633. *The Crystal Structure of* trans-*Dimesitylbis*(*diethylphenylphosphine*)*cobalt*(II).

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The three-dimensional *X*-ray analysis of [Co(mesityl)$_2$(PEt$_2$Ph)$_2$] has confirmed its *trans*-square-planar configuration. The mesityl groups are planar, and perpendicular to the co-ordination plane of the cobalt atom, but are not exactly symmetrical about this plane; the Co–C bonds are not co-planar with the mesityl groups, which lie in two parallel planes 0·44 Å apart and the cobalt atom is thus 0·22 Å from each mesityl plane. The *ortho*-methyl groups are in contact (C–C = 4 Å) above and below the cobalt atom. The tetrahedral angles of the phosphine groups are distorted to give larger cobalt–phosphorus–carbon angles (mean value 116·4°), and the Co–P bond-length (2·237 ± 0·004 Å) shows considerable double-bond character. The Co–C bond-length (1·96 ± 0·01 Å) indicates that there is no appreciable π-bonding between the cobalt atom and the mesityl group; this may be the result of steric hindrance which prevents the mesityl group from approaching the cobalt atom more closely without further distortion.

It is concluded that the principal requirement for the existence of the complexes [MR$_2$(PR$_3'$)$_2$] is a square-planar configuration, other factors being of minor importance. Where the metal atom has a tendency to form tetrahedral complexes, stability is achieved only as the combined result of the steric hindrance of the *trans*-phosphine groups acting on the R groups, and of the mutual steric interaction of the R groups to keep R–M–R linear; this is fully effective only when these ligands have sufficiently bulky *ortho*-substituents.

Chatt and Shaw [1,2] have described the preparation and properties of a series of alkyl and aryl complexes of transition metals and have discussed the factors which affect their stability. The cobalt complexes [CoR$_2$(PR'$_3$)$_2$] are stable only when R is a di-*ortho*-substituted aryl group or an aryl group with one very bulky *ortho*-substituent. They have dipole moments of zero, and magnetic moments of 2·3—2·7 B.M., indicating that they have

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[1] Chatt and Shaw, *J.*, 1959, 705, 4020.
[2] Chatt and Shaw, *J.*, 1960, 1718; 1961, 285.

a centrosymmetric *trans*-square-planar configuration; this is unusual in complexes of cobalt(II) and occurs only as a result of steric hindrance.[3]

We have examined the structure of the complex [Co(mesityl)$_2$(PEt$_2$Ph)$_2$] to confirm that it has a square-planar configuration and to obtain more precise information about the bonding in the molecule and the steric factors which affect its stability.

EXPERIMENTAL AND RESULTS

Crystal data for this and for the corresponding nickel compound, which is isomorphous, are given. The compounds were prepared by Dr. B. L. Shaw, using the published methods.[2]

[Co(mesityl)$_2$(PEt$_2$Ph)$_2$], lemon-yellow platy crystals. $C_{38}H_{52}CoP_2$, $M = 629·7$, m. p. 124—127°, monoclinic, $a = 10·69 \pm 0·03$, $b = 9·33 \pm 0·03$, $c = 18·25 \pm 0·06$ Å, $\beta = 107·6 \pm 0·1°$; $U = 1734·3$ Å^3, $D_m = 1·198 \pm 0·010$ (by flotation), $Z = 2$, $D_c = 1·206$, $F(000) = 674$. Space group, $P2_1/c$ (C^5_{2h} No. 14). Molecular symmetry $\bar{1}$. Co-K_α radiation, single-crystal oscillation and Weissenberg photographs.

[Ni(mesityl)$_2$(PEt$_2$Ph)$_2$], orange-yellow platy crystals. $C_{38}H_{52}NiP_2$, $M = 629·5$, m. p. 154—156°, monoclinic, $a = 10·67 \pm 0·03$, $b = 9·40 \pm 0·03$, $c = 18·54 \pm 0·06$ Å, $\beta = 107·3 \pm 0·1°$; $U = 1774·1$ Å^3, $D_m = 1·198 \pm 0·010$ (by flotation), $Z = 2$, $D_c = 1·178$, $F(000) = 676$. Space group, $P2_1/c$ (C^5_{2h} No. 14). Molecular symmetry $\bar{1}$. Co-K_α radiation, single-crystal oscillation and Weissenberg photographs.

The molecular symmetry requires the metal atom to lie on a centre of symmetry, and the co-ordination round the metal must therefore be *trans*-square-planar and not tetrahedral.

The intensities of thd $h0l$, $h1l$, $h2l$, $0kl$, $1kl$, $2kl$ reflections of the cobalt complex were measured by visual comparison with a standard scale; multiple-film techniques were used. For each zone the structure factors were put on an approximately absolute scale, and the mean Debye temperature factor for the molecule was determined, by Wilson's method;[4] however, the special position of the heavy metal atom invalidated the statistical assumptions of this method, and correct scale factors were obtained only by the comparison of observed and calculated structure factors for each layer line separately.

TABLE 1.

Final atomic parameters, temperature factors (Å^2), and standard deviations of position.

	x/a	y/b	z/c	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Co	0	0	0	2·631	0	0	0
P	0·1570	0·1638	0·0116	3·367	0·0033	0·0308	0·0029
C(1)	−0·0964	0·1381	0·0434	3·691	0·0125	0·0144	0·0111
C(2)	−0·0742	0·1326	0·1261	4·419	0·0137	0·0161	0·0123
C(3)	−0·1501	0·2154	0·1649	5·216	0·0158	0·0173	0·0138
C(4)	−0·2484	0·3075	0·1200	5·063	0·0152	0·0175	0·0131
C(5)	−0·2712	0·3201	0·0419	4·855	0·0150	0·0166	0·0132
C(6)	−0·1981	0·2306	0·0071	4·012	0·0134	0·0147	0·0116
C(7)	0·0294	0·0316	0·1783	6·241	0·0181	0·0195	0·0165
C(8)	−0·3278	0·4003	0·1626	6·622	0·0181	0·0207	0·0161
C(9)	−0·2310	0·2424	−0·0815	5·112	0·0156	0·0170	0·0137
C(10)	0·2406	0·2164	0·1113	5·551	0·0162	0·0185	0·0141
C(11)	0·1977	0·3325	0·1455	6·796	0·0184	0·0203	0·0169
C(12)	0·2673	0·3687	0·2228	6·684	0·0186	0·0206	0·0163
C(13)	0·3743	0·2921	0·2607	7·684	0·0204	0·0236	0·0183
C(14)	0·4240	0·1780	0·2314	6·076	0·0173	0·0184	0·0156
C(15)	0·3540	0·1421	0·1531	5·955	0·0173	0·0190	0·0152
C(16)	0·2944	0·1165	−0·0227	5·488	0·0164	0·0187	0·0142
C(17)	0·4003	0·2281	−0·0158	5·711	0·0168	0·0188	0·0143
C(18)	0·1063	0·3468	−0·0304	5·231	0·0155	0·0167	0·0138
C(19)	0·0777	0·3486	−0·1192	6·927	0·0185	0·0211	0·0172

Structure Analysis.—The position of the phosphorus atom was found from the two-dimensional Patterson functions $P(UW)$ and $P(VW)$. Three successive three-dimensional electron-density maps were then calculated, the phases of the structure factors being determined

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[3] Figgis and Nyholm, *J.*, 1954, 12.

