$ReNCl_2(PEt_2Ph)_3$ (Corfield, Doedens & Ibers, 1967). In this case, however, the authors suggested that this 'rather long' distance could be attributed to steric effects.

Deviations from the idealized geometry in the coordination octahedron appear to be largely determined by repulsions between N and ligands. All P atoms, but especially the highly electronegative *cis* Cl atom, are bent away from the N atom until the $N\cdots L$ (*cis*) distances are at the optimum values (about 3·0 Å for $N\cdots P$ but 3·26 Å for $N\cdots Cl$). The bending away of the *cis* Cl atom in turn forces the *trans* Cl atom toward P(2), as can be appreciated from the values of the bond angles.

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Tri-μ-chloro-bis[(η-*p*-cymene)ruthenium(II)] Tetraphenylborate Methanol Solvate

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Abstract. $[Ru_2Cl_3\{p\text{-}CH_3.C_6H_4.CH(CH_3)_2\}_2]BPh_4$. MeOH, $C_{44}H_{48}BCl_3Ru_2.CH_3OH$, $M_r = 928$, monoclinic, $I2$ (non-standard setting of $C2$), $a = 27{\cdot}331$ (5), $b = 9{\cdot}765$ (5), $c = 16{\cdot}923$ (2) Å, $\beta = 112{\cdot}748$ (14)°, $U = 4165$ Å^3, $D_m = 1{\cdot}46$, $D_c = 1{\cdot}48$ g cm^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 9·3 cm^{-1}. $R = 0{\cdot}064$ for 2783 observed data with $I > 2{\cdot}5\sigma(I)$. There are two crystallographically independent Ru–Ru dimers each lying across a twofold rotation axis. Ru and Cl atoms were refined anisotropically, all benzene rings were constrained to have ideal geometries. Both $Ru\cdots Ru$ distances are 3·283 Å; $Ru\cdots Cl$ distances lie between 2·41 and 2·45 Å with Ru—Cl—Ru angles in the range 84·1 to 86·1°.

Introduction. The title compound was prepared during studies of binuclear triply bridged arene ruthenium(II) complexes (Arthur & Stephenson, 1981). A number of binuclear triply bridged ruthenium compounds have been examined by X-ray crystallography (Laing & Pope, 1976) and show $Ru\cdots Ru$ distances between 3·44 and 3·08 Å depending on the oxidation state of the Ru atoms and also the nature of the bridging ligands. NMR studies indicated a binuclear diamagnetic complex in which bridging ligands were Cl and terminal ligands π-bonded arenes with both Ru atoms in oxidation state (II). This structure determination is the first to show the nature of the binuclear Ru^{II}–π-arene interaction.

Experimental. Dark-red needles were grown from a 313–333 K petroleum ether–methylene chloride mixture. Preliminary photography showed that the space group was $I2$ or $I2/m$ (alternative settings for $C2$ and $C2/m$; the symmetry operators for $I2$ are x,y,z; $\bar{x},y,\bar{z}$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$). A crystal of dimensions 0·15 × 0·15 × 0·25 (needle) mm was mounted along the needle axis. Data were collected in the ω–2θ scan mode using a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation for θ out to 25°. Of the 3869 unique reflections measured, 2783 had $I > 2{\cdot}5\sigma(I)$. No crystal decay was observed and no absorption correction was applied. The two Ru atoms were located from a Patterson map and all remaining non-H atoms were found from subsequent Fourier maps. The structure consists of two crystallographically unrelated dimers. Each $Ru\cdots Ru$ bond is bisected by a twofold rotation axis which also runs through one of the bridging chlorides. One of these molecules was found to show a significant oscillation about the $Ru\cdots Ru$ axis. Disorder was also apparent in one of the phenyl rings of the tetraphenylborate anion and also in the position of the methanol solvent

