nmr spectra.[7] Evidence from this source indicates that the unique group is less labile than the other two.

The shortest nonbonded contacts are listed in Table VIII. The cyclopentadienyl group has a staggered conformation with respect to the five equatorial oxygen atoms and the carbon–oxygen contacts that result are extremely regular. There is a similar regularity in the five O_{axial}–$O_{equatorial}$ distances which reinforces the observation that regularity in the coordination polyhedron has been achieved at the expense of slight distortions in the coordination of individual chelate rings. Intermolecular contacts all involve fluorine–fluorine or fluorine to cyclopentadienyl carbon contacts. None is abnormally short in view of the fluorine van der Waals radius of 1.35 Å.[19] It is not evident from these contacts why one $-CF_3$ group should show greater disordering than the others. The number of short F···F contacts per $-CF_3$ group varies from 2 to 8, however, which would account for the considerable variation in the amplitudes of thermal motion of the various groups.

Acknowledgment.—This work was supported financially by the National Research Council of Canada. Helpful discussions with Dr. W. A. G. Graham and Mr. J. G. Evans of this department are gratefully acknowledged.

[19] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260.

CONTRIBUTION FROM ISTITUTO DI CHIMICA GENERALE ED INORGANICA,
UNIVERSITÀ DEGLI STUDI, MILAN 20133, ITALY

A Tetrahedral Platinum(0) Carbonyl. The Crystal and Molecular Structure of Tris(triphenylphosphine)carbonylplatinum[1]

BY V. G. ALBANO, G. M. BASSO RICCI, AND P. L. BELLON[2]

Received December 4, 1968

The crystal and molecular structure of tris(triphenylphosphine)carbonylplatinum, $Pt(P(C_6H_5)_3)_3CO$, was determined from three-dimensional X-ray data measured by counter methods. The structure was refined by full-matrix least squares using 1408 reflections, to an R factor of 0.051. The complex crystallizes in the monoclinic space group $P2_1/n$ ($C_{2h}{}^5$) with the cell parameters: $a = 11.275$ (5) Å, $b = 30.904$ (8) Å, $c = 13.298$ (5) Å, $\beta = 91.6$ (1)°. There are four monomeric molecules per cell; the coordination around the metal atom is approximately tetrahedral. The three metal–phosphorus bond lengths are 2.333 (8), 2.335 (6), and 2.352 (8) Å, and the metal–carbon distance is 1.86 (3) Å. On the basis of these and other results for noncarbonylated and carbonylated phosphine–platinum complexes, it is suggested that d_π–d_π interactions play an important role in metal–phosphorus bonds whenever no π acceptors competing with phosphorus are present.

It is known that compounds of zerovalent platinum such as $Pt(P(C_6H_5)_3)_3$ and $Pt(P(C_6H_5)_3)_4$ react in solution with carbon monoxide to give variously carbonylated products.[3–5] Booth, *et al.*,[6] have characterized, among the number of mono- and polynuclear platinum carbonyls, the complex $Pt(P(C_6H_5)_3)_3CO$, an orange-yellow monoclinic solid decomposing at 95°. The metal–carbon interaction deduced from the CO stretching band (at 1908 cm^{-1}) is not as weak as should be expected in view of the very high ionization potential, 8.2 eV,[7] of the spin-paired d^{10} state of Pt(0). This value suggests that metal-to-carbon back-donation would take place with difficulty.

An explanation of the stability of compounds such as $Pt(PR_3)_3CO$ and $Pt(PR_3)_2(CO)_2$ has been proposed by Nyholm:[8] the availability of d_π electrons on Pt is increased by the presence of donor bonds from PR_3 ligands which create an excess of negative charge on the metal.

At the beginning of the present investigation no structural reports of any kind on platinum(0) carbonyls had yet appeared. However, two papers dealing with structures and properties of platinum(II) carbonyls were available. In $PtCl(P(C_2H_5)_3)_2CO^+$ [9] and in $PtCl_2(ONC_2H_4OCH_3)CO$,[10] a pyridine N-oxide complex, distances of 1.78 and 1.74 Å and CO stretching frequencies of about 2100 cm^{-1} have been reported. These metal–carbon distances are the shortest interactions reported for a group VIII metal carbonyl of the second and third transition series.[11] On the basis of the lower stretching frequency, one should expect a more pronounced, d_π–π^* interaction in $Pt(P(C_6H_5)_3)_3CO$; therefore, the existence of a metal–carbonyl interaction significantly shorter than the above ones would be expected.

Recently Chini has obtained, by carbonylation of $Pt(P(C_6H_5)_3)_3$ in presence of an excess of triphenylphosphine, a pale yellow polymorph of $Pt(P(C_6H_5)_3)_3CO$

---

[1] Work performed under the auspices of the Italian National Research Council.

[2] Author to whom inquiries should be addressed.

[3] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

[4] L. Malatesta and R. Ugo, *ibid.*, 2080 (1963).

[5] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

[6] G. Booth, J. Chatt, and P. Chini, *Chem. Commun.*, 639 (1965).

[7] "Atomic Energy Levels," National Bureau of Standards Circular No. 467, Vol. III, U. S. Government Printing Office, Washington, D. C., 1952.

[8] R. S. Nyholm, *J. Chem. Soc.*, 273 (1961).

[9] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Am. Chem. Soc.*, **89**, 3360 (1967).

[10] M. Orchin and P. J. Schimdt, *Coord. Chem. Rev.*, **3**, 345 (1968).

[11] F. Calderazzo in "Organic Synthesis *via* Metal Carbonyls," Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1968.

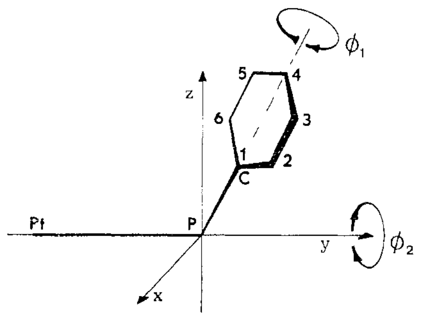

Figure 1.—Model group used in minimum residual computations.

which crystallizes with a different habit and displays the stretching band of the CO group at 1940 cm^{-1}.[12] The question of whether the metal atom is differently coordinated in the two species is interesting. A structural investigation of the new compound has been undertaken and will be reported at a later date.

Experimental Section

Crystals of $Pt(P(C_6H_5)_3)_3CO$ were kindly supplied by P. Chini. The polymorph reported in this paper crystallizes in a truncated bipyramidal habit of monoclinic symmetry. The space group, as determined from systematic absences on Weissenberg and precession films, is $P2_1/n$ (C_{2h}^5).[13]

The unit cell parameters, determined from film data, were subsequently refined by an ω-lag method[14] on a PAILRED diffractometer. The results, assuming λ(Mo Kα) 0.7107 Å, are: a = 11.275 (5) Å, b = 30.904 (8) Å, c = 13.298 (5) Å. β = 91.6 (1)°, V = 4677 Å^3. Agreement between computed and observed densities has been obtained for $Z = 4$ ($\rho_{calcd} = 1.43$ g/cm^3 and $\rho_{measd} = 1.42$ (2) g/cm^3, the latter value being measured by flotation in iodomercurate solutions).

The reflections were collected on a PAILRED linear equi-inclination diffractometer to a limit in $(\sin\theta)/\lambda$ of 0.4. The incident beam, monochromatized by reflection on a silicon single crystal cut normally to [111], was Mo Kα. With a crystal mounted along a it was possible to measure the intensities from $0kl$ to $4kl$. In the $5kl$ level, owing to the very short b^* axis and to the increased ω spread of the reciprocal lattice points, a number of overlaps between adjacent reflections were observed. The collection of data for this crystal was stopped; a second crystal of the same batch was mounted along c and the reflections from $hk0$ to $hk4$ were collected. The scan technique adopted, ω scan or fixed counter-moving crystal, is adequate when monochromatic radiation is used.

After rejection of all of the measurements having a relative counting esd, $\sigma(I)/I$,[15] above 0.25, the two sets of data were independently corrected for geometrical and physical effects. The absorption correction (μ is 32.3 cm^{-1}) was computed with a program based on the Busing and Levy method.[16] Fourteen crystal faces were measured on both samples with a Stoe reflection goniometer equipped with a screw micrometer. The transmission factors were in the range 0.55–0.59 for the first crystal, with dimensions 0.025 cm along the ω axis and 0.025 × 0.026 cm normal to it, and in the range 0.56–0.60 for the second crystal with the respective dimensions, 0.029 × 0.022 × 0.027 cm. The small ranges of transmission factors are very significant in the present case where two sets of data were to be brought to the same scale. Owing to the low absorption, a sampling of 216 (6^3) points was adopted in computing the transmission factors. (For a smaller, random group of reflections a comparison with factors obtained from a 512 (8^3) point sampling was done and no significant variations were detected.)

