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## The Crystal and Molecular Structure of Dichlorotris(tetrahydrofuran)p-tolylchromium(III)

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The structure of dichlorotris(tetrahydrofuran)-p-tolylchromium(III), pCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CrCl<sub>2</sub>,3THF, has been determined by single crystal X-ray diffraction methods. The crystals are orthorhomic, space group Pbca with a = 10.396, b = 18.447 and c = 22.396 Å. The chromium is octahedrally co-ordinated with two chlorine ligands *trans* and two tetrahydrofuran ligands trans: the p-tolyl group, which is sigma-bonded to the chromium (Cr-C =  $2.014 \pm$ 0.010 Å), is trans to the third tetrahydrofuran ligand. The Cr-O bonds which are trans to one another are essentially equal and are normal in length ( $2.045 \pm 0.008$  Å). However, the Cr–O bond to the tetrahydrofuran group trans to the p-tolyl group is much longer  $(2.214 \pm 0.007 \text{ Å})$  than the other two.

SOLVATED organochromium compounds of the general type  $R_n CrCl_{3-n}S_x$  (where n = 1-3, R = alkyl, aryl, aralkyl, and allyl, and S = tetrahydrofuran or pyridine)are readily accessible by the interaction of the appropriate stoicheiometric ratios of the organomagnesium halides and CrCl<sub>3</sub>,3THF in tetrahydrofuran.<sup>1,2</sup> In many instances the solvated organochromium compound is a relatively stable crystalline material. However, despite the fact that most of their chemical reactions

<sup>1</sup> H. Zeiss, "Organometallic Chemistry," Reinhold, New York, 1960, p. 380.

are consistent with their formulation as sigma-bonded organochromium complexes, no X-ray structural work has been carried out until now.

The present Paper describes the determination of the structure<sup>3</sup> of p-MeC<sub>6</sub>H<sub>5</sub>CrCl<sub>2</sub>,3THF by single crystal X-ray diffraction methods. The compound was prepared from p-MeC<sub>6</sub>H<sub>4</sub>MgCl and CrCl<sub>3</sub>,3THF and it has a magnetic moment of 3.87 B.M. It is readily hydrolysed

<sup>2</sup> H. H. Zeiss and R. P. A. Sneeden, Angew. Chem., in the

press. <sup>3</sup> J. J. Daly, R. P. A. Sneeden, and H. H. Zeiss, J. Amer. Chem. Soc., 1966, 88, 4287.

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(giving toluene) and reacts with mercuric chloride (giving p-tolylmercuric chloride).

### EXPERIMENTAL

Crystal Data.—C<sub>19</sub>H<sub>31</sub>Cl<sub>2</sub>CrO<sub>3</sub>,  $M = 430 \cdot 4$ . Orthorhombic,  $a = 10 \cdot 396 \pm 0 \cdot 012$ ,  $b = 18 \cdot 447 \pm 0 \cdot 022$ ,  $c = 22 \cdot 396 \pm 0 \cdot 028$  Å,  $U = 4295 \cdot 0$  Å<sup>3</sup>,  $D_{\rm m} = 1 \cdot 315$ , Z = 8,  $D_c = 1 \cdot 331$ . Space group Pbca ( $D_{2h}^{15}$  No. 61). MoK<sub> $\alpha$ </sub>

radiation,  $\lambda = 0.71069$  Å. The cell dimensions were obtained from precession photographs.

The pale green plate-like crystals have the b axis perpendicular to the plate while the short a and long c axes are the plate diagonals. The crystals are unstable to the atmosphere and were sealed in Lindemann glass capillaries under a stream of argon. Eventually, a crystal was placed with axis a parallel to the capillary and the intensities produced from it were measured. A Hilger and Watts linear



FIGURE 1 The labelling of the atoms in the [a]-axis projection of the molecule



FIGURE 2 The unit cell contents projected down [a]