[4] Wilson, *Nature*, 1942, **150**, 152.

TABLE 2.

Bond lengths and angles, with standard deviations.

Atoms	Length (Å)	s.d. (Å)	Atoms	Angle	s.d.	Atoms	Angle	s.d.
Co–P	2·232	0·004	P–Co–C(1)	89·08°	0·41°	Co–P–C(10)	113·79°	0·6°
Co–C(1)	1·961	0·012				P–C(10)–C(11)	121·6	1·1
			Co–C(1)–C(2)	117·1	0·8	P–C(10)–C(15)	119·3	1·0
C(1)–C(2)	1·46	0·017	Co–C(1)–C(6)	130·2	0·9	C(11)–C(10)–C(15)	119·1	1·4
C(2)–C(3)	1·45	0·019	C(2)–C(1)–C(6)	112·1	1·0	C(10)–C(11)–C(12)	119·0	1·4
C(3)–C(4)	1·41	0·025	C(1)–C(2)–C(3)	123·2	1·1	C(11)–C(12)–C(13)	119·4	1·6
C(4)–C(5)	1·38	0·020	C(1)–C(2)–C(7)	121·5	1·1	C(12)–C(13)–C(14)	125·5	1·6
C(5)–C(6)	1·42	0·019	C(3)–C(2)–C(7)	115·2	1·2	C(13)–C(14)–C(15)	115·0	1·4
C(6)–C(1)	1·39	0·021	C(2)–C(3)–C(4)	117·9	1·2	C(14)–C(15)–C(10)	122·0	1·4
			C(3)–C(4)–C(5)	121·4	1·2			
C(2)–C(7)	1·55	0·026	C(3)–C(4)–C(8)	117·8	1·2	Co–P–C(16)	117·64	0·6
C(4)–C(8)	1·57	0·022	C(5)–C(4)–C(8)	120·8	1·2	P–C(16)–C(17)	117·7	1·0
C(6)–C(9)	1·55	0·019	C(4)–C(5)–C(6)	117·7	1·2			
			C(5)–C(6)–C(1)	127·5	1·2	Co–P–C(18)	117·82	0·6
P–C(10)	1·835	0·017	C(1)–C(6)–C(9)	116·1	1·0	P–C(18)–C(19)	112·0	1·1
C(10)–C(11)	1·39	0·025	C(5)–C(6)–C(9)	116·13	1·1			
C(11)–C(12)	1·42	0·028				C(10)–P–C(16)	101·8	0·7
C(12)–C(13)	1·35	0·031				C(10)–P–C(18)	98·9	0·7
C(13)–C(14)	1·37	0·027				C(16)–P–C(18)	104·1	0·8
C(14)–C(15)	1·44	0·026						
C(15)–C(10)	1·40	0·026						
P–C(16)	1·817	0·015						
C(16)–C(17)	1·51	0·025						
P–C(18)	1·883	0·017						
C(18)–C(19)	1·56	0·023						

TABLE 3.

Intermolecular non-bonding distances (Å) of less than 3·5 Å.

Cobalt–mesityl	Co–C(7)	3·19	Phenyl–ethyl	C(10)–C(17)	3·27
	Co–C(9)	3·35		C(11)–C(18)	3·06
Mesityl–phosphine–phenyl	C(2)–C(11)	3·38		C(15)–C(16)	3·09
	C(7)–C(10)	3·35		C(15)–C(17)	3·36
	C(7)–C(11)	3·48	Ethyl–ethyl	C(16)–C(19)	3·27
Mesityl–phosphine–ethyl	C(1)–C(16′)	3·13		C(17)–C(18)	3·27
	C(1)–C(18)	3·47			
	C(2)–C(16′)	3·44			
	C(6)–C(16′)	3·44			

at each stage by the contributions of the atoms located in previous stages. An increased number of terms was used in successive maps. The phenyl group of the phosphine appeared in the first map, and most of the carbon atoms in the second; the mesityl group did not become clearly visible until the third map. The scale factors for each layer were then adjusted to make $\sum F^2_{\text{calc}} = \sum F^2_{\text{obs}}$, one cycle of least-square refinement was calculated, giving an R-value of 0·285, and a difference-Fourier synthesis in which all the terms were used showed the one remaining ethyl-carbon atom.

Seven cycles of least-squares refinement, including one more layer-scaling cycle, were then computed. Isotropic temperature factors were refined for each atom, but only the diagonal terms of the least-squares matrix were used. No hydrogen atoms were included. The final R-value, including the non-observed terms, was 0·161 for the 1345 reflections, while the sum $\sum w\Delta F^2$ was less than one-tenth of the value for the first cycle. The changes in atomic parameters indicated by the final cycle were less than the calculated standard deviations, and neither $\sum \Delta F$ nor $\sum w\Delta F^2$ had decreased from the previous cycle. The final difference map had no areas of more than $\pm 0{\cdot}7$ e/Å^3. The atomic parameters are given in Table 1, and the observed and calculated structure factors in Table 4.

Throughout the refinement, bond length and angle calculations were made between cycles, and frequent checks were made on the planarity of the aryl groups. These results showed a steady improvement in consistency.

The Mercury computer library programmes used included data reduction (J. A. Bland

TABLE 4.

Observed and calculated values of structure factors.