The two sets of reflections were finally brought to the same scale with an interlayer scaling procedure outlined by Hamilton, *et al.*[17] Before combining them into a unique set, a survey was made to see whether some effect—*e.g.*, extinction—was affecting differently equivalent reflections of either set; however, nothing systematic was noticed. The final set was one consisting of 1408 reflections, measured on two crystals, out of 2200 reflections possible within the range 0–0.4 for $(\sin\theta)/\lambda$.

Structure Solution and Refinement

Metal and phosphorus atoms were located by conventional Patterson and Fourier analysis and their positions were refined by least squares. The conventional R based on their contribution only was 0.23.

The phenyl rings were approximately located by a "minimum R" technique.[18–20] With reference to Figure 1, the procedure can be briefly outlined in this way: if the P–C bond length and the Pt–P–C angles are known (as they are approximately) and further if the assumption is made that the phenyl ring does not distort, then the approximate position of the ring in crystal space is known if one determines the rotation angles Φ_1 and Φ_2, around the P–C and Pt–P bonds. These angles can be determined if a map of R factors is computed as a function of Φ_1 and Φ_2. In such a map, if the phosphorus atom belongs to a triphenylphosphine group, three well-developed minima of R appear at the appropriate values of ϕ_1 and ϕ_2 for each of the three rings. At this point, the approximate location of the phenyl carbon atoms and also the group parameters for a rigid-group refinement can be computed.

After location of the 54 phenyl carbonyl atoms by the above method, a Fourier difference synthesis disclosed the position of the CO group. The R factor based on the contribution of all of the atoms before the complete refinement was 0.15.

The refinement was done by full-matrix least squares. A total of 88 parameters were taken into account: 1 over-all scale factor, 24 positional and thermal isotropic temperature factors for Pt, P, C, and O atoms, and 63 group positional and thermal parameters for the 9 phenyl rings which were treated as rigid groups.[21] The group constraints are that a phenyl ring is a planar, regular hexagon with a C–C bond length of 1.395 Å.

The atomic scattering factors used in least-squares as well as in structure factor computations were for Pt the TFD statistical model curve[22] corrected for the real

---

(12) P. Chini, private communication.

(13) This space group refers to the reduced cell. The cell of the standard setting, having space group $P2_1/c$, is related to the present one in the following way: $a_1 = -a$, $b_1 = b$, $c_1 = a + c$.

(14) J. Hornstra, Report 4021, N. V. Philips Gloeilampen Fabrik, Eindhoven, Netherlands, 1965.

(15) The counting statistical variance of an intensity measurement, on which $V(F_o^2)$ is based, is $V_{cs}(I) = N_P + (t_P/t_B)^2N_B$, N_P and N_B being the number of counts on peak and background and t_P and t_B being the times spent on peak and background.

(16) W. R. Busing and H. A. Levy, *Acta Cryst.*, **10**, 180 (1957).

(17) W. C. Hamilton, J. S. Rollet, and R. A. Sparks, *ibid.*, **18**, 129 (1965).

(18) A. K. Bhuiya and E. Stanley, Abstracts of Communications, Internation Union of Crystallography, VI Congress, Rome, 1963, Section 1, Paper 7.

(19) V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, Abstracts of Communications, International Union of Crystallography, VI Congress, Rome, 1963, Symposium 1, Paper 13.

(20) V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *Istituto Lombardo*, A100, 337 (1966).

(21) C. Scheringer, *Acta Cryst.*, **16**, 546 (1963).

(22) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 239 (1957).