	The <i>R</i> -factor a	as a function	of the layer inde	ex and the mag	nitude of $ F_{o} $	
h		$\Sigma  F_{o} $	$\Sigma  F_{\rm c} $	$\Sigma[\Delta]$	No. planes	R
0		9551.72	8988.65	1045.65	$\overline{204}$	0.109
1		11,830.63	11,458.48	1220.41	348	0.103
<b>2</b>		11,843.48	11,915.98	1344.94	360	0.114
3		10,191.38	$9803 \cdot 34$	1180.74	332	0.116
4		9492-29	$8808 \cdot 52$	1066.75	320	0.112
5		$6667 \cdot 80$	6330.36	818.72	257	0.123
6		$6147 \cdot 47$	5977.86	865.01	249	0.141
7		$4913 \cdot 88$	$4481 \cdot 84$	807.14	214	0.164
8		$4136 \cdot 80$	$3624 \cdot 99$	715.89	187	0.173
9		2286.39	$2053 \cdot 16$	505.25	125	0.221
10		1214.91	$1131 \cdot 19$	303.06	65	0.249
A11		78,276.75	74,574·37	$9873 \cdot 56$	2661	0.126
$9.00 <  F_0  \leq$	18.00	$1473 \cdot 73$	$1227 \cdot 95$	$531 \cdot 14$	192	0.360
$18.00 <  F_0  \leq$	27.00	$14,127 \cdot 28$	$11,937 \cdot 24$	3989.94	1068	0.282
$27.00 <  F_0  \leq$	36.00	$12,279 \cdot 26$	$11,985 \cdot 24$	1611.30	555	0.131
$36.00 <  F_0  \leq$	45.00	8240.50	8214.50	887.18	264	0.108
$45.00 <  F_0  \leq$	450.00	42,055.98	41,209.44	2854.00	582	0.068

TABLE 1

TABLE 2

Atomic co-ordinates (in Å) with their standard deviations as units in the last place

	X	Y	Ζ
Cr	2.0674(16)	4.6347(15)	$2 \cdot 8039(14)$
Cl(1)	2.3574(30)	5.5409(28)	4.9059(23)
Cl(2)	1.8356(28)	3.8267(27)	0.6296(23)
O(1)	0.3142(72)	5.6689(64)	2.6138(60)
C(12)	-0.6821 (117)	5.7837(124)	3.6603(117)
C(13)	-1.7287 (168)	6.7904(176)	3.1069(146)
C(14)	-1.1509(155)	7.3057(119)	1.8339(120)
C(15)	-0.1930 (128)	$6 \cdot 2157 (124)$	1.3555(123)
O(2)	3.9243 (80)	3.7807(74)	2.8991(66)
C(8)	$4 \cdot 2569 (136)$	$2 \cdot 4564 (129)$	2.3109(145)
C(9)	5.7189 (164)	$2 \cdot 3043$ (166)	$2 \cdot 5564$ (161)
C(10)	$6 \cdot 2906 (112)$	3.6061 (132)	3.0668(144)
C(11)	5.0201 (116)	$4 \cdot 2784 (139)$	3.6720(149)
O(3)	3.0361(72)	6.4398(65)	1.9638(70)
C(16)	3.8873 (168)	$6 \cdot 4229$ (126)	0.8101(141)
C(17)	$4 \cdot 3436 (235)$	$7 \cdot 8246 \ (136)$	0.6285(189)
C(18)	$3 \cdot 3291 (193)$	$8 \cdot 6229$ (135)	1.3675(177)
C(19)	2.9163(133)	7.7605(106)	2.5456(133)

XYΖ  $\begin{array}{c} X \\ 1 \cdot 1830 \ (93) \\ 1 \cdot 7234 \ (109) \\ 1 \cdot 1581 \ (129) \\ - 0 \cdot 0622 \ (126) \\ - 0 \cdot 6674 \ (127) \\ - 0 \cdot 0876 \ (118) \\ - 0 \cdot 6944 \ (169) \end{array}$  $\begin{array}{c} Y\\ 2\cdot 9831 \ (97)\\ 2\cdot 2460 \ (97)\\ 1\cdot 0960 \ (119)\\ 0\cdot 6816 \ (114)\\ 1\cdot 3534 \ (94)\\ 2\cdot 5051 \ (104)\\ -0\cdot 6164 \ (144) \end{array}$  $\begin{array}{c} C(1) \ \dots \\ C(2) \ \dots \\ C(3) \ \dots \end{array}$ 3.5430 (97) 3.6430 (37) 4.6110 (102) 5.1110 (126) 4.6411 (129) 3.6091 (117) 3.0902 (111)C(4) ..... C(5) ..... C(6) ..... C(7) ..... 5.1980 (169)

