
		2.333(8)	
Pt–C	1.92(2)	1.86(3)	1.84(2)
C–O	1.14(2)	1.12(4)	1.13(3)
Pt–O	3.06(2)	2.98(3)	2.97(2)
P–P	3.56(1)	3.92(1)	3.76(1)
		3.86(1)	
		3.81(1)	
P–C	3.62(2)	3.42(3)	3.51(2)
	3.40(2)	3.41(3)	
		3.36(4)	
C–C	3.28(3)		
Angles (°)			
P–Pt–P	97.9(2)	113.7(3)	105.7(7)
		110.9(3)	
		109.6(2)	
P–Pt–C	115.1(8)	109(1)	113(1)
	105.0(6)	108(1)	
		105(1)	
C–Pt–C	117(1)		
Pt–C–O	174(3)	171(3)	180

[a] Present work. [b] Monoclinic, ref. 2. [c] Trigonal, ref. 3.

the metal–ligand distances is negligible, as is probably the case when the coordination number is low). As can be seen in Table 5, the metal–phosphorus distance in the present compound [2.360(4) Å] is essentially the same as in the mono-carbonyl species; on this basis, one might assume this figure as a limit value, probably corresponding to an essentially pure Pt–P σ bond.

The value of the P–Pt–P angle [97.9(2)°] is comparatively low. It is probably determined by the overall molecular conformation and by the packing; we suggest that such a situation reflects the low P–P repulsion, which is a result of the low electron population of the phosphorus d_π orbitals.

The metal–carbonyl interaction is essentially linear, the angle Pt–C–O being 174(3)°. The Pt–C distance of 1.92(2) Å found here is longer than the corresponding interactions in the two monocarbonyl polymorphs, for which an average of 1.85(1) Å was observed. The strict similarity of the stereochemistry of the three species suggests that the only effect which can be responsible for the longer interaction in the present molecule is a lower amount of π-back-donation towards the carbon atoms, due to the presence of two competing carbonyl groups. This view is confirmed when the stretching frequencies of the carbonyl groups are compared: for solutions in tetrahydrofuran of both polymorphs of $Pt(CO)P(C_6H_5)_3$ a single band is observed at 1930 cm^{-1}, whereas a solution of $Pt(CO)_2[P(C_6H_5)_2C_2H_5]_2$ displays two bands at 1982 and at 1940 cm^{-1} (ref. 1).

TABLE 6

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)[a]

Atom	Min	Intermed	Max	Mean *esd.*
Pt	0.230	0.265	0.331	0.001
P	0.225	0.264	0.318	0.007
C(1)	0.22	0.30	0.44	0.03
O	0.27	0.35	0.51	0.03
C(2)	0.24	0.29	0.33	0.02
C(3)	0.25	0.29	0.47	0.02

[a] Measured along the principal axes of the thermal ellipsoids.

The principal axes of the thermal ellipsoids of C and O atoms have significantly different magnitudes (see Table 6). Their orientations, shown in Fig. 2b, do not indicate the essentially bending motion which one would expect: the major axis of the thermal vibration of the C atom makes an angle of about 45° with the Pt–C and C–O bonds. This implies that the equivalence of the two carbonyl groups, imposed by the overall symmetry of the packing, is probably only a statistically averaged situation. If this is the case, then one single molecule of $Pt(CO)_2[P(C_6H_5)_2C_2H_5]_2$ would not possess, in the solid state, a rigorous C_2 symmetry, since the two Pt–CO interactions are in effect different.

ACKNOWLEDGEMENTS

The Authors wish to thank Dr. P. Chini for the gift of crystal samples and Dr. M. Sansoni for a number of helpful discussions. This work was made possible by the financial support of the Italian "Consiglio Nazionale delle Ricerche".

REFERENCES

1 P. Chini and G. Longoni, *J. Chem. Soc. A*, (1970) 1542.
2 V. G. Albano, G. M. Basso Ricci and P. L. Bellon, *Inorg. Chem.*, 8 (1969) 2109.
3 V. G. Albano, P. L. Bellon and M. Sansoni, *Chem. Commun.*, (1969) 899; see also *errata, ibid.*, (1970) 188.
4 V. G. Albano, P. L. Bellon and M. Sansoni, *J. Chem. Soc. A*, (1971) 2420.
5 Th. Kruck, *Angew. Chem., Int. Ed., Engl.*, 6 (1967) 53.
6 J. Hornstra, *Report 4021*, N.V. Philips Gloeilampen Fabriek, Eindhoven, Netherlands, 1965.
7 W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10 (1957) 180.
8 W. L. Bond, *Acta Crystallogr.*, 12 (1959) 375.
9 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24 (1968) 321.
10 J. B. Forsyth and M. Wells, *Acta Crystallogr.*, 12 (1959) 412.
11 *Int. Tables for X-Ray Crystallogr.*, Vol. III, Kynoch Press, Birmingham, 1962.
12 W. C. Hamilton, *Acta Crystallogr.*, 18 (1965) 502.
13 G. Ciani, M. Manassero and M. Sonsoni, *J. Appl. Cryst.*, 4 (1971) 173.