TABLE I

COMPUTED AND OBSERVED STRUCTURE FACTOR MODULI IN ELECTRONS

H	K	FO	/FC/
	L = 0		
2	-0	374	385
4	-0	70	74
6	-0	206	221
8	-0	110	108
2	1	185	195
3	1	106	103
4	1	177	177
5	1	67	67
8	1	51	53
9	1	76	69
2	2	124	132
3	2	104	114
5	2	124	117
6	2	51	61
7	2	132	133
8	2	48	52
2	3	344	354
3	3	191	207
4	3	228	221
5	3	133	141
8	3	61	61
3	4	51	65
4	4	36	31
6	4	100	102
7	4	68	66
8	4	67	65
1	5	39	36
2	5	128	126
3	5	210	213
4	5	79	72
5	5	115	127
9	5	66	67
0	6	184	184
1	6	106	102
2	6	177	169
4	6	58	53
5	6	45	47
6	6	64	66
7	6	85	91
8	6	92	96
1	7	87	90
2	7	104	101
3	7	57	59
4	7	212	213
6	7	102	110
-0	8	64	60
1	8	151	151
3	8	68	57
4	8	73	62
7	8	103	104
9	8	44	47
1	9	53	49
3	9	171	171
4	9	89	86
5	9	131	141
9	9	55	54
-0	10	155	161
1	10	46	47
2	10	171	167
3	10	56	52
6	10	141	134
8	10	84	80
1	11	114	125
2	11	78	75
3	11	167	165
4	11	100	97
5	11	105	108
6	11	75	81
-0	12	45	51
1	12	197	203
4	12	53	55
5	12	90	93
6	12	68	73
7	12	109	107
1	13	101	93
2	13	231	215
3	13	119	115
4	13	248	247
5	13	58	50
6	13	86	85
-0	14	178	171
2	14	112	118
5	14	53	53
6	14	110	104
7	14	56	53
8	14	72	65
1	15	137	133
2	15	52	55
3	15	289	285
4	15	44	44
5	15	125	128
-0	16	59	64
1	16	212	206
2	16	91	95
3	16	63	55
5	16	81	84
6	16	51	51
7	16	66	61
2	17	166	164
4	17	148	145
5	17	46	48
-0	18	180	186
1	18	162	156
2	18	131	122
5	18	69	66
6	18	55	62
7	18	63	70
1	19	53	49
2	19	53	55
3	19	112	115
5	19	54	55
-0	20	144	162
1	20	82	83
2	20	129	119
6	20	69	66
1	21	53	46
2	21	60	66
3	21	72	67
4	21	60	65
5	21	66	78
1	22	146	145
3	22	69	74
2	23	71	70
4	23	76	79
-0	24	131	132
1	24	62	68
2	24	98	104
1	25	61	69
3	25	92	93
-0	26	89	99
1	26	89	90
2	26	75	74
	L = 1		
3	-0	104	103
-3	0	84	100
5	-0	72	74
-5	0	247	269
7	-0	113	121
-7	0	202	212
2	1	129	132
-2	-1	59	55
3	1	243	249
-3	-1	169	163
4	1	171	162
-4	-1	164	163
5	1	117	116
-5	-1	155	158
-6	-1	70	69
8	1	94	91
9	1	71	68
-9	-1	53	55
2	2	124	119
-2	-2	174	173
3	2	112	102
4	2	36	41
-5	-2	70	68
6	2	121	124
-6	-2	175	179
7	2	46	51
-7	-2	61	54
8	2	99	102
-8	-2	123	125
2	3	252	259
3	3	170	170
-3	-3	267	263
4	3	127	120
-4	-3	136	131
5	3	72	80
-5	-3	102	103
7	3	43	41
9	3	85	83
-9	-3	64	69
-2	-4	85	85
-3	-4	92	81
4	4	79	84
5	4	71	74
-5	-4	77	80
-6	-4	71	63
7	4	134	132
-7	-4	136	132
8	4	58	55
-8	-4	84	70
0	5	55	45
2	5	161	172
-2	-5	291	286
-3	-5	54	49
4	5	179	177
-4	-5	263	262
6	5	40	41
-6	-5	115	126
8	5	71	65
-0	6	180	158
1	6	268	262
-1	-6	164	164
2	6	124	130
-2	-6	148	145
3	6	96	93
4	6	75	76
-4	-6	38	36
-5	-6	60	70
6	6	109	113
-6	-6	73	71
7	6	74	74
-7	-6	105	97
8	6	49	56
-9	-6	53	52
-0	7	234	247
1	7	135	132
-1	-7	211	200
-2	-7	67	68
3	7	197	192
-3	-7	261	241
4	7	36	36
-4	-7	50	43
5	7	123	124
-5	-7	169	162
9	7	69	80
-9	-7	66	54
-0	8	335	326
1	8	72	78
-1	-8	134	123
2	8	245	227
-2	-8	49	49
6	8	114	114
-6	-8	152	146
-7	-8	45	34
8	8	86	86
-8	-8	81	86
-0	9	94	104
1	9	156	149
-1	-9	106	95
2	9	95	92
-2	-9	209	207
3	9	91	85
-3	-9	75	81
4	9	168	176
-4	-9	154	155
5	9	51	54
-5	-9	72	73
6	9	52	52
-6	-9	61	68
1	10	332	315
-1	-10	200	182
2	10	50	49
3	10	63	62
4	10	42	35
5	10	123	126
-5	-10	74	67
7	10	115	108
-7	-10	107	116
-0	11	48	48
1	11	54	43
-1	-11	106	106
2	11	135	134
-2	-11	161	170
3	11	142	147
-3	-11	137	135
4	11	130	145
-4	-11	172	175
5	11	98	96
-5	-11	113	114
-6	-11	58	56
8	11	58	52
-0	12	231	227
1	12	64	66
-1	-12	105	104
2	12	127	130
-2	-12	169	166
4	12	101	97
5	12	51	51
6	12	161	167
-6	-12	123	133
-7	-12	50	46
8	12	66	67
-8	-12	73	86
-0	13	50	49
1	13	107	106
-1	-13	162	157
2	13	63	58
-2	-13	117	109
3	13	165	170
-3	-13	274	275
4	13	94	93
-4	-13	105	112
5	13	104	108
-5	-13	131	130
-0	14	70	73
1	14	139	141
-1	-14	178	171
2	14	83	73
-2	-14	82	86
-3	-14	43	51
4	14	51	45
5	14	125	122
6	14	59	55
7	14	95	104
-7	-14	99	108
2	15	128	125
-2	-15	205	212
3	15	54	59
4	15	135	142
-4	-15	260	248
-6	-15	85	80
8	15	49	59
-8	-15	54	48
-0	16	171	172
1	16	71	72
-1	-16	154	159
2	16	78	82
-2	-16	130	128
5	16	51	56
6	16	86	87
-6	-16	89	89
-7	-16	53	59
0	17	37	37
1	17	74	73
-1	-17	80	86
3	17	106	113
-3	-17	194	195
-5	-17	147	148
6	17	48	42
-0	18	79	89
1	18	88	87
-1	-18	143	135
2	18	100	86
-2	-18	120	115
-3	-18	49	42
5	18	62	54
-5	-18	58	65
6	18	58	65
-6	-18	80	84
-7	-18	69	69
2	19	115	119
-2	-19	119	108
3	19	44	42
-3	-19	61	64
4	19	91	105
-4	-19	155	144
-5	-19	57	52
-6	-19	54	61
-0	20	71	76
1	20	107	109
-1	-20	135	136
2	20	69	64
-3	-20	64	60
-5	-20	73	64
-6	-20	63	61
1	21	58	55
-2	-21	65	66
3	21	77	77
-3	-21	80	83
-4	-21	65	59
-5	-21	105	88
6	21	49	49
-0	22	144	146
2	22	104	102
-2	-22	85	91
1	23	62	51
-1	-23	51	50
2	23	49	43
3	23	88	90
-3	-23	81	89
-4	-23	55	57
5	23	53	49
-0	24	58	49
1	24	114	117
-1	-24	78	79
3	24	58	63
2	25	111	110
-2	-25	98	102
-0	26	110	112
1	26	100	104
-1	-26	73	77
2	26	77	79
	L = 2		
0	-0	212	218
2	-0	172	168
-2	0	136	137
-4	0	59	61
6	-0	160	165
-6	0	220	235
8	-0	119	122
-8	0	179	157
0	1	54	62
1	1	109	107
-1	-1	92	111
2	1	47	47
-2	-1	174	179
3	1	128	126
-3	-1	99	101
4	1	190	185
-4	-1	152	153
5	1	80	87
-5	-1	128	139
-6	-1	89	102
8	1	72	73
9	1	83	91
1	2	102	104
-1	-2	103	111
-2	-2	133	139
3	2	107	98
-3	-2	40	32
-4	-2	66	70
5	2	136	144
-5	-2	134	130
6	2	49	51
-6	-2	50	55
7	2	128	130
-7	-2	182	186
8	2	44	47
-8	-2	53	52
9	2	50	54
0	3	25	24
1	3	69	66
-1	-3	163	168
2	3	148	180
-2	-3	249	253
3	3	64	71
-3	-3	177	185
4	3	165	164
-4	-3	223	223
-5	-3	90	89
-6	-3	65	68
8	3	109	111
0	4	90	90
1	4	207	215
2	4	74	75
-2	-4	179	182
3	4	75	71
4	4	67	75
-5	-4	110	94
6	4	154	162
-6	-4	146	149
7	4	89	89
-7	-4	97	91
8	4	86	89
-8	-4	105	116
0	5	62	56
1	5	74	75
-1	-5	208	207
2	5	69	64
3	5	151	155
-3	-5	276	276
5	5	119	130
-5	-5	106	107
9	5	108	100
-9	-5	74	73
-0	6	314	312
1	6	188	187
-1	-6	228	224
2	6	84	83
-2	-6	105	93
4	6	61	54
-4	-6	88	85
5	6	46	46
-5	-6	81	102
6	6	85	102
-6	-6	130	134
7	6	89	93
-7	-6	90	103
8	6	98	86
-8	-6	79	79
2	7	252	243
-2	-7	182	184
3	7	54	64
-3	-7	62	56
4	7	165	157
-4	-7	200	197
5	7	67	73
6	7	59	72
-6	-7	69	68
8	7	61	61
1	8	87	107
-1	-8	238	230
2	8	121	120
-2	-8	69	84