TABLE 3

Thermal parameters (in Å<sup>2</sup>) with their standard deviations as units in the last place

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011	$U_{22}$	$U_{33}$	$2U_{12}$	$2{U_{23}}$	$2U_{13}$
0.0485(9)	0.0436 (8)	0.0390 (8)	-0.0097 (15)	-0.0059(12)	0.0002 (13)
0.0680(18)	0.0638(16)	0.0445(12)	-0.0040 (28)	-0.0227 (23)	-0.0085(23)
0.0645(17)	0.0640(15)	0.0405(12)	-0.0027 (27)	-0.0187(22)	-0.0062(23)
0.0610(44)	0.0485 (37)	0.0464(34)	0.0055(68)	0.0063(56)	0.0151(65)
0.0547 (68)	0.0863(82)	0.0673(68)	0.0434(124)	0.0070(124)	0.0165(113)
0.1086(121)	0.1239(131)	0.0835 (90)	0.0921(211)	0.0718 (178)	0.0622 (171)
0.1145(116)	0.0602(70)	0.0733 (76)	0.0653(156)	0.0127(121)	-0.0099(152)
0.0675(81)	0.0784(80)	0.0749(72)	0.0350(138)	0.0167(127)	-0.0381(129)
0.0683(51)	0.0612(46)	0.0615(44)	-0.0209 (83)	-0.0277 (68)	0.0012 (73)
0.0755 (86)	0.0680(76)	0.1068 (94)	0.0274(137)	-0.0646(146)	0.0081(157)
0.0974(114)	0.1076(119)	0.1138(113)	0.0609(192)	-0.0639(186)	-0.0709(185)
0.0324(61)	0.0849(89)	0.1246(110)	0.0168(121)	-0.0224 (155)	-0.0109(129)
0.0384 (64)	0.1058(102)	0.1176(108)	-0.0270(130)	-0.0783(174)	-0.0630(139)
0.0605(47)	0.0451(37)	0.0692(44)	-0.0172(68)	-0.0099(67)	0.0403 (72)
0.1382 (129)	0.0661 (77)	0.0995 (95)	-0.0324 (168)	-0.0363(140)	0.1617(193)
0.2185(216)	0.0550 (82)	0.1545 (153)	-0.0745(219)	-0.0257 (178)	0.2067(310)
0.1467 (160)	0.0591 (82)	0.1358(131)	-0.0058 (181)	0.0166 (167)	0.0883(236)
0.0850 (92)	0.0396 (56)	0.1022 (89)	-0.0268 (117)	-0.0333 (116)	0.0647(147)
0.0318 (49)	0.0581 (59)	0.0572 (56)	-0.0094(92)	-0.0014 (95)	0.0196 (87)
0.0588 (67)	0.0465 (55)	0.0567(57)	-0.0055 (103)	0.0058 (89)	0.0041(103)
0.0652 (81)	0.0624 (68)	0.0936 (85)	0.0217(124)	0.0209(123)	0.0069(133)
0.0667 (79)	0.0590 (66)	0.0957 (86)	-0.0192 (126)	0.0172(122)	0.0416 (143)
0.0808(81)	0.0354 (50)	0.0771 (71)	-0.0013 (106)	0.0128(100)	0.0134(127)
0.0591 (69)	0.0512 (60)	0.0744(71)	0.0085(108)	0.0050(103)	-0.0202(112)
0.1009(118)	0.0808 (95)	0.1433(137)	-0.0473 (171)	0.0888 (185)	-0.0002 (204)
	$U_{11}$ 0.0485 (9) 0.0680 (18) 0.0645 (17) 0.0610 (44) 0.0547 (68) 0.1086 (121) 0.0675 (81) 0.0675 (81) 0.0755 (86) 0.0974 (114) 0.0324 (61) 0.0324 (61) 0.0384 (64) 0.0605 (47) 0.1382 (129) 0.2185 (216) 0.1467 (160) 0.0550 (92) 0.0318 (49) 0.0588 (67) 0.0667 (79) 0.0890 (81) 0.0591 (69) 0.1009 (118)	$\begin{array}{cccc} U_{11} & U_{22} \\ 0.0485 & (9) & 0.0436 & (8) \\ 0.0680 & (18) & 0.0638 & (16) \\ 0.0645 & (17) & 0.0640 & (15) \\ 0.0645 & (17) & 0.0640 & (15) \\ 0.0547 & (68) & 0.0863 & (82) \\ 0.1086 & (121) & 0.1239 & (131) \\ 0.1145 & (116) & 0.0602 & (70) \\ 0.0675 & (81) & 0.0784 & (80) \\ 0.0683 & (51) & 0.0612 & (46) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (86) & 0.0680 & (76) \\ 0.0755 & (81) & 0.0651 & (37) \\ 0.0384 & (64) & 0.1058 & (102) \\ 0.0665 & (47) & 0.0451 & (37) \\ 0.2185 & (216) & 0.0550 & (82) \\ 0.1467 & (160) & 0.0591 & (82) \\ 0.0388 & (67) & 0.0465 & (55) \\ 0.0652 & (81) & 0.0624 & (68) \\ 0.0667 & (79) & 0.0590 & (66) \\ 0.0808 & (81) & 0.0354 & (50) \\ 0.0591 & (69) & 0.0512 & (60) \\ 0.1009 & (118) & 0.0808 & (95) \\ \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