h	k	l	$10F_o$	$10F_c$	$10\Delta F$
0	0				
		2	1398	1292	107
		4	859	794	65
		6	1225	1133	92
		8	1186	1011	175
		10	223	244	-20
		12	248	282	-34
		14	175	145	31
		16	120	131	-12
		18	150	155	-6
0	1				
		1	640	899	-259
		2	-679	-1035	356
		3	679	695	-16
		4	594	452	142
		5	766	715	51
		6	99	111	-12
		7	457	492	-36
		8	-341	-335	-6
		9	293	326	-33
		10	-220	-234	14
		11	345	338	7
		12	63	1	62
		13	280	216	65
		14	-75	-63	-11
		15	150	163	-14
		16	50*	16	35
		17	178	144	34
		18	-37*	-51	14
		19	55	71	-16
0	2				
		0	-1375	-1326	-49
		1	-103	-134	31
		2	-237	-198	-39
		3	-342	-375	33
		4	123	81	42
		5	27*	27	0
		6	324	241	82
		7	-121	-96	-24
		8	-187	-216	30
		9	-217	-183	-33
		10	188	120	68
		11	-172	-179	7
		12	117	93	24
		13	-105	-107	2
		14	121	93	28
		15	-48	-39	-9
		16	121	89	31
		17	-82	-80	-1
		18	41	52	-11
		19	-17*	-69	52
0	3				
		1	-77	-26	-51
		2	-209	-148	-61
		3	-152	-168	16
		4	146	110	36
		5	-46	-91	46
		6	-103	-113	11
		7	-92	-10	-81
		8	40*	28	12
		9	-38*	-33	-5
		10	77	93	-16
		11	41*	15	26
		12	94	95	-1
		13	-42	-52	10
		14	-41*	-29	-12
		15	76	63	13
		16	-42*	-19	-23
		17	36*	41	-5
		18	27*	2	25
0	4				
		0	-199	-178	-21
		1	58	63	-5
		2	138	146	-7
		3	102	73	29
		4	181	178	3
		5	48	25	24
		6	76	43	33
		7	94	114	-20
		8	65	50	15
		9	113	129	-16
		10	248	291	-43
		11	159	115	44
		12	292	284	7
		13	113	141	-28
		14	101	109	-8
		15	115	115	0
		16	121	126	-6
		17	36	47	-11
0	5				
		1	363	344	19
		2	179	190	-12
		3	233	187	46
		4	85	110	-25
		5	512	471	40
		6	120	122	-2
		7	231	227	4
		8	64	77	-14
		9	300	270	30
		10	120	150	-31
		11	306	296	10
		12	-45	-36	-9
		13	292	271	21
		14	103	86	17
		15	52	79	-27
		16	107	81	26
0	6				
		0	564	583	-19
		1	-39*	-11	-28
		2	385	351	34
		3	149	158	-10
		4	347	347	-0
		5	84	70	14
		6	325	321	4
		7	-42*	-42	0
		8	319	324	-5
		9	105	111	-6
		10	120	133	-13
		11	39*	38	1
		12	49	66	-17
		13	-74	-59	-15
		14	71	99	-27
		15	-36*	-32	-4
0	7				
		1	203	219	-16
		2	-84	-97	14
		3	235	237	-3
		4	-74	-86	12
		5	185	186	-1
		6	-84	-100	16
		7	197	214	-18
		8	-58	-69	11
		9	71	106	-34
		10	-55	-74	19
		11	66	96	-30
		12	-77	-73	-4
		13	65	76	-11
		14	-54	-70	16
0	8				
		0	130	166	-37
		1	-41	-74	33
		2	116	154	-38
		3	-60	-52	-8
		4	80	94	-13
		5	-73	-87	14
		6	77	109	-32
		7	-123	-94	-29
		8	46	72	-26
		9	-93	-104	11
		10	66	80	-15
		11	-61	-75	14
		12	40	65	-26
0	9				
		1	132	121	11
		2	42*	11	31
		3	41*	40	1
		4	51	34	18
		5	39*	10	29
		6	-37*	-31	-15
		7	54	63	-9
		8	-29*	-24	-5
		9	31	32	-0
0	10				
		0	-29*	-13	-16
		1	-42	-27	-15
		2	-28	-15	-13
		3	-35	-41	6
1	0				
		0	1415	1168	247
		2	1107	1212	-105
		4	245	316	-72
		6	953	836	117
		8	773	674	99
		10	407	402	5
		12	126	161	-35
		14	-45*	-19	-26
		16	42	43	-0
		18	71	51	21
1	1				
		0	-537	-482	-55
		1	494	545	-51
		2	27	34	-7
		3	85	119	-34
		4	-618	-592	-26
		5	678	627	51
		6	-366	-262	-105
		7	262	272	-10
		8	-565	-605	40
		9	113	138	-25
		10	-156	-202	46
		11	269	244	26
		12	-141	-161	20
		13	78	63	16
		14	-103	-109	6
		15	169	122	47
		16	-42*	-55	13
		17	126	107	20
		18	-79	-53	-26
1	2				
		0	427	444	-17
		1	-785	-759	-27
		2	138	121	17
		3	-698	-728	30
		4	598	564	33
		5	-420	-387	-33
		6	80	52	29
		7	-465	-486	22
		8	32*	45	-13
		9	-337	-317	-20
		10	127	115	12
		11	-346	-339	-7
		12	227	162	64
		13	-175	-151	-25
		14	181	152	29
		15	-45*	-9	-36
		16	193	166	28
		17	-120	-76	-44
		18	78	80	-2
1	3				
		0	-379	-309	-70
		1	335	284	51
		2	-197	-187	-10
		3	317	340	-22
		4	-216	-186	-30
		5	345	320	25
		6	-138	-88	-50
		7	217	165	52
		8	86	65	21
		9	268	277	-8
		10	-30*	-54	24
		11	269	266	3
		12	-32*	-57	25
		13	232	223	9
		14	37*	8	29
		15	83	86	-4
		16	59	22	37
		17	126	119	8
1	4				
		0	112	68	43
		1	229	197	32
		2	-211	-176	-35
		3	410	417	-8
		4	-126	-114	-13
		5	235	191	43
		6	331	307	23
		7	108	121	-12
		8	115	74	41
		9	354	340	14
		10	216	203	13
		11	180	137	43
		12	198	215	-17
		13	79	54	26
		14	252	214	38
		15	66	61	5
		16	126	118	8
		17	102	84	17
1	5				
		0	415	450	-34
		1	208	224	-16
		2	141	99	41
		3	61	95	-33
		4	352	326	26
		5	121	98	23
		6	226	218	8
		7	265	288	-23
		8	214	187	28
		9	120	76	44
		10	150	154	-4
		11	70	62	9
		12	184	177	7
		13	174	123	52