5	8	100	103
-5	-8	129	134
6	8	55	63
-6	-8	40	38
7	8	131	123
-7	-8	118	113
8	8	73	63
0	9	42	43
-1	-9	65	74
2	9	59	63
-2	-9	108	103
3	9	141	132
-3	-9	242	239
4	9	78	80
-4	-9	87	96
5	9	122	117
-5	-9	131	127
-0	10	284	272
-1	-10	43	37
2	10	107	109
-2	-10	188	180
4	10	99	105
-4	-10	48	42
-6	-10	141	138
-8	-10	73	75
-0	11	89	85
1	11	125	108
2	11	46	49
-2	-11	160	156
3	11	67	68
-3	-11	168	181
4	11	86	84
-4	-11	121	128
-5	-11	111	120
-6	-11	49	45
-0	12	118	107
1	12	183	169
-1	-12	245	235
-3	-12	51	49
5	12	115	124
-5	-12	109	110
-7	-12	116	127
-1	-13	75	69
2	13	148	159
-2	-13	165	164
3	13	94	99
-3	-13	118	123
4	13	114	115
-4	-13	205	207
-5	-13	72	80
-6	-13	81	74
-8	-13	56	57
-0	14	158	157
1	14	129	128
-1	-14	117	125
-2	-14	106	104
4	14	81	77
-4	-14	64	61
6	14	121	138
-6	-14	96	100
-7	-14	49	48
-8	-14	91	103
-1	-15	118	117
2	15	51	47
3	15	168	171
-3	-15	206	203
-4	-15	68	65
-5	-15	143	147
6	15	57	46
-0	16	88	88
1	16	108	114
-1	-16	114	117
2	16	82	91
-2	-16	72	76
-3	-16	40	37
-5	-16	100	103
-6	-16	61	66
-7	-16	111	112
2	17	116	126
-2	-17	139	143
4	17	117	126
-4	-17	174	172
-6	-17	65	60
-0	18	99	100
1	18	142	143
-1	-18	89	86
-2	-18	81	80
-4	-18	55	44
5	18	94	89
-5	-18	64	67
6	18	67	57
-6	-18	75	71
7	18	97	97
-7	-18	65	60
-1	-19	81	80
-2	-19	58	57
3	19	130	138
-3	-19	156	158
-4	-19	47	41
5	19	78	77
-5	-19	116	110
-0	20	118	131
1	20	51	52
2	20	95	87
-2	-20	69	64
-4	-20	57	54
-5	-20	75	72
-6	-20	98	93
-1	-21	64	60
2	21	63	74
-2	-21	81	78
3	21	84	71
-3	-21	76	73
4	21	86	80
-4	-21	96	105
-5	-21	54	56
1	22	100	108
-1	-22	91	97
5	22	84	63
-5	-22	73	88
-2	-23	66	72
-3	-23	64	60
4	23	83	74
-4	-23	82	81
-0	24	93	102
2	24	53	60
1	25	60	55
-1	-25	47	43
-3	-25	97	100
-0	26	63	70
1	26	76	75
-1	-26	87	85
-2	-26	54	56
	L = 3		
1	-0	279	297
-1	0	329	337
5	-0	176	175
-5	0	213	227
7	-0	96	91
-7	0	199	206
-9	0	88	100
0	1	241	258
1	1	159	164
-1	-1	184	189
2	1	151	166
3	1	92	100
-3	-1	136	139
4	1	108	103
-4	-1	137	132
5	1	66	70
-5	-1	103	110
-6	-1	94	103
8	1	86	76
0	2	250	256
1	2	121	124
-1	-2	39	40
-2	-2	140	138
3	2	43	38
4	2	104	97
-4	-2	57	52
-5	-2	78	81
6	2	160	159
-6	-2	181	184
-7	-2	55	53
8	2	84	83
-8	-2	154	160
0	3	54	56
1	3	314	332
-1	-3	133	125
2	3	57	59
-2	-3	79	98
3	3	190	189
-3	-3	159	155
-4	-3	121	124
5	3	115	120
-5	-3	118	107
-9	-3	78	76
1	4	191	197
-1	-4	53	49
2	4	97	93
-2	-4	46	40
-4	-4	98	93
5	4	149	149
-5	-4	113	109
6	4	72	66
-6	-4	81	78
7	4	111	112
-7	-4	127	117
8	4	78	70
-8	-4	64	72
-9	-4	81	88
-0	5	47	41
1	5	96	90
2	5	231	223
-2	-5	245	236
-3	-5	85	84
4	5	191	192
-4	-5	205	214
6	5	77	68
-6	-5	59	63
8	5	89	93
1	6	156	162
-1	-6	129	122
2	6	84	76
-2	-6	116	109
3	6	76	72
-3	-6	58	56
4	6	77	80
5	6	59	60
-5	-6	134	140
6	6	112	112
-6	-6	101	105
7	6	149	150
-7	-6	127	117
8	6	89	81
0	7	59	60
-1	-7	213	208
2	7	40	41
3	7	206	205
-3	-7	242	233
4	7	77	69
5	7	163	167
-5	-7	119	124
-0	8	159	157
1	8	113	113
-1	-8	153	140
2	8	154	156
-2	-8	131	133
3	8	39	39
4	8	62	65
-4	-8	54	44
5	8	68	74
6	8	125	130
-6	-8	110	111
7	8	99	100
8	8	106	114
-8	-8	81	76
1	9	63	64
-1	-9	49	56
2	9	173	116
-2	-9	165	159
3	9	73	80
-3	-9	117	114
4	9	97	100
-4	-9	88	91
5	9	94	94
-5	-9	70	67
6	9	74	78
-8	-9	58	64
-0	10	49	52
1	10	105	105
-1	-10	221	221
2	10	110	105
5	10	123	130
-5	-10	99	91
6	10	53	49
7	10	150	155
-7	-10	137	138
1	11	44	44
-1	-11	99	98
2	11	87	90
-2	-11	121	125
3	11	55	48
-3	-11	129	137
4	11	92	91
-4	-11	119	118
5	11	75	69
-5	-11	71	74
-6	-11	57	54
-0	12	178	177
-1	-12	41	34
-2	-12	124	119
-3	-12	45	43
4	12	97	104
-4	-12	54	45
-5	-12	51	52
6	12	154	157
-6	-12	122	120
-8	-12	105	103
1	13	77	66
-2	-13	83	82
3	13	157	159
-3	-13	169	172
4	13	71	65
5	13	81	80
-5	-13	118	120
-0	14	81	84
1	14	91	75
-1	-14	143	145
-2	-14	59	57
-3	-14	60	58
5	14	110	118
-5	-14	105	98
7	14	114	106
-7	-14	126	119
1	15	140	129
2	15	193	190
-2	-15	157	161
4	15	128	127
-4	-15	169	164
-6	-15	56	55
-0	16	119	110
1	16	101	105
-1	-16	123	126
-2	-16	65	63
-3	-16	53	48
4	16	57	63
-4	-16	68	68
5	16	81	81
6	16	85	76
-6	-16	88	85
-7	-16	58	59
0	17	41	42
3	17	165	173
-3	-17	166	161
5	17	71	64
-5	-17	107	111
-0	18	181	167
1	18	68	65
-1	-18	75	73
2	18	72	79
-2	-18	76	74
4	18	71	66
-4	-18	55	49
5	18	68	69
-5	-18	81	88
6	18	133	125
-6	-18	96	82
2	19	109	110
-2	-19	109	104
4	19	125	118
-4	-19	87	84
0	20	40	41
1	20	138	132
-1	-20	114	108
-5	-20	98	88
3	21	134	135
-3	-21	90	86
4	21	92	96
-4	-21	61	61
-0	22	114	112
-4	-22	67	63
1	23	56	61
2	23	67	67
3	23	102	104
-3	-23	68	73
1	24	68	78
-1	-24	63	58
	L = 4		
0	-0	174	192
-2	0	253	251
4	-0	128	131
-4	0	108	117
6	-0	83	82
-6	0	158	165
-8	0	108	108
0	1	21	8
1	1	206	217
-1	-1	162	158
2	1	207	191
-2	-1	94	93
3	1	240	240
-3	-1	180	193
4	1	111	103
-4	-1	117	119
5	1	134	147
-5	-1	162	158
-6	-1	76	64
-8	-1	69	67
-9	-1	77	75
1	2	222	213
-1	-2	239	240
-3	-2	36	34
5	2	146	145
-5	-2	126	127
6	2	59	57
7	2	94	97
-7	-2	141	142
0	3	127	133
1	3	82	86
-1	-3	64	64
2	3	102	186
-2	-3	87	87
3	3	53	46
-3	-3	53	49
4	3	194	199
-4	-3	175	181
-5	-3	57	53
6	3	80	79
-6	-3	64	52
-8	-3	60	53
0	4	142	144
1	4	135	136
-1	-4	52	50
2	4	109	123
-2	-4	92	83
3	4	92	81
4	4	119	126
-4	-4	56	60
5	4	68	63
-5	-4	79	88
6	4	127	125
-6	-4	98	95
7	4	92	85
8	4	88	87
-8	-4	82	81
1	5	201	199
-1	-5	108	106
3	5	230	230
-3	-5	124	127
4	5	64	58
5	5	163	172
-5	-5	119	123
-0	6	117	109
1	6	86	94
-1	-6	124	120
2	6	130	126
5	6	118	119
-5	-6	68	65
6	6	112	112
-6	-6	87	81
7	6	100	103
-7	-6	89	81
8	6	79	79
1	7	47	55
2	7	230	214
-2	-7	160	164
3	7	47	48
4	7	187	203
-4	-7	101	101
5	7	61	65
-5	-7	51	54
6	7	93	98
-8	-7	85	80
-0	8	47	49
1	8	216	222
-1	-8	152	149
2	8	97	102
-2	-8	70	82
5	8	124	127
-5	-8	77	85
6	8	90	96
-6	-8	51	57
7	8	141	139
-7	-8	109	102
8	8	78	68
1	9	65	63
2	9	50	59
-2	-9	95	97
3	9	169	174
-3	-9	77	92
4	9	49	55
-4	-9	63	60
5	9	117	116
-5	-9	76	75
-6	-9	57	55
-0	10	200	210
1	10	119	117
-1	-10	53	56
2	10	121	128
-2	-10	93	104
4	10	84	91
6	10	156	151
-6	-10	137	131
8	10	108	113
-8	-10	112	121
1	11	125	122
2	11	70	74
3	11	114	123