diffractometer <sup>4</sup> equipped with balanced filters was used to measure the diffracted intensities up to a  $\theta$  value of about 26°. 2661 Intensities were accepted as having a significant value and the analysis was carried out with them. No correction was made for absorption ( $\mu = 8.15$  cm.<sup>-1</sup> for MoK<sub> $\alpha$ </sub> radiation).

Determination of the Structure and Refinement.—The positions of the chromium atom and the two chlorine atoms were found from a three-dimensional sharpened Patterson function. At this stage the co-ordinates were Cr at x, 1/4, 1/8; Cl(1) at  $x_{Cr}$ ,  $y_1$ ,  $z_1$ ; Cl(2) at  $x_{Cr}$ ,  $y_2$ ,  $z_2$ . The chlorines were trans to one another and a Fourier map based on the phases of these heavy atoms exhibited false symmetry. Thus there were two sets of four light atoms around the chromium atom instead of one. One set was chosen and the electron density recalculated; from this map the remaining light atoms were successfully located. The structure was then refined by the least-squares block diagonal method. The temperature factors were anisotropic and in the form

$$\begin{split} \exp &- 2\pi^2 (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + \\ & 2hka^* b^* U_{12} + 2klb^* c^* U_{23} + 2hla^* c^* U_{13}) \end{split}$$

the atomic scattering factors were taken from International Tables.<sup>5</sup> The weighting scheme was

$$W = 1/(6.35 + |F_{\rm o}| + 0.0016|F_{\rm o}|^2)$$

and has been described by Cruickshank.<sup>6</sup> The final value of R(2661 planes) was 0.126 and R'(2509 planes) was 0.0259. The calculations were carried out on an Elliott 803B computer with programmes written by Daly *et al.*? The agreement between observed and calculated structure factors is analysed in Table 1 where R is given as a function of the layer index and then of the magnitude of  $|F_0|$ . The increase of R with h in Table 1 is due partly to geometrical factors and partly to the decrease of the average value of  $|F_0|$ . The R factor for planes with l odd (which have no contribution from the chromium atom) is 0.148.

### RESULTS AND DISCUSSION

The atomic parameters and their standard deviations are given in Tables 2 and 3. The bond lengths and angles with their standard deviations are in Table 4. Figure 1 shows the labelling of the atoms and is the projection of the molecule down a. The unit cell contents projected down a are shown in Figure 2. There are three isomers of octahedral compounds of the type  $MA_3B_2C$  and the analysis shows that the p-MeC<sub>6</sub>H<sub>4</sub>CrCl<sub>2</sub>,3THF molecule has the configuration (I). If no rearrangement occurs, then the compound is



derived from a *trans*-CrCl<sub>3</sub>,**3**THF. Although the molecule is not required to have any symmetry by the spacegroup data, it does approach the symmetry 2  $(C_2)$  with the axis passing through the methyl group, the chromium atom and O(3); there are significant departures from this symmetry. In the solid state the ligands adopt an orientation such that the molecule may exist in d and l forms and so, since the space-group contains symmetry centres and glide planes, there