		14	135	101	34
		15	130	119	11
		16	42	39	4
1	6				
		0	421	423	-2
		1	-59	-50	-10
		2	400	411	-11
		3	157	138	19
		4	382	383	-1
		5	195	157	38
		6	230	262	-32
		7	64	58	6
		8	96	94	2
		9	-60	-33	-28
		10	124	111	13
		11	181	155	26
		12	89	61	29
		13	29*	44	-15
		14	-80	-35	-45
		15	-40	-5	-35
1	7				
		0	-192	-166	-26
		1	227	243	-16
		2	-78	-86	8
		3	290	295	-4
		4	-32*	-33	0
		5	162	176	-14
		6	-128	-112	-16
		7	31*	40	-9
		8	-156	-108	-48
		9	128	108	20
		10	-32*	-25	-7
		11	103	90	13
		12	-165	-137	-28
1	8				
		0	153	161	-8
		1	-76	-73	-3
		2	87	79	8
		3	-216	-184	-32
		4	90	113	-23
		5	-216	-168	-47
		6	59	79	-20
		7	-123	-115	-7
		8	180	161	19
		9	-73	-65	-7
		10	93	101	-8
		11	-143	-146	3
1	9				
		0	-32*	-43	11
		1	98	87	12
		2	-31*	-20	-11
		3	31*	21	10
		4	-30*	-8	-22
		5	131	117	14
		6	-59	-71	11
		7	146	135	11
1	10				
		0	21*	0	21
		1	55	48	7
		2	51	67	-16
		3	65	67	-2
1	0				
		-2	856	999	-143
		-4	-273	-230	-43
		-6	538	568	-29
		-8	-86	-101	15
		-10	306	284	22
		-12	121	69	52
		-14	359	279	80
		-16	419	353	66
		-18	156	173	-17
1	1				
		-1	625	734	-108
		-2	163	233	-70
		-3	532	550	-19
		-4	-486	-453	-33
		-5	363	369	-6
		-6	-23*	-39	16
		-7	474	468	5
		-8	-293	-236	-57
		-9	245	210	35
		-10	-34*	-30	-4
		-11	390	336	53
		-12	90	73	17
		-13	355	244	112
		-14	-58	-3	-55
		-15	270	189	81
		-16	55	83	-28
		-17	199	177	22
		-18	42	75	-32
		-19	122	128	-6
1	2				
		-1	-123	-149	26
		-2	-38	-27	-11
		-3	157	119	38
		-4	410	472	-62
		-5	-190	-150	-40
		-6	389	322	67
		-7	-28*	-74	47
		-8	346	385	-39
		-9	157	134	24
		-10	267	236	31
		-11	37*	53	-16
		-12	185	181	4
		-13	47	22	24
		-14	48	38	10
		-15	-57	-12	-45
		-16	54	45	9
		-17	48	21	27
		-18	80	62	18
		-19	57	36	21
1	3				
		-1	304	260	43
		-2	-290	-259	-31
		-3	-398	-363	-35
		-4	-63	-54	-9
		-5	198	211	-13
		-6	-65	-80	16
		-7	147	109	39
		-8	-52	-48	-5
		-9	88	62	26
		-10	-114	-71	-43
		-11	-111	-79	-32
		-12	-64	-66	2
1	4				
		-1	190	258	-68
		-2	88	104	-15
		-3	104	91	13
		-4	467	427	40
		-5	-78	-94	16
		-6	285	215	69
		-7	-27*	-13	-14
		-8	-29*	-19	-10
		-9	85	100	-15
		-10	69	80	-11
		-11	-89	-110	20
		-12	284	282	1
		-13	-95	-82	-13
1	5				
		-1	322	302	20
		-2	255	235	19
		-3	525	475	50
		-4	77	72	6
		-5	429	456	-27
		-6	273	237	35
		-7	226	209	16
		-8	151	146	4
		-9	213	205	9
		-10	32*	65	-33
		-11	400	434	-34
		-12	166	152	14
		-13	116	131	-15
		-14	166	142	25
1	6				
		-1	-30*	-17	-13
		-2	380	409	-29
		-3	-60	-52	-8
		-4	125	133	-8
		-5	61	51	10
		-6	333	390	-57
		-7	146	139	7
		-8	364	391	-27
		-9	-155	-148	-8
		-10	281	271	10
		-11	37*	49	-12
		-12	140	174	-28
		-13	138	148	-9
1	7				
		-1	197	203	-6
		-2	-130	-66	-64
		-3	199	221	-22
		-4	-140	-111	-29
		-5	192	218	-26
		-6	-137	-104	-33
		-7	302	254	47
		-8	-38*	-40	2
		-9	232	237	-4
		-10	-105	-104	-1
		-11	118	107	11
		-12	-118	-84	-35
		-13	189	167	22
1	8				
		-1	-69	-80	11
		-2	132	128	3
		-3	-65	-64	-1
		-4	130	96	33
		-5	-133	-93	-40
		-6	71	28	44
1	9				
		-1	32*	41	-8
		-2	32*	28	4
		-3	-31*	-7	-24
		-4	31*	9	22
		-5	-67	-51	-16
1	10				
		-1	117	125	-7
		-2	-21*	-10	-11
		-3	20*	65	-45
		-4	68	45	23
2	0				
		0	-602	-732	130
		2	150	191	-42
		4	258	233	25
		6	-45	-19	-26
		8	-32*	-34	1
		10	73	80	-7
		12	-101	-81	-20
		14	-89	-97	8
		16	-29*	-23	-6
		18	-15*	-40	26
2	1				
		0	366	396	-30
		1	593	643	-50
		2	55	60	-5
		3	-57	-42	-15
		4	52	14	38
		5	189	91	98
		6	-314	-281	-33
		7	124	129	-5
		8	99	106	-7
		9	118	103	16
		10	46	31	15
		11	-59	-68	9
		12	70	69	1
		13	48*	9	39
		14	-46*	-16	-30
		15	42*	31	12
		16	-37*	-30	-7
		17	50*	31	-1
		18	16*	23	-7
2	2				
		0	829	1145	-316
		1	-55	-62	7
		2	345	428	-83
		3	-532	-576	44
		4	333	347	-14
		5	-212	-176	-37
		6	409	405	4
		7	65	13	52
		8	279	250	29
		9	-295	-318	23
		10	329	374	-44
		11	-279	-275	-5
		12	273	255	18
		13	-47*	-16	-31
		14	199	161	38
		15	-40*	-47	7
		16	203	194	9
		17	28*	10	18
2	3				
		0	-404	-336	-68
		1	189	166	23
		2	-102	-78	-24
		3	470	502	-32
		4	-237	-193	-44
		5	614	691	-77
		6	-63	-98	36
		7	392	382	10
		8	-214	-165	-49
		9	342	326	15
		10	-146	-144	-2
		11	558	591	-32
		12	-192	-220	28
		13	341	321	19
		14	32*	22	10
		15	191	225	-34
		16	25*	14	10