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molecule. Smooth convergence of this partially disordered structure was facilitated using a constrained least-squares refinement in which all phenyl groups were input as idealized planar rings with C—C bond lengths of 1·395 Å. All other C—C bonds were constrained to 1·54 Å with a weight of 0·01 (*SHELX*, Sheldrick, 1976). H atoms bonded to phenyl groups were included in their calculated positions with a common fixed temperature factor of U = 0·08 Å^2. In the final cycles of refinement the two independent Ru atoms and four independent Cl atoms were refined anisotropically. All other non-H atoms were given individual isotropic temperature factors providing a total of 163 refinable parameters. The weighting scheme applied was $w = 1/[\sigma^2(F_o) + 0{\cdot}0009F_o^2]$ and the final R factor was R = 0·064, R' = 0·083 for the 2783 observed data. A final difference map showed five peaks each of about 1 e Å^{-3} which occurred near the disordered MeOH solvent molecule, near the rotationally disordered bridging chlorines of dimer *B*, and near the disordered phenyl group of the tetraphenylborate. The three residual peaks associated with this phenyl group are consistent with a possible vibrational disorder in the plane of the ring. Final positions and thermal parameters are given in Table 1, bond lengths and angles in Table 2.* A drawing of one of the dimeric molecules is shown in Fig. 1(*a*), and a packing diagram for the whole cell is shown in Fig. 2.

Table 1. *Fractional coordinates with e.s.d.'s in parentheses and isotropic thermal parameters*

$U_{eq} = \frac{1}{3}$ trace $\bar{\mathbf{U}}$.