### TABLE 4

# Bond lengths (in Å) and angles (in degrees) with their standard deviations

Cr-Cl(1)	2.307(3)	O(3)-C(16)		1.434 (16)
Cr-Cl(2)	2.331(3)	O(3) - C(19)		1.448(14)
Cr - O(1)	2.044(7)	C(16) - C(17)	)	1.485(24)
Cr-O(2)	2.046(8)	C(17)-C(18	ý <b></b>	1.488 (26)
Cr - O(3)	$2 \cdot 214(7)$	C(18)C(19	ý	1.517 (21)
Cr - C(1)	2.014(10)		,	
01 0(1)	= 011 (10)	C(1) - C(2)	•••••	1.406(14)
O(1)-C(12)	$1 \cdot 450 (14)$	C(2) - C(3)	•••••	1.376(16)
$O(1) - C(15) \dots$	1.463(14)	C(3) - C(4)		1.372(18)
C(12)-C(13)	1.554(20)	C(4) - C(5)		1.372(17)
$C(13) - C(14) \dots$	1.490(21)	C(5) - C(6)		1.390(16)
$C(14) - C(15) \dots$	1.528(18)	C(6) - C(1)		1.431(15)
O(22) = C(8)	1.497 (16)	C(4) = C(7)		1.548 (90)
$O(2) = O(0) \dots \dots$	1.490 (10)	C(4) = C(1)		1.940 (20)
$C(2) = C(11) \dots$	1.400 (10)	Mean C–C	(benzenoid	) 1·391 Å
$C(8) - C(9) \dots \dots$	1.490(21)	Mean C-C	(in THF)	.́. 1∙514 Å
$C(9) = C(10) \dots$	1.511(21)	Mean C-O	、	. 1·452 Å
C(10)-C(11)	1.560(19)			
$C_{1}(1) - C_{1}(2)$	176.71(12)	Cr-O(1)-O(1)	C(12)	$124 \cdot 22 \ (62)$
O(1) = Cr = O(2)	172.50 (20)	O(1)-C(12)	-C(13) 1	104.90(98)
O(1) - O(2)	170.00 (20)	C(12) - C(1)	3)-C(14)	$105 \cdot 49 (119)$
C(1) - Cr - O(3)	. 179.23 (34)	C(13) - C(1)	4) - C(15) = 1	105.30(112)
Cl(1)-Cr-O(1)	. 89.65 (20)	C(14) - C(1)	5(-O(1))	102·40 (93)
Cl(1) - Cr - O(2)	90.43 (22)	$\tilde{C}(15) = \tilde{O}(1$	-C(12)	110.68 (80)
$C_1(1) = C_r = O(3)$	88.31 (20)	C(15) - O(1)	$) \sim Cr$	124.50 (63)
Cl(2) = Cr = O(1)	<u>00.10</u> (20)	0(10) 0(1	) 01	12100 (00)
$C_1(2) = C_{\pi} = O(2)$	. 00.10 (20)	Cr-O(2)-O(2)	C(8) I	$123 \cdot 81 (68)$
C1(2) = C1 = O(2)	. 09.37 (22)	O(2) - C(8)	-C(9) 1	104·19 (108)
CI(2) = CI = O(3)	. 88.41 (20)	C(8) - C(9)	-C(10) ]	109.81(125)
CI(I) - Cr - C(I)	. 92.40 (29)	C(9)-C(10	)Ċ(11) 1	101·20 (109)
CI(2) - Cr - C(1)	.90.82(29)	$\dot{C}(10) - \dot{C}(1)$	$1) - \dot{O}(2)$	105-33 (100
O(1) - Cr - O(3)	. 85.84(26)	$-\tilde{c}(\tilde{u}) - \tilde{o}(\tilde{v})$	-C(8)	110-63 (89)
O(2)-Cr- $O(3)$	. 87.76 (28)	-C(11) - O(2)	-Cr	125.11(70)
O(1)-Cr-C(1)	. 94.15(33)	0(11) 0(2	) CI	20 11 (10)
O(2) - Cr - C(1)	$. 92 \cdot 24 (35)$	Cr-C(1)-C	C(2) 1	122.68(72)
$C_{T-O}(3) = C(16)$	199.74 (71)	C(1) - C(2)-	-C(3) I	123.82 (99)
O(2) = O(16) = O(17)	105.64 (12)	C(2) - C(3)	C(4) I	119·58 (112)
C(10) = C(10) = C(11)	100.04(121)	( C(3)C(4)-	-C(5) I	120.14 (114)
C(10) - C(17) - C(18)	5) 103.00(144)	C(4) - C(5)	-C(6) 1	120.17(107)
C(17) = C(18) = C(19)	(105.44(130))	2 C(5)−C(6)-	-C(1) 1	121.94 (99)
C(18) - C(19) - O(3)	100.60(102)	C(6) - C(1) -	-C(2) 1	113.99 (89)
C(19) - O(3) - C(16)	) $112.53$ (89)	C(6) - C(1)-	-Cr 1	23.21 (73)
C(19) - O(3) - Cr	. 123.70 (64)	C(3) - C(4)	-C(7)	19.57 (115)
Mean C-C-C/ben	zenoid) 110.0	C(5) - C(4)	-C(7) 1	20.08 (113)
Moon $C = C = C / T$	IE = 105.9	$C(0) C(4)^{-}$	C(1) J	20.00 (119)
Mean C-O-C	117 100.2			
Mean $C = O = C$	111.3			
Mean O - C - C	103.8			