-3	-11	126	127
4	11	95	94
-4	-11	51	42
5	11	61	60
-5	-11	77	80
-8	-11	60	64
1	12	127	133
-1	-12	162	155
2	12	46	40
-3	-12	69	76
5	12	138	136
-5	-12	84	85
7	12	116	116
-7	-12	141	149
1	13	50	45
-1	-13	63	65
2	13	162	166
-2	-13	84	88
3	13	104	104
-3	-13	79	81
4	13	105	107
-4	-13	112	113
5	13	66	61
-0	14	153	154
-1	-14	97	109
-2	-14	110	120
-3	-14	69	69
4	14	86	89
6	14	126	130
-6	-14	101	114
7	14	59	65
-7	-14	68	59
3	15	113	115
-3	-15	135	130
4	15	55	52
-4	-15	68	61
5	15	79	74
-5	-15	91	92
-0	16	133	133
1	16	98	90
-1	-16	118	113
2	16	54	48
-2	-16	106	100
-3	-16	58	51
5	16	88	98
-5	-16	68	74
6	16	88	85
-6	-16	66	77
-7	-16	88	90
2	17	152	152
-2	-17	89	90
4	17	129	138
-4	-17	114	120
0	18	51	50
1	18	127	119
-1	-18	142	136
1	19	73	80
-2	-19	58	60
3	19	165	161
-3	-19	84	85
4	19	64	61
5	19	113	115
-5	-19	76	75
-0	20	141	147
2	20	68	71
-2	-20	82	70
2	21	106	104
-2	-21	61	61
3	21	84	90
-3	-21	56	65
4	21	110	105
-4	-21	77	72
1	22	79	86
-1	-22	80	80
2	23	96	85
-2	-23	61	69
3	23	99	99
-3	-23	62	53
-0	24	79	85
	L = 5		
1	-0	161	135
-1	0	260	258
-3	0	129	142
0	1	22	23
1	1	155	138
-1	-1	81	79
2	1	184	166
-2	-1	117	125
-3	-1	140	134
4	1	240	231
0	2	212	221
2	2	128	129
-2	-2	190	192
0	3	31	36
1	3	237	227
-1	-3	65	66
-3	-3	164	144
4	3	70	69
1	4	146	131
-1	-4	219	223
-1	-5	72	61
2	5	187	186
-2	-5	148	156
-4	-5	147	166
0	6	113	112
1	6	159	154
-1	-6	149	158
2	6	76	78
-4	-6	54	53
1	7	54	54
-1	-7	63	57
2	7	61	56
-3	-7	121	131
4	7	63	68
0	8	197	198
1	8	145	134
-1	-8	76	79
2	8	90	94
-2	-8	169	156
1	9	50	52
2	9	141	151
3	9	100	111
-3	-9	81	82
4	9	133	135
-4	-9	79	74
1	10	207	213
-1	-10	195	190
2	10	55	58
3	10	60	62
2	11	81	86
-2	-11	76	80
3	11	147	151
-3	-11	102	110
4	11	81	78
-4	-11	101	101
0	12	228	232
2	12	128	143
-2	-12	158	154
1	13	122	120
3	13	157	141
-3	-13	115	108
4	13	105	91
1	14	147	149
-1	-14	191	180
-2	-14	63	61
-3	-14	73	73
2	15	173	154
3	15	59	54
4	15	106	114
-4	-15	130	117
0	16	95	101
1	16	107	113
-1	-16	107	101
-2	-16	104	102
-3	-16	62	60
1	17	97	98
3	17	110	122
-3	-17	113	124
0	18	128	138
1	18	55	59
-1	-18	80	67
2	18	130	109
-2	-18	100	99
-3	-18	72	67
2	19	118	118
4	19	125	125
-4	-19	115	117
1	20	112	114
-1	-20	122	123
1	21	73	77
3	21	128	128
-3	-21	101	97
0	22	97	106
1	23	72	63
	L = 6		
0	-0	189	205
-2	0	149	134
1	1	53	62
-1	-1	67	68
-3	-1	113	122
4	1	95	89
-4	-1	97	83
0	2	39	45
1	2	105	110
-1	-2	173	170
-3	-2	103	114
1	3	53	63
-1	-3	89	80
2	3	128	130
-2	-3	144	151
3	3	55	60
4	3	135	143
-4	-3	176	181
0	4	205	217
1	4	58	65
-1	-4	96	104
-2	-4	94	94
-3	-4	50	56
1	5	86	99
-1	-5	102	103
-2	-5	52	44
3	5	199	202
-3	-5	205	199
0	6	174	171
1	6	158	148
-1	-6	148	147
2	6	119	104
-2	-6	103	98
-3	-6	83	85
-1	-7	83	86
2	7	214	204
-2	-7	195	201
4	7	157	161
-4	-7	121	132
0	8	167	161
1	8	189	189
-1	-8	277	266
2	8	119	116
-2	-8	78	69
-3	-8	90	97
1	9	70	63
3	9	185	163
-3	-9	124	124
4	9	87	81
0	10	258	252
1	10	80	84
2	10	153	135
-2	-10	179	172
1	11	104	93
2	11	116	117
-2	-11	108	106
3	11	136	126
-3	-11	86	81
4	11	115	113
-4	-11	91	91
1	12	152	164
-1	-12	180	172
2	13	137	131
-2	-13	98	88
3	13	73	78
-3	-13	74	69
4	13	106	103
-4	-13	114	113
1	14	91	101
-1	-14	64	71
2	14	126	107
-2	-14	115	120
1	15	104	100
3	15	110	112
-3	-15	93	109
0	16	125	118
1	16	88	81
-1	-16	98	92
2	16	101	104
-2	-16	79	78
2	17	92	89
-2	-17	71	74
4	17	90	98
-4	-17	126	130
0	18	41	47
1	18	144	143
-1	-18	133	133
1	19	59	55
-1	-19	60	56
3	19	119	111
-3	-19	124	119
0	20	120	118
-1	-20	59	60
1	22	93	104
-1	-22	94	94
	L = 7		
1	-0	67	70
-1	0	157	164
-3	0	97	100
0	1	85	80
-2	-1	131	122
-3	-1	102	113
4	1	94	91
0	2	178	200
-1	-2	99	103
-2	-2	108	112
0	3	28	23
-1	-3	57	62
3	3	143	135
-3	-3	146	154
0	4	130	129
1	4	114	122
-1	-4	145	149
2	4	68	83
-1	-5	71	74
2	5	165	149
-2	-5	165	172
4	5	146	134
-4	-5	169	178
0	6	125	130
1	6	155	164
-1	-6	164	165
2	6	62	68
-2	-6	69	66
1	7	94	90
-1	-7	116	101
3	7	189	177
-3	-7	183	189
0	8	211	209
1	8	84	87
-1	-8	58	54
2	8	106	85
-2	-8	124	120
1	9	54	57
2	9	168	155
-2	-9	150	148
-3	-9	75	77
4	9	144	144
-4	-9	134	131
1	10	137	143
-1	-10	137	137
1	11	58	55
2	11	69	69
-2	-11	71	59
3	11	118	122
-3	-11	115	111
4	11	66	54
-4	-11	112	102
2	12	91	101
-2	-12	102	106
1	13	63	58
-2	-13	66	63
3	13	101	98
-3	-13	93	92
1	14	115	119
-1	-14	104	97
2	15	75	88
4	15	84	81
-4	-15	111	122
1	16	100	106
-1	-16	86	89
-2	-16	79	71
-1	-17	58	58
3	17	79	82
-3	-17	95	94
0	18	125	136
-1	-18	56	50
0	20	37	38
1	20	114	111
-1	-20	111	109
	L = 8		
0	-0	168	186
-2	0	99	86
-1	-1	76	69
-2	-1	78	84
-3	-1	116	120
4	1	71	66
-4	-1	110	91
0	2	60	69
1	2	78	83
-1	-2	136	131
2	3	111	113
-2	-3	137	134
4	3	113	107
0	4	136	138
1	4	67	68
-1	-4	86	101
-2	-4	86	92
1	5	53	56
3	5	128	105
-3	-5	158	163
0	6	158	154
1	6	86	91
-1	-6	63	59
2	6	77	74
-2	-6	67	66
2	7	113	124
-2	-7	146	142
4	7	110	119
-4	-7	166	167
1	8	112	114
-1	-8	120	136
-1	-9	56	59
0	10	113	120
3	9	156	139
-3	-9	149	153
4	9	66	63
2	10	63	57
-2	-10	83	88
2	11	73	73
-3	-11	59	74
4	11	84	74
-4	-11	104	106
1	12	79	93
-1	-12	73	71
2	13	62	72
-2	-13	68	64
3	13	57	62
-3	-13	68	72
4	13	83	70
-4	-13	100	94
1	15	62	58
3	15	79	87
-3	-15	94	88
0	18	40	43
1	18	86	89
-1	-18	111	98
	L = 9		
1	-0	129	136
-1	0	126	129
-2	-1	74	71
-3	-1	66	66
4	1	65	66
-4	-1	106	84
0	2	125	128
-1	-2	78	76
2	2	56	53
-2	-2	75	87
1	3	67	69
-3	-3	115	122
0	4	131	128
-1	-4	71	57
-2	-4	63	71
2	5	118	121
-2	-5	89	84
4	5	97	94
-4	-5	131	121
1	6	94	93
-1	-6	139	141
1	7	96	86
3	7	157	135
-3	-7	113	108
0	8	110	118
-2	-8	87	85
2	9	138	116
-2	-9	96	95
4	9	119	109
-4	-9	114	109
1	10	68	75
-1	-10	90	91
1	11	70	68
2	11	72	61
-3	-11	97	85
1	13	59	52
1	14	61	53
-1	-16	59	62
	L = 10		
0	-0	113	110
2	-0	82	94
-2	0	59	63
0	2	50	50
1	2	104	110
-1	-2	87	96
0	3	45	39
2	3	86	92
4	3	104	87
0	4	84	85
1	4	61	57
-1	-4	76	76
-2	-4	62	65
1	5	94	97
-3	-5	62	68
0	6	129	121
-1	-6	58	61
-2	-6	60	65
-4	-7	110	112
-1	-8	100	104
1	9	82	87
0	10	88	94
-1	-12	68	70
	L = 11		
1	-0	100	114
0	2	96	98
1	3	75	74
0	4	70	74
1	4	75	69
-1	-4	97	90
-1	-6	73	86

