Fig. 1. View of the molecular packing, with atom-numbering scheme indicated.

The basal plane of the $Cu_2Ac_4(PPh_3)_2$ complex shows remarkable differences between the Cu—O bond distances. The long Cu—O(3) bond distance [1·976 (6) Å] corresponds to the long distance C(3')—O(3') [1·288 (9) Å] of the acetate group and indicates a weaker coordination of the O(3') oxygen atom in comparison with O(4) which occupies the *trans* position in the basal plane with bond distance Cu—O(4) 1·934 (5) Å.

The selected interatomic distances and Cu—basal plane distances (see Table 3) show that replacement of water molecules in $Cu_2Ac_4(H_2O)_2$ by triphenylphosphine ligands led to an elongation of the Cu—Cu distance through displacement of the Cu atoms from the basal planes. The elongation of the Cu—Cu distance is followed by shortening of the Cu—O$_{av}$ (in basal plane) distance. The replacement of water molecules

Table 3. *Selected distances (Å) for aqua and for triphenylphosphine copper(II) carboxylates*

| | | Interatomic distances | | | Cu–basal |
Complex	Ligand	Cu—L	Cu—Cu	Cu—O$_{av}$	plane distance
$Cu_2Ac_4L_2$	H$_2$O*	2·156 (4)	2·616 (1)	1·969 (3)	0·192
		2·161 (1)	2·614 (2)	1·969 (2)	0·191
	PPh$_3$	2·570 (2)	2·709 (1)	1·956 (5)	0·245
Cu_2YL_2	H$_2$O†	2·140 (3)	2·626 (2)	1·955 (4)	0·258
	PPh$_3$	2·570 (2)	2·676 (1)	1·967 (3)	0·226

Y = 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioate-(2−) anion.

* de Meester, Fletcher & Skapski (1973); Brown & Chidambaram (1973).

† McCrindle, Ferguson, McAlees & Roberts (1981).

in $Cu_2Y_2(H_2O)_2$ [Y = 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedionato(2−) anion] by triphenylphosphine (McCrindle, Ferguson, McAlees & Roberts, 1981) causes smaller changes in Cu—Cu and Cu—O$_{av}$ (in basal plane) distances. However, the displacements of the Cu atoms from the basal planes (see Cu—basal plane distance in Table 3) are in opposite directions. These differences can be explained by the different basicity of the ligands.

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The Structure of Di-μ-chloro-bis[chloro(η⁶-hexamethylbenzene)ruthenium(II)]–Chloroform (1/2)

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Abstract. [Ru$_2$Cl$_2$(C$_{12}$H$_{18}$)$_2$].2CHCl$_3$, M_r = 907·26, triclinic, $P\bar{1}$, a = 10·192 (1), b = 10·953 (1), c = 8·529 (2) Å, α = 100·26 (1), β = 106·64 (1), γ = 104·74 (1)°, V = 849·2 (5) Å^3, Z = 1, D_x = 1·77 g cm^{-3}, Mo $K\alpha$ radiation (λ = 0·71073 Å), μ = 16·9 cm^{-1}, $F(000)$ = 452, R_1 = 0·025 for 2732 re-

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flections collected at 296 (1) K. The molecule is essentially a dimer of the (η^6-hexamethylbenzene)-RuCl₂ moiety; each Ru is bonded to two symmetry-related bridging Cl [Ru–Cl=2·460(1)Å, Cl–Ru–Cl' = 80·90 (2)°] forming a planar four-membered ring. A terminal Cl [Ru–Cl=2·394(1)Å], and an η^6-hexamethylbenzene ring [Ru–ring plane = 1·654 (1) Å] is also attached to each Ru. The hexamethylbenzene ring is planar with the methyl groups all displaced slightly towards Ru. The distance between the Ru atoms [3·743 (1) Å] indicates no bonding interaction.

Introduction. Complexes of the general formula [(η^6-arene)RuCl₂]₂ have been useful starting materials for organoruthenium studies since their original synthesis from RuCl₃.xH₂O and cyclohexadienes (Winkhaus & Singer, 1967; Zelonka & Baird, 1972; Bennett & Smith, 1974). Although it would provide a valuable structural model for the wealth of chemistry based on these complexes (Bennett, Bruce & Matheson, 1982), the structure of an [(η^6-arene)RuCl₂]₂ complex had not been determined by X-ray diffraction techniques. In our current investigations of organoruthenium chemistry, we have obtained single crystals of [{η^6-C₆(CH₃)₆}-RuCl₂]₂ (Bennett, Matheson, Robertson, Smith & Tucker, 1980) and have undertaken its X-ray diffraction analysis.