TABLE 4. (*Continued.*)

h k l	10F_o	10F_c	10ΔF
2 4			
0	300	285	16
1	22*	15	8
2	-22*	-27	5
3	381	317	63
4	384	364	21
5	126	131	-5
6	415	408	7
7	51	5	46
8	202	206	-4
9	178	145	33
10	109	75	34
11	155	123	32
12	267	217	50
13	-67	-56	-11
14	200	199	1
15	66	19	47
2 5			
0	285	261	24
1	202	180	22
2	204	200	4
3	173	178	-5
4	247	257	-11
5	195	164	31
6	182	165	17
7	173	135	38
8	162	161	1
9	30*	43	-13
10	207	173	33
11	35*	24	10
12	99	106	-6
13	30*	24	6
14	26*	17	9
15	40	52	-11
2 6			
0	171	193	-23
1	-29*	-22	-7
2	199	188	11
3	88	76	13
4	133	99	34
5	127	107	20
6	77	45	32
7	-37*	-28	-9
8	37*	37	-0
9	109	99	11
10	135	93	43
11	135	103	32
12	28*	46	-18
13	71	73	-2
2 7			
0	-261	-229	-32
1	206	183	22
2	-181	-161	-20
3	90	81	10
4	-37*	-1	-36
5	37*	96	-59
6	-181	-153	-28
7	35*	21	14
8	-34*	-56	23
9	106	96	10
10	-29*	-21	-8
2 8			
0	171	151	19
1	-159	-166	7
2	201	215	-14
3	-159	-127	-32
4	83	97	-15
5	-154	-134	-20
6	94	137	-44
7	-68	-89	21
8	161	166	-5
9	-55	-71	16
10	66	105	-39
2 9			
0	30*	28	3
1	102	96	6
2	-29*	-41	12
3	145	159	-14
4	-59	-55	-4
5	140	116	24
6	22*	21	1
7	125	155	-30
2 10			
0	48	70	-22
1	85	110	-25
2 0			
-2	-364	-465	101
-4	438	433	4
-6	629	401	228
-8	128	112	16
-10	125	148	-23
-12	348	318	31
-14	306	272	34
-16	363	347	16
-18	178	187	-9
2 1			
-1	197	261	-65
-2	-726	-994	268
-3	-201	-146	-55
-4	294	209	85
-5	666	716	-51
-6	-131	-62	-69
-7	264	205	57
-8	-342	-249	-93
-9	190	159	31
-10	-545	-482	-63
-11	385	316	69
-12	-64	-90	27
-13	421	286	135
-14	-58	-61	3
-15	243	177	67
-16	-56	-28	-28
-17	270	233	37
-18	-45	-19	-26
-19	147	137	10
2 2			
-1	889	1138	-249
-2	634	782	-147
-3	-393	-353	-40
-4	-165	-122	-43
-5	-65	-73	9
-6	292	328	-36
-7	118	98	20
-8	380	359	21
-9	-31*	-55	24
-10	231	205	26
-11	-366	-292	-74
-12	213	172	41
-13	-245	-198	-47
-14	200	96	104
-15	-214	-203	-12
-16	108	63	45
-17	-98	-98	-0
-18	42	71	-29
-19	-32	-44	12
2 3			
-1	639	627	11
-2	207	167	39
-3	388	480	-93
-4	-128	-97	-31
-5	92	75	17
-6	-219	-207	-12
-7	404	419	-14
-8	77	101	-24
-9	146	156	-10
-10	88	100	-12
-11	200	175	25
-12	-73	-31	-41
-13	37*	7	30
-14	-37*	-55	18
2 4			
-1	-116	-154	38
-2	318	337	-18
-3	250	197	54
-4	522	596	-75
-5	-23*	-10	-14
-6	422	436	-14
-7	283	225	57
-8	104	108	-4
-9	68	53	15
-10	246	217	29
-11	239	200	39
-12	138	113	26
-13	214	175	40
2 5			
-1	315	288	27
-2	455	500	-45
-3	348	292	57
-4	261	254	7
-5	242	248	-6
-6	302	289	13
-7	191	193	-2
-8	295	216	79
-9	241	185	56
-10	207	163	44
-11	122	125	-4
-12	149	132	17
-13	111	108	3
-14	131	107	24
2 6			
-1	-94	-107	14
-2	69	52	17
-3	29*	27	2
-4	138	142	-3
-5	36*	67	-31
-6	150	119	31
-7	-37*	-13	-24
-8	191	158	33
-9	37*	1	35
-10	203	177	26
-11	36*	12	24
-12	216	232	-16
-13	88	76	12
-14	159	148	11
2 7			
-1	156	141	16
-2	-389	-331	-57
-3	74	94	-21
-4	-309	-274	-35
-5	169	121	48
-6	-192	-160	-33
-7	191	161	30
-8	-199	-164	-35
-9	206	132	74
-10	-171	-154	-17
-11	162	147	15
-12	-28*	-62	34
-13	173	171	3
2 8			
-1	-36*	-56	20
-2	117	114	3
-3	-112	-107	-5
-4	35*	42	-7
-5	-210	-192	-18
-6	138	138	1
-7	-142	-124	-18
-8	94	80	14
-9	-71	-77	5
-10	27*	26	1
-11	-116	-121	5
2 9			
-1	30*	76	-46
-2	115	91	24
-3	83	82	1
-4	-29*	-3	-26
-5	121	128	-8
-6	-27*	-11	-16
2 10			
-1	86	109	-23
-2	106	117	-11
-3	49	72	-23
-4	93	119	-27
3 0			
0	240	184	56
2	178	152	25
4	200	204	-4
6	-38	-67	29
8	-73	-88	15
10	46*	39	7
12	58*	13	45
14	-52*	-20	-32
16	40*	27	14
-2	-900	-822	-78
-4	-194	-194	-0
-6	229	199	30
-8	104	95	9
-10	-140	-173	33
-12	84	65	19
-14	58*	44	15
-16	69	66	4
-18	65	86	-21
3 1			
0	-558	-564	6
1	104	122	-18
2	-190	-190	0
3	240	286	-46
4	-245	-240	-5
5	204	160	45
6	104	110	-6
7	178	129	48
8	60	39	22
9	73	94	-22
10	235	122	112
11	117	90	28
12	58*	53	5
13	56*	24	32
14	138	107	32
15	46*	19	27
16	76	70	6
-1	408	428	-20
-2	-394	-365	-30
-3	-79	-105	26
-4	-381	-449	68
-5	243	240	3
-6	-128	-120	-8