and imaginary part of anomalous dispersion[23] and for P (also corrected for anomalous dispersion), O, and C the curves from the self-consistent variational field method.[24] The function minimized was $\Sigma w(F_o - |F_c|)^2$, w being the reciprocal of the variance in F. This latter was computed from the corresponding variance on F_o^2 assumed as[25] $V(F_o^2) = V_{cs}(F_o^2) + (AF_o^2)$. V_{cs} is the counting statistical variance of F_o^2.[15] The value of A, a bias or "ignorance" factor,[26] was chosen in such a way as to render the function $\Sigma w\Delta^2$ approximately constant over the entire range of F. In the present case $A = 0.12$ was satisfactory; the value 1.1 of the error fit function was obtained using this value. The refinement converged in five cycles to the following

---

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

[24] R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

[25] P. A. Agron, R. D. Ellison, and H. A. Levy, *ibid.*, **23**, 1079 (1967).

[26] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

TABLE II[a–c]

POSITIONAL AND THERMAL PARAMETERS OF NONGROUP ATOMS

	x	y	z	β_{11} or B, Å^2	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Pt	1776(1)	1021(0)	2477(1)	74(1)	−2(0)	1(2)	7(0)	0(0)	49(1)
P_1	3003(7)	610(2)	1449(6)	99(8)	14(4)	−29(14)	10(1)	1(4)	52(6)
P_2	2420(6)	1046(2)	4158(6)	74(7)	5(4)	3(14)	10(1)	2(4)	69(6)
P_3	1563(6)	1718(2)	1853(6)	69(7)	−2(4)	4(13)	9(1)	2(4)	49(5)
C	301(30)	755(10)	2399(26)	6.9(8)					
O	−581(23)	594(8)	2482(20)	9.9(6)					

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

TABLE III[a–c]

RIGID-GROUP PARAMETERS AND MEAN ISOTROPIC TEMPERATURE FACTORS OF PHENYL RINGS

	x	y	z	α, deg	β, deg	γ, deg	B, Å^2
P_1R_1	2032(7)	510(3)	−864(8)	12.3(6)	−86.0(6)	−17.9(7)	5.2(3)
P_1R_2	3328(11)	−398(4)	2090(10)	94.4(7)	98.8(7)	−106.4(9)	7.9(4)
P_1R_3	5718(8)	940(3)	1249(7)	8.6(2.5)	164.5(6)	75.9(2.5)	5.0(3)
P_2R_1	5042(9)	1410(3)	4814(9)	13.1(7)	62.4(6)	103.7(8)	5.6(3)
P_2R_2	2518(7)	1175(3)	5270(7)	−125.2(1.1)	41.5(7)	132.1(1.1)	6.5(4)
P_2R_3	620(8)	1588(4)	5518(8)	102.1(1.0)	43.2(7)	137.1(1.0)	6.2(3)
P_3R_1	2999(7)	2492(3)	3005(7)	142.6(1.5)	151.8(7)	176.9(1.5)	5.5(3)
P_3R_2	−1131(8)	2081(4)	1869(4)	157.1(7)	58.6(6)	92.0(8)	5.3(3)
P_3R_3	2197(7)	1832(3)	−468(8)	137.0(6)	97.8(6)	−13.4(8)	7.0(3)

[a] P_1R_1 is the first phenyl ring attached to phosphorus 1. [b] (x, y, z) is the displacement vector of the center of each phenyl ring with respect to the cell origin, in crystal coordinates. All values $\times 10^4$. [c] α, β, and γ are three eulerian angles which bring about alignment of an orthogonal system fixed on the ring with a right-handed system defined in crystal space as follows: $X = a$; y coplanar with a and b; Z orthogonal to a and b. The system defined on the ring has x parallel to the vector C_2–C_6, y parallel to C_1–C_4, and z orthogonal to both (see labeling of carbon atoms in Figure 1). The angles α, β, and γ have the same meaning as in ref 29.

reliability indices: $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.056$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.081$.

The possibility of a significant anisotropic thermal motion for Pt and P atoms was subsequently tested by resuming the refinement on a larger set of parameters (108 parameters in the anisotropic refinement as compared with 88 in the isotropic one). This refinement converged after three more cycles with the following indices: $R' = 0.051$ and $R'_w = 0.074$. Following Hamilton,[27] the ratio R_w/R'_w (1.096 in this case) must be more than 1.015 before the hypothesis of isotropic thermal motion can be rejected at a 99.5% confidence level. The anisotropic motion of the Pt–P_3 group in this structure is therefore significant.

A final electron density difference map showed two peaks of 0.5 e$^-$/Å^3 and a number of minor peaks (maximum height 0.3 e$^-$/Å^3). The two stronger peaks are quite far apart and do not seem related to a definite atomic position.[28] Table I gives the final list of computed and observed structure factor moduli in electrons, all obtained after convergence of the anisotropic refinement. A survey of this list does not reveal extinction effects to an appreciable extent. The positional and thermal parameters of nongroup atoms are given in Table II, and Table III[29] lists the group and mean isotropic thermal parameters of the phenyl rings. The atomic coordinates of the 54 phenyl carbon atoms are collected in Table IV. The esd's reported in Tables II and III are derived from the inverse matrix of the final anisotropic least-squares cycle. The esd's of Table IV are functionally related to those of Table III; as stated by Ibers,[26] these "are meant to be used in error analysis of inter-ring distances. Intraring distances, of course, are fixed."

Description of the Structure

The crystal structure of monoclinic $Pt(P(C_6H_5)_3)_3CO$ consists of the packing of discrete molecules related by the space group symmetry operations. No unusual features have been noticed in a survey of the intra- and intermolecular contacts. As in triphenylphosphne itself[30] and in its complexes, the packing is essentially dictated by a number of inter-ring contacts.

The over-all appearance of the molecule is shown in Figure 2; the most important bond lengths and angles and some of the nonbonding distances are collected in Table V.

The nearest neighbors of platinum are three phosphorus atoms and the carbon atom of the CO group. The four ligands occupy the apices of a slightly distorted tetrahedron. To our knowledge, the present one is the first X-ray structural report on a tetrahedrally coordinated Pt compound, although this coordination is not surprising for a four-coordinated d^{10} metal atom. The next nearest neighbors are all found at nonbonding distances from the metal. Apart from the oxygen of the CO group, the shortest nonbonding

---

(27) W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964.

(28) All of the computations discussed in this paper were done on an IBM 7040 computer. The programs used were local versions of the following entries of the "1966 International World List of Crystallographic Programs": 7528, 7531, 7532, 7535 for Fourier analysis, structure factor, and least squares. The least-squares program (entry 7528) was extensively modified in the author's laboratory to accept chemical constraints. Counter data reduction, absorption corrections, and group locating procedure were based upon Fortran 4 programs prepared in the author's laboratory. The interlayer scaling program was written by A. Domenicano, Istituto di Chimica Farmaceutica, University of Rome.

(29) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1955.

(30) J. J. Daly, *J. Chem. Soc.*, 2799 (1964).

TABLE IV[a,b]

POSITIONAL PARAMETERS OF GROUP ATOMS

	x	*y*	*z*		*x*	*y*	*z*
C_{111}	2416 (19)	597 (12)	128 (12)	C_{224}	2515 (32)	−282 (13)	5734 (17)
C_{112}	3212 (12)	608 (12)	−647 (18)	C_{225}	1602 (22)	−170 (15)	5056 (18)
C_{113}	2826 (17)	550 (12)	−1640 (15)	C_{226}	1603 (19)	229 (16)	4593 (15)
C_{114}	1647 (19)	452 (12)	−1857 (12)	C_{231}	1422 (19)	1342 (14)	4994 (16)
C_{115}	849 (12)	410 (12)	−1082 (18)	C_{232}	680 (29)	1148 (11)	5679 (17)
C_{116}	1233 (17)	466 (12)	−88 (15)	C_{233}	−121 (20)	1395 (14)	6203 (15)
C_{121}	3177 (18)	49 (10)	1800 (19)	C_{234}	−182 (19)	1835 (14)	6042 (16)
C_{122}	3093 (18)	−276 (12)	1085 (11)	C_{235}	560 (29)	2030 (11)	5358 (17)
C_{123}	3246 (19)	−701 (11)	1377 (16)	C_{236}	1366 (20)	1784 (14)	4834 (15)
C_{124}	3480 (18)	−801 (10)	2380 (19)	C_{311}	2378 (38)	2166 (14)	2511 (16)
C_{125}	3568 (18)	−475 (12)	3097 (11)	C_{312}	3568 (41)	2110 (13)	2782 (17)
C_{126}	3419 (19)	−49 (11)	2807 (16)	C_{313}	4188 (12)	2437 (19)	3275 (17)
C_{131}	4567 (28)	787 (27)	1316 (16)	C_{314}	3621 (38)	2819 (14)	3500 (16)
C_{132}	5524 (74)	515 (11)	1517 (15)	C_{315}	2430 (41)	2876 (13)	3229 (17)
C_{133}	6675 (48)	669 (23)	1449 (15)	C_{316}	1807 (12)	2550 (19)	2732 (17)
C_{134}	6871 (28)	1093 (27)	1182 (16)	C_{321}	11 (13)	1916 (12)	1838 (16)
C_{135}	5915 (74)	1366 (11)	979 (15)	C_{322}	−716 (21)	1808 (11)	2628 (14)
C_{136}	4761 (48)	1213 (23)	1043 (15)	C_{323}	−1858 (17)	1974 (12)	2658 (13)
C_{211}	3091 (14)	1263 (13)	4595 (18)	C_{324}	−2272 (13)	2247 (12)	1901 (16)
C_{212}	4144 (17)	1485 (13)	5486 (16)	C_{325}	−1543 (21)	2356 (11)	1111 (14)
C_{213}	5286 (23)	1631 (13)	5705 (13)	C_{326}	−399 (17)	2192 (12)	1080 (13)
C_{214}	6184 (14)	1556 (13)	5038 (18)	C_{331}	1910 (15)	1805 (12)	539 (18)
C_{215}	5944 (17)	1333 (13)	4143 (16)	C_{332}	1310 (18)	1553 (12)	174 (18)
C_{216}	4803 (23)	1185 (13)	3923 (13)	C_{333}	1597 (19)	1581 (13)	1182 (12)
C_{221}	2522 (32)	517 (13)	4805 (17)	C_{334}	2483 (19)	1859 (12)	1477 (12)
C_{222}	3432 (32)	405 (15)	5484 (18)	C_{335}	3084 (15)	2112 (15)	765 (12)
C_{223}	3426 (19)	5 (16)	5948 (15)	C_{336}	2796 (18)	2086 (12)	244 (16)

[a] All values ×10^4. [b] Atoms from C_{111} to C_{116} belong to the phenyl ring P_1R_1.

interaction is a Pt–H contact 3.2 Å long (the hydrogen being in its postulated position 1.08 Å from a ring carbon).