	x	y	z	U_{eq}/U_{iso} (Å^2)
Dimer *A*				
Ru(1)	0·05840 (4)	0·00000	−0·00650 (7)	0·0339
Cl(3)	0·50000	0·3192 (7)	0·50000	0·1324
Cl(4)	0·52661 (19)	0·5901 (8)	0·5972 (4)	0·1129
C(7)	0·6666 (7)	0·5893 (19)	0·6667 (7)	0·062 (5)
C(8)	0·5631 (6)	0·4211 (17)	0·3064 (7)	0·059 (5)
C(9)	0·5337 (9)	0·2829 (19)	0·2904 (15)	0·096 (7)
C(10)	0·6042 (10)	0·432 (3)	0·2645 (17)	0·129 (10)
C(1)	0·6354 (4)	0·4014 (7)	0·5520 (4)	0·043 (4)
C(2)	0·6112 (4)	0·3616 (7)	0·4664 (4)	0·039 (4)
C(3)	0·5930 (4)	0·4605 (7)	0·4021 (4)	0·037 (3)
C(4)	0·5990 (4)	0·5992 (7)	0·4234 (4)	0·036 (3)
C(5)	0·6232 (4)	0·6391 (7)	0·5090 (4)	0·037 (4)
C(6)	0·6414 (4)	0·5401 (7)	0·5733 (4)	0·034 (3)
Dimer *B*				
Ru(2)	0·06102 (5)	0·44759 (17)	0·50422 (9)	0·055
Cl(1)	0·02103 (18)	0·5395 (7)	0·5987 (3)	0·091
Cl(2)	0·00000	0·2614 (8)	0·50000	0·098
C(17)	0·1542 (9)	0·519 (3)	0·6901 (9)	0·097 (7)
C(18)	0·0855 (9)	0·3289 (23)	0·3372 (11)	0·108 (8)
C(19)	0·0383 (10)	0·228 (3)	0·3065 (18)	0·129 (10)
C(20)	0·0695 (12)	0·444 (3)	0·2706 (18)	0·144 (12)
C(11)	0·1339 (5)	0·3430 (10)	0·5731 (6)	0·065 (5)
C(12)	0·1406 (5)	0·4811 (10)	0·5958 (6)	0·066 (5)
C(13)	0·1290 (5)	0·5814 (10)	0·5325 (6)	0·053 (4)
C(14)	0·1107 (5)	0·5435 (10)	0·4464 (6)	0·071 (6)
C(15)	0·1040 (5)	0·4054 (10)	0·4237 (6)	0·083 (6)
C(16)	0·1156 (5)	0·3051 (10)	0·4870 (6)	0·074 (6)
Tetraphenylborate				
B(1)	0·2589 (6)	0·0085 (21)	0·4857 (9)	0·039 (4)
C(21)	0·2149 (3)	−0·0709 (11)	0·4030 (6)	0·040 (4)
C(22)	0·1616 (3)	−0·0380 (11)	0·3812 (6)	0·058 (5)
C(23)	0·1223 (3)	−0·1079 (11)	0·3149 (6)	0·072 (5)
C(24)	0·1363 (3)	−0·2106 (11)	0·2703 (6)	0·068 (5)
C(25)	0·1896 (3)	−0·2434 (11)	0·2920 (6)	0·075 (6)
C(26)	0·2289 (3)	−0·1736 (11)	0·3584 (6)	0·055 (4)
C(27)	0·3219 (3)	−0·0023 (14)	0·4946 (6)	0·041 (3)
C(28)	0·3332 (3)	0·0129 (14)	0·4214 (6)	0·069 (5)
C(29)	0·3858 (3)	0·0123 (14)	0·4283 (6)	0·100 (7)
C(30)	0·4270 (3)	−0·0034 (14)	0·5083 (6)	0·101 (7)
C(31)	0·4157 (3)	−0·0186 (14)	0·5814 (6)	0·097 (7)
C(32)	0·3631 (3)	−0·0181 (14)	0·5746 (6)	0·065 (5)
C(33)	0·2508 (4)	0·1836 (8)	0·4790 (6)	0·042 (4)
C(34)	0·2301 (4)	0·2443 (8)	0·3981 (6)	0·048 (4)
C(35)	0·2258 (4)	0·3865 (8)	0·3906 (6)	0·060 (5)
C(36)	0·2421 (4)	0·4679 (8)	0·4640 (6)	0·073 (5)
C(37)	0·2628 (4)	0·4072 (8)	0·5449 (6)	0·059 (5)
C(38)	0·2671 (4)	0·2651 (8)	0·5524 (6)	0·047 (4)
C(39)	0·2491 (4)	−0·0572 (11)	0·5686 (6)	0·048 (4)
C(40)	0·2173 (4)	0·0081 (11)	0·6047 (6)	0·047 (3)
C(41)	0·2075 (4)	−0·0543 (11)	0·6714 (6)	0·070 (5)
C(42)	0·2296 (4)	−0·1821 (11)	0·7019 (6)	0·073 (5)
C(43)	0·2614 (4)	−0·2474 (11)	0·6658 (6)	0·085 (6)
C(44)	0·2711 (4)	−0·1849 (11)	0·5991 (6)	0·053 (4)
Methanol solvate				
C(45)	0·5656 (8)	0·429 (3)	0·0328 (12)	0·099 (6)
C(46)	0·5301 (8)	0·414 (3)	−0·0492 (11)	0·099 (7)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Dimer *B*		Dimer *A*	
Ru(2)—Ru(2′)	3·282 (3)	Ru(1)—Ru(1′)	3·283 (3)
Ru(2)—Cl(1)	2·431 (7)	Ru(1)—Cl(3)	2·411 (5)
Ru(2)—Cl(2)	2·449 (6)	Ru(1)—Cl(4)	2·406 (7)
Ru(2)—C(11)	2·139 (11)	Ru(1)—C(1)	2·174 (8)
Ru(2)—C(12)	2·153 (11)	Ru(1)—C(2)	2·152 (9)
Ru(2)—C(13)	2·168 (12)	Ru(1)—C(3)	2·137 (10)
Ru(2)—C(14)	2·169 (14)	Ru(1)—C(4)	2·144 (10)
Ru(2)—C(15)	2·155 (14)	Ru(1)—C(5)	2·166 (9)
Ru(2)—C(16)	2·141 (13)	Ru(1)—C(6)	2·180 (8)
Tetraphenylborate			
B(1)—C(21)	1·644 (17)		
B(1)—C(27)	1·673 (19)		
B(1)—C(33)	1·722 (22)		
B(1)—C(39)	1·656 (21)		

Dimer *B*		Dimer *A*	
Ru(2)—Cl(1)—Ru(2′)	85·21 (20)	Ru(1)—Cl(3)—Ru(1′)	85·84 (13)
Ru(2)—Cl(2)—Ru(2′)	84·13 (15)	Ru(1)—Cl(4)—Ru(1′)	86·15 (22)
Cl(1)—Ru(2)—Cl(1′)	79·01 (20)	Cl(3)—Ru(1)—Cl(4)	78·60 (18)
Cl(1)—Ru(2)—Cl(2)	79·57 (18)	Cl(3)—Ru(1)—Cl(4′)	78·68 (18)
Cl(1′)—Ru(2)—Cl(2)	79·84 (18)	Cl(4)—Ru(1)—Cl(4′)	78·42 (22)