are equal numbers of these d and l forms in the unit cell; they can be seen in Figure 2.

The Cr–Cl(1) bond  $(2\cdot307 \pm 0.003$  Å) is significantly shorter than the Cr–Cl(2) bond  $(2\cdot331 \pm 0.003$  Å); these lengths may be compared with the Cr–Cl length in [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl,2H<sub>2</sub>O where <sup>8</sup> it is  $2\cdot286 \pm 0.001$  Å. The chromium–carbon length found was  $2\cdot014 \pm 0.010$ 

<sup>6</sup> D. W. J. Cruickshank, D. E. Pilling, and (in part) A. Bujosa, F. M. Lovell, and M. R. Truter, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, 1962, p. 32.

<sup>7</sup> J. J. Daly, F. S. Stephens, and P. J. Wheatley, unpublished work.

<sup>8</sup> B. Morosin, Acta Cryst., 1966, 21, 280.

 <sup>&</sup>lt;sup>4</sup> U. W. Arndt and D. C. Phillips, Acta Cryst., 1961, 14, 807.
 <sup>5</sup> "International Tables for X-Ray Crystallography," vol. III, Kynoch Press, Birmingham, 1962.

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Å; no other chromium-carbon sigma bond lengths are available for comparison (but the Co-C sigma bond in trans square planar [Co(mesityl), (PEt, Ph),] was 91.961 + 0.012 Å). Chromium-carbon bonds in carbonyls <sup>10-14</sup> are shorter than that reported here; for example in  $Cr(C_{e}H_{e})(CO)_{3}$  the chromium-carbonyl length <sup>14</sup> is 1.84 Å. The shortening is presumably due to back donation of electrons from the carbonyl group. The Cr-O(1) and Cr-O(2) lengths are essentially equal (average 2.045 + 0.008 Å) and are slightly longer than those found in other octahedral complexes,4,15-19 values of 2.002 and 2.013 + 0.003 Å have been reported <sup>4</sup> for Cr-O in  $[Cr(H_2O)_4Cl_2]Cl_2H_2O$ . However, the Cr-O(3)bond, which is *trans* to the p-tolyl group, is  $2 \cdot 214 +$ 0.007 Å long and this is 21  $\sigma$  more than the other Cr-O bonds.

Other departures from octahedral co-ordination are illustrated by the bond angles in Table 4; thus the angles which should be 90° vary from 85.8 to 94.1° and the O(1)-Cr-O(2) angle is 173.6 instead of 180°.