The Metal–Ligand Interactions

In the present compound and in Clark's cation,[9] $PtCl(P(C_2H_5)_3)_2CO^+$, the Pt–P bond distances are the same (2.34 Å). The bonding scheme however is different because in the two complexes the acceptor orbitals of platinum are different in geometry as well in energy: in $Pt(P(C_6H_5)_3)_3CO$, these orbitals are sp hybrids, whereas in Clark's cation—a square-planar d^8 complex—the lower energy d orbitals come into play.

It seems reasonable to assume the latter orbitals closer in energy to the donor orbitals of the phosphorus atoms, so that Pt–P σ bonds will be more stable in the planar complex. From this point of view the Pt(II)–P bonds should probably be shorter than the Pt(0)–P ones. However, metal-to-ligand back-donation through π bonding is easier for Pt(0) than for Pt(II). Therefore the observed equivalence of the metal–phosphorus distances in the two complexes is due to a different balance of σ and π bonding.

In regard to the amount of π character in metal–phosphorus bonds, it is interesting to observe that, when no π-acceptor groups are present other than phosphorus, the Pt–P bonds are significantly shorter than the distance of 2.34 Å found in the present complex and in Clark's cation. Thus the Pt(II)–P bonds found in $PtHCl(PR_3)_2$[31] and in $PtHBr(PR_3)_2$[32] are in the range 2.26–2.27 Å. This fact suggests that in substituted phosphine–platinum(II) compounds π bonding plays an important role in M–P bonds when no competing π acceptors are present. The same is true for Pt(0)–P bonds: in the trigonal-planar complex $Pt(PR_3)_3$,[33] the Pt–P distances are 2.26–2.27 Å. Here again the comparison with the present carbonyl compounds suggests that a more extensive d_π–d_π interaction is present in the noncarbonylated species.

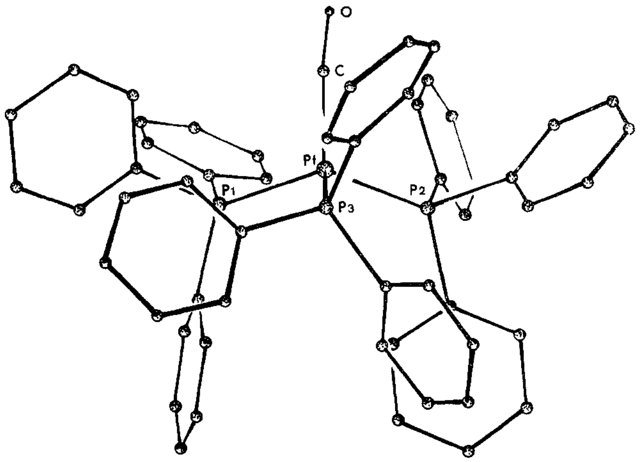

Figure 2.—An over-all view of the molecule of $Pt(P(C_6H_5)_3)_3CO$.

In the present Pt–C–O group the bonding parameters are affected by fairly high esd's. These are probably due to the unusually high thermal motion of the carbon and oxygen atoms (B_C = 6.9 (8) Å^2, B_O = 9.8 (9)

---

(31) R. Eisemberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(32) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.* (Amsterdam), **7**, 9 (1967).

(33) V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966).

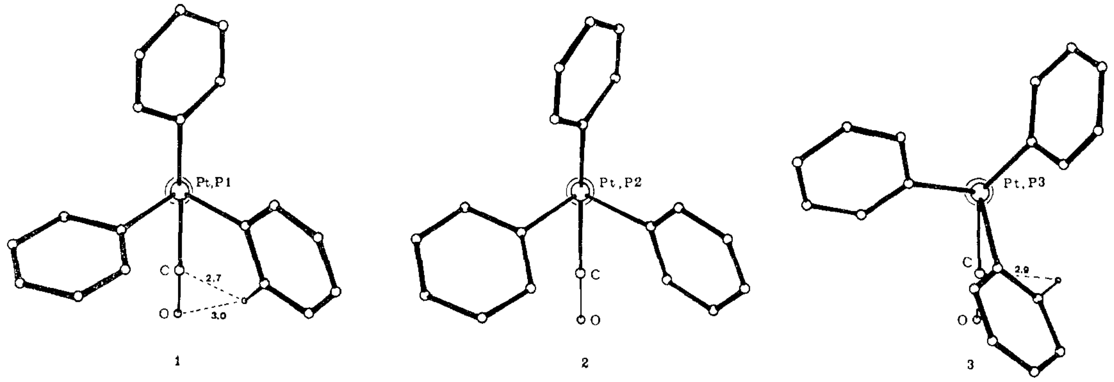

Figure 3.—The triphenylphosphine groups projected along the Pt–P axes. The hydrogen atoms nearest to carbon and oxygen atoms are also shown.

Table V

Selected Interatomic Distances and Angles in $Pt(P(C_6H_5)_3)_3CO$

Atoms	Dist, Å	Atoms	Angles, deg
$Pt–P_1$	2.352 (8)	$Pt–C–O$	171 (3)
$Pt–P_2$	2.333 (8)	$P_1–Pt–P_2$	113.7 (3)
$Pt–P_3$	2.335 (8)	$P_1–Pt–P_3$	110.9 (3)
$Pt–C$	1.86 (3)	$P_2–Pt–P_3$	109.6 (2)
$Pt–O$	2.98 (3)	$P_1–Pt–C$	105 (1)
$Pt–H_{116}$[a]	3.4	$P_2–Pt–C$	109 (1)
$Pt–H_{126}$	3.4	$P_3–Pt–C$	108 (1)
$Pt–H_{136}$	3.6	$Pt–P_1–C_{111}$	113 (1)
$Pt–H_{216}$	3.8	$Pt–P_1–C_{121}$	116 (1)
$Pt–H_{236}$	3.7	$Pt–P_1–C_{131}$	118 (1)
$Pt–H_{322}$	3.5	$Pt–P_2–C_{211}$	124 (1)
$Pt–H_{332}$	3.2	$Pt–P_2–C_{221}$	115 (1)
$P_1–C_{111}$	1.86 (2)	$Pt–P_2–C_{231}$	114 (1)
$P_1–C_{121}$	1.82 (3)	$Pt–P_3–C_{311}$	119 (1)
$P_1–C_{131}$	1.86 (4)	$Pt–P_3–C_{321}$	114 (1)
$P_2–C_{211}$	1.88 (3)	$Pt–P_3–C_{331}$	117 (1)
$P_2–C_{221}$	1.86 (4)	$C_{111}–P_1–C_{121}$	102 (1)
$P_2–C_{231}$	1.85 (3)	$C_{111}–P_1–C_{131}$	104 (1)
$P_3–C_{311}$	1.87 (4)	$C_{121}–P_1–C_{131}$	102 (2)
$P_3–C_{321}$	1.86 (2)	$C_{211}–P_2–C_{221}$	98 (2)
$P_3–C_{331}$	1.82 (2)	$C_{211}–P_2–C_{231}$	101 (2)
$P_1–P_2$	3.92 (1)	$C_{221}–P_2–C_{231}$	101 (1)
$P_1–P_3$	3.86 (1)	$C_{311}–P_3–C_{321}$	102 (1)
$P_2–P_3$	3.81 (1)	$C_{311}–P_3–C_{331}$	103 (4)
$P_1–C$	3.36 (4)	$C_{321}–P_3–C_{331}$	100 (2)
$P_2–C$	3.42 (3)	$P_1–C_{111}–C_{114}$	176 (2)
$P_3–C$	3.41 (3)	$P_1–C_{121}–C_{124}$	178 (2)
$C–O$	1.12 (4)	$P_1–C_{131}–C_{134}$	177 (2)
$C–H_{112}$	2.7	$P_2–C_{211}–C_{214}$	174 (2)
$C–H_{332}$	2.9	$P_2–C_{221}–C_{224}$	176 (2)
$O–H_{112}$	3.0	$P_2–C_{231}–C_{234}$	173 (2)
		$P_3–C_{311}–C_{314}$	179 (2)
		$P_3–C_{321}–C_{324}$	177 (2)
		$P_3–C_{331}–C_{334}$	175 (2)

[a] The hydrogen atoms, in their postulated positions at 1.08 Å from the ring carbon atoms, are labeled according to the same scheme adopted for ring carbons (see footnotes in Table IV).