-7	274	309	-36
-8	-346	-363	17
-9	197	138	59
-10	-317	-307	-10
-11	190	148	41
-12	-245	-295	50
-13	191	171	20
-14	-203	-192	-11
-15	240	199	41
-16	-193	-144	-49
-17	51*	94	-42
-18	-90	-103	17
-19	90	76	15
3 2			
0	660	852	-192
1	508	536	-28
2	238	249	-11
3	188	171	17
4	284	265	18
5	73	72	0
6	552	567	-15
7	275	311	-37
8	273	269	3
9	98	109	-11
10	316	307	9
11	95	53	42
12	230	219	11
13	-55*	-44	-11
14	151	118	32
15	44*	65	-22
16	131	98	32
-1	386	403	-17
-2	602	826	-224
-3	191	127	64
-4	312	389	-77
-5	-571	-751	181
-6	585	679	-94
-7	-140	-112	-28
-8	323	291	32
-9	-265	-285	20
-10	266	280	-14
-11	-300	-331	30
-12	331	399	-68
-13	-434	-523	89
-14	280	248	33
-15	-162	-144	-17
-16	164	159	6
-17	-99	-79	-21
-18	161	136	25
-19	-135	-110	-25
4 0			
0	52	54	-2
2	553	533	20
4	159	149	9
6	-41*	-61	20
8	92	167	-76
10	460	414	46
12	67	79	-12
14	69	98	-29
16	84	114	-30
-2	-319	-338	18
-4	-525	-481	-44
-6	-212	-185	-27
-8	-118	-132	13
-10	-41*	-21	-20
-12	-46*	-41	-5
-14	58	59	-1
-16	60	81	-21
-18	44*	34	10
4 1			
0	246	224	21
1	46	48	-2
2	89	32	57
3	217	192	25
4	106	76	30
5	354	385	-31
6	150	120	30
7	153	119	34
8	208	223	-15
9	160	169	-10
10	-132	-120	-12
11	310	273	38
12	-56*	-15	-41
13	51*	86	-34
14	151	103	48
15	99	98	1
-1	289	253	36
-2	132	124	8
-3	264	252	12
-4	227	195	31
-5	-133	-113	-20
-6	34*	26	7
-7	252	299	-47
-8	-38*	-24	-14
-9	40*	31	9
-10	189	184	5
-11	154	129	25
-12	-46*	-12	-34
-13	124	80	44
-14	-117	-112	-6
-15	58*	64	-5
-16	-55*	-82	27
-17	102	31	71
-18	-45*	-12	-33
-19	36*	20	15
4 2			
0	426	420	6
1	427	444	-18
2	85	70	15
3	405	432	-26
4	472	472	1
5	204	173	31
6	373	394	-21
7	232	183	49
8	252	237	15
9	364	418	-54
10	117	94	23
11	140	103	37
12	217	185	32
13	122	19	103
14	87	102	-15
15	130	85	44
-1	-109	-90	-19
-2	249	350	-101
-3	-31*	-22	-9
-4	496	722	-226
-5	-217	-171	-46
-6	487	603	-116
-7	-230	-251	21
-8	203	219	-16
-9	41*	44	-3
-10	201	221	-20
-11	-487	-204	-283
-12	259	305	-46
-13	-67	-70	3
-14	132	144	-12
-15	-57*	-23	-34
-16	143	120	23
-17	97	58	39
-18	146	120	27
-19	-66	-55	-11
5 0			
0	342	302	40
2	150	137	12
4	488	524	-36
6	185	207	-22
8	488	452	36
10	399	436	-37
12	327	364	-37
14	137	169	-32
-2	108	136	-27
-4	89	85	5
-6	465	431	34
-8	121	99	22
-10	77	59	18
-12	229	300	-72
-14	337	333	4
-16	55*	29	26
-18	41*	29	12
5 1			
0	275	287	-12
1	264	289	-25
2	287	367	-80
3	195	200	-4
4	228	221	6
5	275	298	-23
6	131	156	-25
7	235	226	8
8	117	100	17
9	296	248	48
10	57*	6	51
11	242	195	48
12	-50*	-11	-39
13	145	151	-6
-1	266	303	-37
-2	383	456	-73
-3	165	181	-16
-4	161	130	31
-5	338	368	-30
-6	38*	29	9
-7	117	122	-5
-8	238	259	-21
-9	121	123	-3
-10	145	173	-28
-11	198	198	-1
-12	121	125	-4
-13	203	159	45
-14	190	159	30
-15	-57*	-31	-26
-16	152	130	22
-17	109	83	26
-18	42*	4	39
-19	34*	44	-11
5 2			
0	-38*	-3	-35
1	201	248	-47
2	181	150	31
3	207	230	-23
4	105	79	26
5	126	130	-4
6	122	105	17
7	142	143	-1
8	-83	-72	-11
9	174	153	22
10	56*	8	48
11	52*	65	-12
12	-48*	-20	-28
13	41*	36	6
14	32*	40	-8
-1	188	223	-35
-2	155	149	7
-3	-126	-122	-4
-4	132	95	37
-5	281	272	10
-6	223	222	1
-7	337	309	28
-8	182	191	-9
-9	115	96	20
-10	207	200	7
-11	93	68	25
-12	112	128	-16
-13	229	256	-27
-14	58*	23	35
-15	181	164	16
-16	188	144	43
-17	47*	33	14
-18	160	126	34
-19	85	69	16
6 0			
0	89	86	3
2	44	61	-17
4	308	329	-21
6	467	495	-28
8	58	58	0
10	229	259	-30
12	271	295	-23
-2	494	524	-30
-4	491	457	35
-6	890	788	103
-8	390	410	-20
-10	84	117	-33
-12	503	517	-14
-14	243	259	-15
-16	50*	63	-13
-18	38*	14	24
6 1			
0	51*	10	41
1	289	290	-1
2	223	156	68
3	273	312	-39
4	169	158	11
5	297	308	-11
6	-58*	-31	-27
7	226	194	32
8	-123	-83	-40
9	231	221	10
10	152	131	21
11	175	170	5
12	-40*	-42	2
13	31*	108	-76
-1	355	401	-46
-2	254	249	4
-3	346	326	20
-4	185	195	-9
-5	337	329	8
-6	157	105	52
-7	304	350	-46
-8	345	360	-15
-9	255	232	23