The atoms in the ring of the p-tolyl group all lie within three standard deviations of a plane equilateral hexagon of side 1.391 Å. The equation of the least squares plane through the six atoms is

### -0.4783X + 0.5652Y + 0.6722Z = 3.5211

The distances of C(7) (the methyl group) and chromium from this plane are 0.043 and 0.006 Å, respectively. The C(4)-C(7) length is somewhat longer than the standard <sup>20</sup> length (1.505 Å). The largest angular distortion (from 120°) in the ring is the C(6)-C(1)-C(2) angle which is  $114.0^{\circ} \pm 1.0^{\circ}$ ; this angle is at the carbon atom which is attached to chromium. It is interesting to note that the largest angular distortion in the mesityl ring in Co(mesityl)<sub>2</sub>(PEt<sub>2</sub>Ph)<sub>2</sub> is at the carbon atom attached to Co; the measured value <sup>9</sup> is  $112 \cdot 1^{\circ} \pm 1 \cdot 0^{\circ}$ .

The three tetrahydrofuran rings are not planar; distortion in the O(2) ring can be seen in Figure 1. The dihedral angles in these rings vary from  $0.4^{\circ}$  to  $33.9^{\circ}$  (Table 5) and have an average value of  $21.2^{\circ}$ . The buckling is associated with the low average value of the ring valence angles [105.8 for the O(1) ring, 106.2]for the O(2) ring and  $105 \cdot 6^{\circ}$  for the O(3) ring] and the rings would be planar if the average valence angles were  $108^{\circ}$  since the sum of the angles in the pentagons would

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then be  $3\pi$ . The carbon-carbon bond lengths in the tetrahydrofuran rings have an average value of 1.514 Å. this is somewhat less than the normal single bond length<sup>20</sup> (1.537 Å). On the other hand all the C-O lengths

#### TABLE 5

### Dihedral angles in the tetrahydrofuran rings in

degrees

$\begin{array}{l} D(1)-C(12)-C(13)-C(14)\\ C(12)-C(13)-C(14)-C(15)\\ C(13)-C(14)-C(15)-O(1)\\ C(14)-C(15)-O(1)-C(12)\\ C(14)-C(15)-O(1)-C(12)\\ C(15)-O(1)-C(12)-C(13)\\ \end{array}$	6.81 24.87 33.37 30.24 15.12	$\begin{array}{c} O(3)-C(16)-C(17)-C(18)\\ C(16)-C(17)-C(18)-C(19)\\ C(17)-C(18)-C(19)-O(3)\\ C(18)-C(19)-O(3)-C(16)\\ C(19)-O(3)-C(16)-C(16)\\ C(19)-O(3)-C(16)-C(16)\\ \end{array}$	$20.81 \\ 33.85 \\ 33.02 \\ 20.57 \\ 0.40$
$\begin{array}{l} (10) & (11) & (12) & (13) \\ (2) & (2) & (2) & (2) \\ (2) & (2) & (2) \\ (2) & (2) & (2) \\ (2) & (2) & (2) \\ (2) & (2) & (2) \\ (2) & (2) & (2) \\ ($	$\begin{array}{r} 9{\cdot}43\\ 23{\cdot}69\\ 29{\cdot}46\\ 25{\cdot}76\\ 10{\cdot}71\end{array}$		0 10

(average 1.452 Å) are rather longer than the normal value for paraffinic and saturated heterocyclic compounds,<sup>20</sup> (1.426 Å). With one exception [O(2)-C(8)], the individual C-C and C-O bond lengths do not differ by more than three standard deviations from their normal values.

The two shortest non-bonded intramolecular contacts, excluding those which subtend a bond angle and those in the p-tolyl group, are  $Cl(1) \cdots Cl(1)$  (3.19 Å) and  $O(2) \cdots C(2)$  (3.18 Å). The molecule makes 24 van der Waals' contacts of less than 4 Å; the shortest  $C \cdots Cl$ is 3.41 Å and the shortest C  $\cdots$  C is 3.51 Å.

The foregoing results confirm that in dichlorotris-(tetrahydrofuran)-p-tolylchromium(III) the aryl group is sigma-bonded to chromium. It is also evident that in the octahedral complex the tetrahydrofuran group trans to the aryl group is more loosely bonded than the other two. This trans effect could account for the fact <sup>21</sup> that tristetrahydrofuran(triphenyl)chromium(III) readily loses one molecule of tetrahydrofuran; it could also be an important factor in the rearrangement of sigma bonded triarylchromium(III) compounds to bisarenechromium(I)- $\pi$ -complexes.

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