Å^2).[34] However the present esd's are not likely to be seriously underestimated: the use of monochromatic radiation is a warranty against important systematic errors,[35] the variance model assumed in the refinement seems to be sound, and the final difference map is one of good quality. These arguments lead to the conclusion that the Pt–C bond length found in the present compound, 1.86 (3) Å, is *significantly* longer than 1.76 Å, the mean of the distances reported in platinum(II) carbonyls.[9,10]

The previous discussion of metal–phosphorus bonds applies as well to the metal–carbon interaction: in tetrahedral d^{10} complexes σ bonding is less and π bonding is more favored than in planar d^8 complexes. This is consistent with the fact that the stretching frequency of CO in the present compound, 1908 cm^{-1}, is lower than in Clark's cation (2100 cm^{-1}).

The observed difference among Pt–P bond lengths in noncarbonylated and carbonylated Pt(II) complexes seems to indicate that d_π–π^* interaction also represents an important contribution to bonding in platinum(II) carbonyls.

In this connection it must be pointed out that a more appropriate comparison of the relative importance of σ and π bonding in M–C–O bonds should be done on the basis of both *frequency* and *intensity* of the CO stretching bands.[36]

The Pt–C–O group in this structure is slightly bent: the Pt–C–O angle is 171 (3)°. Although the nonbonded interactions of carbon and oxygen are all greater than the van der Waals contacts (the shorter of them are reported in Table V and in Figure 3) the observed bending, if significant, may be due to the asymmetry of the environment of CO.

The Triphenylphosphine Ligands

In Figure 3 the three triphenylphosphine groups are projected along the metal–phosphorus axes. The ligands are stereochemically different and differently oriented with respect to the Pt–C–O group, also shown in Figure 3, although some degree of equivalence is apparent for groups 1 and 2. The phosphorus–carbon bonds range from 1.82 to 1.89 Å, their mean value being 1.85 Å. The use of rigid-group constraints for phenyl rings makes it problematic to assign meaningful esd's to the individual P–C distances and to their mean.

In the present compound, in a number of similar

---

(34) A tentative explanation of these high thermal factors is that the CO group is pointing toward a relatively empty cavity. See Table V for the shortest contacts of C and O atoms.

(35) J. Ladell, *Acta Cryst.*, **21**, 103 (1966).

(36) T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 971 (1967).

complexes[37] as well as in pure triphenylphosphine,[30] the C–P–C angle averages 103°. On the other hand, in all of these complexes the M–P–C angles are correspondingly larger than the value expected for sp^3 hybridization of phosphorus. This may indicate that in the pure ligand and in its complexes the P–C bonds have a p character more than sp^3.

Some of the P_i–C_{ij1}–C_{ij4} angles seem to indicate significant bending of the rings when compared with the ideal angle of 180°, although none is less than 173°.

Acknowledgments.—The authors wish to thank the Italian National Research Council for financial support. Thanks are due to Professor V. Scatturin and Dr. P. Chini—who also has supplied us with crystals—for many helpful discussions.

(37) See ref 26 and references therein. See also M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968); F. A. Cotton and B. M. Foxman, *ibid.*, **7**, 1784 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Tungsten-183–Phosphorus-31 Spin–Spin Coupling Interactions in Pentacarbonyltungsten Complexes

BY R. L. KEITER AND J. G. VERKADE[1]

Received March 24, 1969

The magnitudes of ^{183}W–^{31}P nuclear spin–spin coupling constants have been determined in a series of $LW(CO)_5$ complexes and are found to increase linearly with a correlation coefficient of greater than 0.95 as the electronegativity of the substituents on the phosphorus ligand L increases: $P(CH_2O)_3CC_4H_9 < P(SCH_2)_3CC_5H_{11} < P(N(CH_3)CH_2)_3CC_5H_{11} < P(OCH_2)_3CCH_3 < PF_3$. This trend can be interpreted in terms of the increasing s character of the ^{183}W–^{31}P bond and the rise in positive charge on phosphorus as more electronegative substituents are bound to phosphorus. Carbonyl stretching frequencies for these complexes have been assigned to A_1^1, B_1, A_1^2, and E modes and to the ^{13}CO satellites of the E band. The approximate method of Cotton and Kraihanzel was used to obtain the force constants k_1, k_2, and k_i. The stretching frequencies of the E mode were found to increase in the series: $P(N(CH_3)CH_2)_3CC_5H_{11} < P(CH_2O)_3CC_4H_9 < P(OCH_2)_3CC_5H_{11} < P(SCH_2)_3CC_5H_{11} < PF_3$. Attempts to correlate the ^{183}W–^{31}P coupling constants with the A_1^1 or E mode frequencies and k_1 produced correlation coefficients of 0.70, 0.79 and 0.51, respectively. Evaluation of the ligands in terms of σ- and π-donating capacities after the method of Graham resulted in correlation coefficients of 0.55 and 0.35, respectively.

Introduction

The magnitudes of nuclear spin–spin coupling constants for ^{31}P coupled to various heavy-metal nuclei have been measured[2–10] in hopes of gaining further information on the nature of phosphorus–metal bonding. It is generally agreed that spin–spin coupling is transmitted through σ bonds and is a function of the s character of the bonding atoms. Whether or not the s-electron density may be increased by a synergic mechanism which depends upon the π-bonding capacity of the trivalent phosphorus ligand is still under discussion.[11] Theoretical calculations by Schneider and Buckingham[12] suggest that the effect of π bonding on metal–phosphorus coupling constants is extremely small. Pidcock, *et al.*,[2] and Allen and Pidcock[3] have provided further evidence suggesting that a π-bonding coupling mechanism is negligible.

On the other hand, the increase in ^{195}Pt–^{31}P coupling values observed in *cis* and *trans* complexes of the type L_2PtCl_2 has been attributed by Grim and coworkers[5] to an increasing π-acceptor capacity in the series: $R_3P < R_2C_6H_5P < R(C_6H_5)_2P$. Moreover, in complexes of the type $LW(CO)_5$ it has been shown[4] that a linear correlation exists between the increasing ^{183}W–^{31}P coupling constants and the increasing frequency of the carbonyl E mode in the series: $L = R_3P < R_2C_6H_5P < R(C_6H_5)_2P < (C_6H_5)_3P$. More recently Grim, McAllister, and Singer[13] found a similar correlation having a different slope among the phosphites: $(i\text{-}C_3H_7O)_3P < (n\text{-}C_4H_9O)_3P < (C_2H_5O)_3P < (CH_3O)_3P < (C_6H_5O)_3P$.

The purpose of the present study was to determine the extent to which the ^{183}W–^{31}P coupling constant depends upon various parameters which have been used as a measure of the σ- and/or π-bonding characteristics of the phosphorus ligand. In this work are reported ^{183}W–^{31}P constants and carbonyl stretching frequency assignments for complexes of the type LW-

---

(1) Alfred P. Sloan Fellow.

(2) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc., A*, 1707 (1966).

(3) F. H. Allen and A. Pidcock, *ibid.*, *A*, 2700 (1968).

(4) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967); S. O. Grim and D. A. Wheatland, *Inorg. Chem.* **8**, 1716 (1969).

(5) S. O. Grim, R. L. Keiter, and W. McFarlane, *ibid.*, **6**, 1133 (1967).

(6) S. O. Grim, D. A. Wheatland, and P. R. McAllister, *ibid.*, **7**, 161 (1968).

(7) R. L. Keiter and S. O. Grim, *Chem. Commun.*, 521 (1968).

(8) S. O. Grim and D. A. Wheatland, *Inorg. Nucl. Chem. Letters*, **4**, 187 (1968).

(9) R. W. King, T. J. Huttermann, and J. G. Verkade, *Chem. Commun.*, 561 (1965).

(10) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Letters*, **2**, 49 (1966).

(11) *Chem. Eng. News*, **45**, 40 (Oct 30, 1967); work of S. O. Grim.

(12) W. G. Schneider and A. D. Buckingham, *Discussions Faraday Soc.*, **34**, 147 (1962).

(13) S. O. Grim, P. R. McAllister, and R. M. Singer, *Chem. Commun.*, 38 (1969).