TABLE 4. (*Continued.*)

h k l	10F_o	10F_c	10ΔF
-10	114	136	-22
-11	257	236	21
-12	223	192	31
-13	227	188	39
-14	314	319	-6
-15	109	123	-13
-16	228	224	3
-17	65	84	-19
-18	55	69	-14
-19	69	81	-12
6 2			
0	335	343	-8
1	192	152	40
2	259	211	48
3	144	142	2
4	114	106	8
5	-47*	-17	-30
6	-48*	-30	-18
7	58*	7	51
8	114	98	16
9	54*	37	17
10	50*	48	2
11	-45*	-14	-31
12	-38*	-7	-31
13	-27*	-51	25
-1	84	46	38
-2	161	122	39
-3	137	66	71
-4	84	12	71
-5	157	97	60
-6	105	80	25
-7	270	256	14
-8	184	177	7
-9	126	101	26
-10	207	223	-17
-11	113	112	1
-12	103	103	0
-13	169	145	24
-14	113	86	26
-15	223	207	16
-16	170	122	48
-17	98	94	4
-18	169	143	26
-19	71	69	2
7 0			
0	219	258	-39
2	185	221	-36
4	319	365	-45
6	150	170	-21
8	52*	10	42
10	60	58	2
12	21*	75	-54
-2	400	417	-17
-4	680	727	-47
-6	491	502	-11
-8	334	416	-82
-10	440	444	-4
-12	323	345	-22
-14	67	123	-56
-16	89	108	-18
-18	133	158	-25
7 1			
0	-57*	-46	-10
1	190	199	-9
2	-146	-129	-17
3	248	275	-27
4	-58*	-12	-46
5	248	225	23
6	-152	-122	-30
7	131	130	1
8	52*	14	38
9	173	144	30
10	-42*	-17	-25
11	126	140	-14
-1	336	331	5
-2	-149	-119	-30
-3	261	238	23
-4	78	57	21
-5	318	308	11
-6	164	132	32
-7	357	367	-9
-8	-66	-32	-34
-9	227	227	-0
-10	58*	32	26
-11	262	225	38
-12	102	54	48
-13	241	224	17
-14	109	77	32
-15	150	140	10
-16	-47*	-31	-26
-17	123	113	9
-18	108	74	35
7 2			
0	174	158	16
1	-105	-119	14
2	142	128	13
3	-48*	-32	-16
4	95	103	-8
5	-163	-161	-2
6	113	92	20
7	-76	-70	-6
8	192	161	31
9	-46*	-4	-42
10	133	157	-24
11	-31*	-17	-14
-1	-209	-202	-7
-2	145	156	-11
-3	-293	-249	-44
-4	46*	19	27
-5	-192	-155	-37
-6	46*	30	16
-7	-47*	-24	-23
-8	47*	62	-15
-9	-48*	-18	-30
-10	48*	27	21
-11	-48*	-60	12
-12	141	107	34
-13	112	90	22
-14	131	105	26
-15	179	115	64
-16	109	85	25
-17	108	76	33
-18	29*	43	-14
8 0			
0	185	182	3
2	96	115	-19
4	65	94	-29
6	-50	-31	-19
8	41*	18	23
10	-25*	-22	-3
-2	133	170	-37
-4	169	163	5
-6	117	172	-55
-8	94	142	-48
-10	273	295	-23
-12	152	199	-47
-14	50	88	-38
-16	84	99	-15
-18	12	175	-163
8 1			
0	-245	-204	-40
1	117	117	1
2	-242	-204	-38
3	57*	69	-12
4	-216	-207	-9
5	76	64	12
6	-51*	-46	-5
7	47*	68	-21
8	-74	-84	11
9	87	34	53
-1	176	132	45
-2	-216	-182	-34
-3	132	128	3
-4	-304	-261	-42
-5	256	195	61
-6	-199	-163	-36
-7	252	230	22
-8	-242	-169	-73
-9	117	113	4
-10	-160	-160	1
-11	236	207	29
-12	-78	-66	-12
-13	195	170	26
-14	-206	-164	-42
-15	65	88	-23
-16	-166	-113	-54
-17	140	120	20
8 2			
0	48*	81	-33
1	-307	-229	-78
2	57*	70	-13
3	-200	-241	41
4	190	198	-8
5	-105	-105	-0
6	49*	165	-116
7	-165	-151	-14
8	118	104	15
9	-78	-63	-15
10	4*	138	-133
-1	-298	-324	26
-2	233	243	-9
-3	-270	-262	-9
-4	182	175	7
-5	-200	-208	8
-6	191	186	5
-7	-48*	-18	-30
-8	157	158	-0
-9	-142	-128	-14
-10	57*	33	24
-11	-112	-70	-42
-12	144	112	32
-13	132	75	57
-14	183	140	43
-15	44*	11	32
-16	75	55	20
-17	-29*	-43	14
9 0			
0	56*	10	46
2	-69	-53	-16
4	-86	-79	-7
6	-40*	-41	1
-2	86	121	-35
-4	56*	43	13
-6	56	57	-1
-8	56	80	-24
-10	84	114	-30
-12	195	193	2
-14	84	99	-15
-16	75	98	-23
9 1			
0	-56*	-51	-5
1	55*	17	38
2	-52*	-42	-11
3	50*	10	40
4	-48*	-29	-19
5	44*	52	-8
6	-39*	-6	-33
7	-32*	-15	-17
8	-20*	-12	-8
-1	113	90	23
-2	-99	-100	0
-3	82	148	-67
-4	-153	-151	-2
-5	57*	44	13
-6	-181	-139	-42
-7	114	94	20
-8	-137	-112	-25
-9	192	137	55
-10	-132	-96	-36
-11	127	91	36
-12	-122	-96	-25
-13	88	92	-4
-14	-120	-93	-26
-15	74	76	-2
-16	-123	-105	-18
9 2			
0	224	176	49
1	-183	-146	-37
2	170	138	32
3	-49*	-10	-40
4	232	219	14
5	-41*	-56	14
6	143	157	-14
7	-29*	-73	44
-1	-214	-142	-73
-2	231	186	45
-3	-56	-28	-28
-4	209	128	80
-5	183	98	85
-6	267	214	53
-7	-112	-121	9
-8	210	170	40
-9	-202	-48	-154
-10	52*	75	-23
-11	-50*	-12	-38
-12	48*	72	-24
-13	-45*	-29	-16
-14	89	71	19
-15	-126	-103	-23
-16	25*	29	-4
10 0			
0	46*	22	24
2	41*	42	-0
4	73	77	-5
-2	144	181	-37
-4	183	171	12
-6	56	36	20
-8	-50	-13	-37
-10	46*	34	12
-12	-40*	-5	-35
-14	-29	-14	-15
10 1			
0	124	32	92
1	45*	19	26
2	41*	73	-32
3	80	86	-6
4	32*	29	3
5	58	60	-2
-1	128	114	15
-2	-49*	-51	2
-3	101	79	21
-4	51*	21	31
-5	51*	47	4
-6	50*	8	42
-7	50*	36	14
-8	-105	-51	-54
-9	95	72	23
-10	-97	-53	-44
-11	44*	29	14
10 2			
0	183	142	41
1	42*	36	7
2	130	116	14
3	115	91	24
4	98	78	21
-1	46*	14	32
-2	117	79	38
-3	162	113	49
-4	49*	43	7
-5	121	94	26
-6	130	111	18
-7	-48*	-15	-33
-8	157	164	-6
-9	-46*	-58	12
-10	116	108	8
-11	101	17	84
-12	130	129	0
-13	-98	-65	-33
-14	61	72	-11
11 0			
0	58	100	-42
-2	98	120	-22
-4	38*	28	10
-6	-65	-49	-16
-8	38*	32	6
-10	-67	-81	14
-12	-63	-84	21
11 1			
0	30*	49	-19
1	48	81	-33
-1	82	71	11
-2	71	98	-26
-3	37*	60	-23
-4	163	154	9
-5	39*	47	-8
-6	87	90	-2
-7	102	74	28
-8	74	90	-16
-9	99	10	89
-10	32*	87	-55
-11	28*	35	-7
-12	83	41	42
11 2			
0	83	83	-1
-1	67	91	-24
-2	98	94	4
-3	92	119	-27
-4	71	93	-22
-5	125	66	59
-6	114	124	-10
-7	112	88	23
-8	83	108	-26
-9	112	60	51
-10	89	142	-53
-11	87	35	52

Unobserved reflections are given the minimum observable value in the region; these are marked by an asterisk.

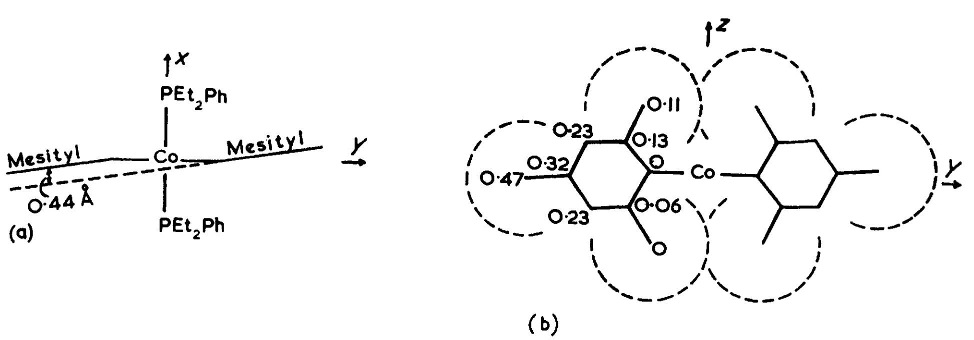

FIG. 2. The molecule viewed down the z- and the x-axis, showing the distortions from ideal symmetry caused by steric hindrance, and the o-methyl groups in contact above and below the cobalt atom. The distances in Å of the carbon atoms from the yz-plane are also shown.

and J. M. R.), $P2_1/c$ isotropic structure factors with least squares, and general Fourier syntheses (O. S. Mills) and distance–angle routine (R. A. Sparks).

Results.—The molecule is illustrated in Fig. 1 and its dimensions are listed in Table 2.* It has, in outline, the expected stereochemical arrangement, but with some significant differences in detail. The co-ordination of the cobalt atom is exactly square-planar, the mesityl groups are planar and perpendicular to the cobalt co-ordination plane, and the *o*-methyl substituents in the two mesityl groups are in contact with each other above and below the co-ordination plane. The steric hindrance of the ligands, however, affects the configuration at the equivalent atoms C(1) and C(1′): the two mesityl groups are thus not coplanar and the cobalt atom lies 0·22 Å from each mesityl plane (Fig. 2a). The mesityl groups are also not mirror-symmetrical about the co-ordination plane (Fig. 2b). Significantly, these distortions leave the two *o*-methyl groups C(7) and C(9′) 4·03 Å apart, a normal distance for methyl groups in unstrained contact, in sharp contrast with the unusually short contact distances found elsewhere in the molecule (Table 3). The cobalt–*o*-methyl distances are 3·19 Å [Co–C(7)] and 3·35 Å [Co–C(9)].