Discussion. There are no significant differences in bond lengths and angles between the two dimers. The apparent shortening of the Ru—Cl bonds in dimer *A* is likely to result from the high anisotropic thermal parameters of the bridging Cl atoms (see Fig. 1*b*). The

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38010 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

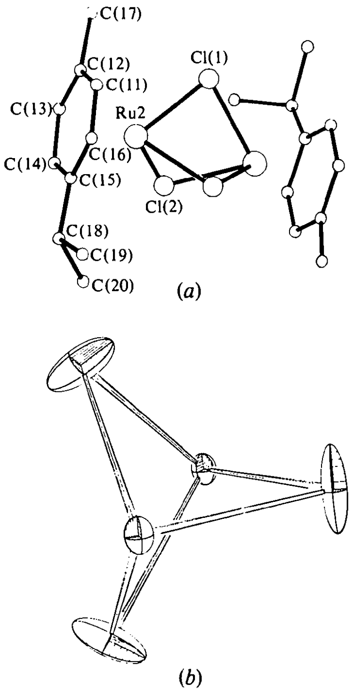

Fig. 1. (*a*) A labelled drawing of dimer *B*. The crystallographic twofold axis at $Oy\frac{1}{2}$ goes through Cl(2) and bisects the Ru(2)–Ru*(2) vector. (*b*) The triple-bridged $Ru(1)Cl_3Ru^*(1)$ group of dimer *A*. The large anisotropic components of Cl(3) and Cl(4) indicate rotational disorder about the Ru–Ru axis.

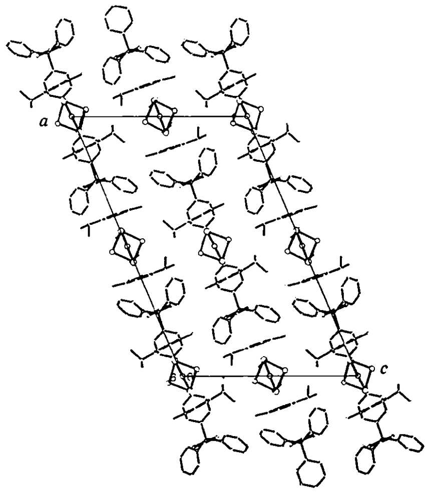

Fig. 2. Unit-cell contents viewed along **b**.

Ru···Ru distance of 3·283 Å is in the middle of the expected Ru···Ru dimer range of 3·44 to 3·08 Å (Laing & Pope, 1976; Crozat & Watkins, 1972). Both Ru atoms are in oxidation state (II) which precludes any metal–metal bonding. The Ru–Cl bond lengths lie between 2·41 and 2·45 Å with Ru–Cl–Ru′ angles in the range 84 to 86° and Cl–Ru–Cl angles of 79(±1)°. These values are in close agreement with the values found in other trichloro-bridged dimers.

The ring centroids of the *η*-bonded *p*-cymene groups are 1·647 and 1·642 Å from the Ru atoms of dimers *A* and *B* respectively. This compares with values of 1·622 Å in the tetranuclear complex $\{Ru(\eta\text{-}C_6H_6)OH\}_4^{4+}$ (Gould, Jones, Robertson, Tocher & Stephenson, 1982) and 1·637 Å in di-*μ*-chloro-bis-[chloro(*η*-*p*-cymene)Os^{II}] (Watkins & Fronczek, 1982). All C–C single bonds refined to within 0·01 Å of their idealized value of 1·54 Å. In neither dimer *A* nor dimer *B* are the isopropyl groups symmetrical with respect to the benzene ring. Dimer *A* has a torsion angle C(2)–C(3)–C(8)–C(9) = 26° which is identical to the conformation of the *p*-cymene in the osmium complex (Watkins & Fronczek, 1982). Dimer *B*, however, shows the corresponding torsion angle C(16)–C(15)–C(18)–C(19) = 57°.

The disordered methanol solvent molecule does not show any close intermolecular contacts.

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