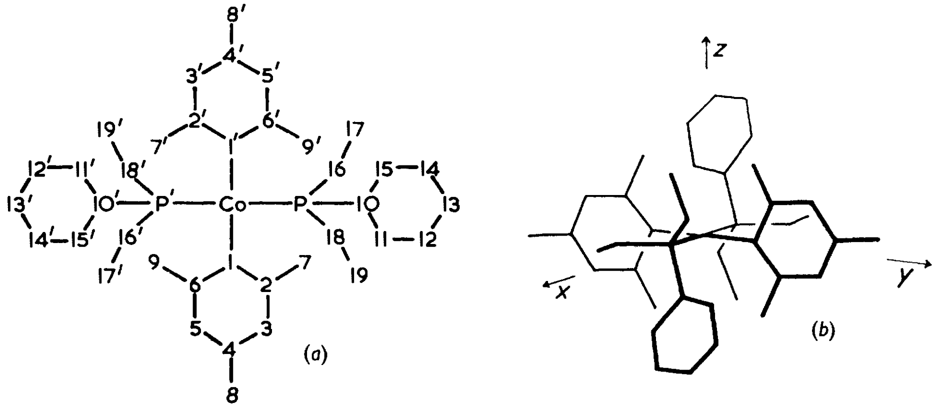

FIG. 1. The molecule as numbered and as viewed in clinographic projection.

The phosphine groups shows distortion of the tetrahedral angles at the phosphorus atom. The metal–phosphorus–carbon angles (mean 116·4°) are all significantly greater than the carbon–phosphorus–carbon angles (mean 101·6°), and the hydrocarbon groups thus project away from the metal atom more than in the ideal tetrahedral arrangement. The phenyl group is planar within the limits of error, and the phosphorus atom lies in this plane; the phosphorus–carbon and carbon–carbon bond lengths in the phosphine group are normal.

DISCUSSION

The cobalt–phosphorus bonds of 2·23 Å are short compared with the radius sum [2·4 Å if the cobalt(II) ion is assumed to have the normal octahedral radius of 1·3 Å and the phosphorus atom to have the tetrahedral radius of 1·10 Å]; they therefore have considerable double-bond character, presumably from d_π–d_π overlap (cf. Fig. 3). The bond-lengths are very similar to the platinum–phosphorus bond-lengths of 2·26 Å in *trans*-$[PtHBr(PEt_3)_2]$.[5]

The radius sum for a cobalt–carbon single bond is 2·0 Å, as found in the vitamin B_{12} co-enzyme[6] (2·05 ± 0·05 Å), and in the cobalt–acetylene carbon bond (1·96 Å) in the π-complex hexacarbonyldiphenylacetylenedicobalt.[7] The cobalt–carbon bond length

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* The relations between the molecular co-ordinates X, Y, Z and the unit cell co-ordinates x, y, z are: $X = 0{\cdot}7393x + 0{\cdot}6685y - 0{\cdot}1323z$: $Y = -0{\cdot}6407x + 0{\cdot}6623y + 0{\cdot}5533z$; $Z = -0{\cdot}2066x + 0{\cdot}3379y - 0{\cdot}8225z$.

[5] Owston, Partridge, and Rowe, *Acta Cryst.*, 1960, **13**, 246.

[6] Lenhert and Hodgkin, *Nature*, 1961, **192**, 937.

[7] Sly, *J. Amer. Chem. Soc.*, 1959, **81**, 18.

of 1·96 Å therefore indicates that the Co–C(1) bond is single; since the cobalt atom is not co-planar with the mesityl group there can be little d_{xy}–$p\pi$-bond formation between the cobalt atom and the mesityl group. The shorter Co–C(1) distance required for π-bond formation could be achieved only by greater distortion at C(1) and a further displacement of the mesityl groups. These groups remain rigidly planar and undistorted and the methyl groups resist any tendency to be forced closer together. In this respect the *ortho*-substituents tend to reduce rather than to increase the stability of the complex.

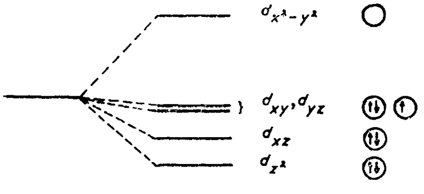

FIG. 3.

Two essential requirements for the stability of alkyl and aryl complexes of Group VIII metals are known to be a square-planar configuration, and the presence of ligands of high field-strength, thus ensuring a large ligand-field stabilisation energy.[1,2,8] These two factors are always present in platinum and palladium complexes of the type $[MR_2(PR'_3)_2]$ which are normally square-planar and therefore stable whatever the nature of R. In four-co-ordinated complexes of nickel, cobalt, and iron, which more readily adopt a tetrahedral configuration, steric hindrance is needed to maintain a square-planar configuration in the compound we have studied the steric hindrance has two components; the aryl groups are restricted to the yz-plane by the bulky phosphine groups; and they are prevented from rotating relative to each other round the P–Co–P axis by the mutual interaction of the *ortho*-substituents.

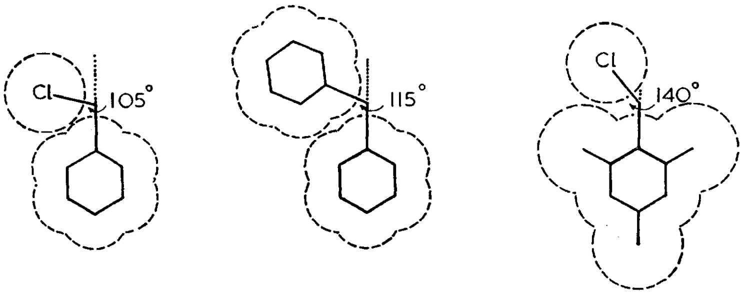

FIG. 4. Scale drawings showing the mutual interaction of the R and X groups in square-planar complexes $[MR_2(PR'_3)_2]$ and $[MRX(PR'_3)_2]$. The R and X groups are approximately coplanar because of the steric hindrance from the phosphine ligands, and the stability of the square-planar configuration is related to the minimum R–M–R or R–M–X angle.

The extent of this mutual interaction can be estimated from scale drawings, as illustrated in Fig. 4 for various complexes; the minimum possible R–M–R or R–M–X angle is shown, and indicates the difficulty with which the tetrahedral configuration could be attained. Thus nickel complexes in which the angle is less than 120° either cannot be isolated or are unstable. In cobalt and iron complexes the planar configuration is so unstable that it exists only when the two R groups are firmly held in opposition with their *ortho*-groups in contact and R–M–R = 180° (Fig. 2b).

It is thus possible to explain the relative stabilities of the complexes $[MR_2(PR'_3)_2]$

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[8] Chatt, *Proc. Chem. Soc.*, 1962, 318.

mainly on stereochemical grounds. The shielding of the z-direction from attack by reagents, which has a major effect on their chemical reactivity in solution,[9] is a further consequence of the close contact of the *ortho*-groups. The stabilisation of the non-bonding d_{xy}-orbital by metal–aryl π-bonding, an effect which was previously thought to be general and of crucial importance, does not occur at all in this compound and will evidently have only a minor effect on stability.

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[*Received, July 5th*, 1962.]

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[9] Basolo, Chatt, Gray, Pearson, and Shaw, *J.*, 1961, 2207.