Experimental. The complex [(η^6-hexamethylbenzene)-RuCl₂]₂ was prepared from hexamethylbenzene and [(η^6-p-cymene)RuCl₂]₂ as previously described (Bennett, Matheson, Robertson, Smith & Tucker, 1980). Dissolution of [(η^6-hexamethylbenzene)RuCl₂]₂ in a minimum amount of hot CHCl₃ and allowing the red solution to cool gradually to room temperature produced red–orange prismatic crystals of the complex. The crystals became opaque within one hour after removal from the mother liquor, indicating probable desolvation. A suitable crystal (0·30 × 0·19 × 0·44 mm) was mounted on a glass fiber and coated with epoxy to prevent desolvation. Intensities were measured with an Enraf–Nonius CAD-4 diffractometer using variable-speed (2–10° min⁻¹) ω–2θ scans of (0·5 + 0·35tanθ)° width and Mo$K\alpha$ ($\lambda = 0·71073$ Å) radiation. Unit-cell constants were determined from a least-squares fit to angular data for 25 reflections in the angular range $10 < \theta < 15°$. Data were collected to (sinθ)/λ of 0·594 Å⁻¹ (maximum 2θ = 50·0°), $-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-10 \leq l \leq 10$. Three standard reflections were monitored after each batch of 97 data; no intensity decay was observed. Of the 5946 reflections measured, 2973 unique [R_{int}(on I) = 3·1%], 2732 reflections with $I > 3\sigma(I)$ were considered observed. An empirical absorption correction (μ = 16·9 cm⁻¹) based on a series of ψ scans (North, Phillips & Mathews, 1968) was applied to the data. Relative

Table 1. *Final fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}(Å^2)$
Ru	0·33308 (2)	0·43845 (2)	0·05216 (2)	2·088 (4)
Cl(1)	0·58612 (6)	0·58144 (7)	0·19396 (7)	2·76 (1)
Cl(2)	0·41551 (8)	0·25825 (7)	0·10309 (8)	3·73 (2)
Cl(3)	0·59590 (12)	0·06784 (9)	0·24669 (13)	6·18 (3)
Cl(4)	0·70430 (14)	−0·05211 (12)	0·50492 (12)	6·75 (3)
Cl(5)	0·88234 (12)	0·05096 (14)	0·32059 (13)	6·94 (3)
C(1)	0·1937 (3)	0·4023 (3)	0·2028 (3)	2·84 (6)
C(2)	0·2638 (3)	0·5393 (3)	0·2418 (3)	2·96 (6)
C(3)	0·2520 (3)	0·6043 (3)	0·1058 (3)	2·90 (6)
C(4)	0·1752 (3)	0·5279 (3)	−0·0648 (3)	2·85 (5)
C(5)	0·1070 (3)	0·3897 (3)	−0·1035 (3)	2·75 (6)
C(6)	0·1141 (3)	0·3273 (3)	0·0301 (3)	2·76 (6)
C(7)	0·2069 (4)	0·3313 (4)	0·3409 (4)	4·39 (8)
C(8)	0·3543 (4)	0·6193 (4)	0·4223 (4)	4·63 (8)
C(9)	0·3278 (3)	0·7481 (3)	0·1469 (5)	4·40 (8)
C(10)	0·1687 (3)	0·5944 (3)	−0·2064 (4)	4·19 (7)
C(11)	0·0323 (3)	0·3094 (4)	−0·2859 (4)	4·30 (8)
C(12)	0·0451 (4)	0·1812 (3)	−0·0069 (5)	4·37 (8)
C(13)	0·7043 (4)	−0·0271 (3)	0·3071 (4)	4·09 (8)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as

$$\tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)].$$

transmission coefficients ranged from 0·860 to 0·999 with an average value of 0·939. The structure was solved by Patterson and Fourier methods. Full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$. H atoms at calculated positions ($r_{C-H} = 0·95$ Å, $B_{iso} = 5·0$ Å²) were included in the structure-factor calculations but were not refined, all other atoms refined anisotropically for 172 variables. Final $R = 0·025$, $wR = 0·039$, $S = 1·65$. Final $(\Delta/\sigma)_{max} = 0·01$, $\Delta\rho_{max} = \pm0·5$ (1) e Å⁻³ on the final difference map. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982). Final atomic parameters are given in Table 1.*

Discussion. The molecular structure and atomic labeling scheme are shown in Fig. 1 and the crystal packing in the unit cell is shown in Fig. 2. The bond lengths and angles are given in Table 2. The only crystallographically imposed symmetry is an inversion center midway between Cl(1) and Cl(1'). The two chloroform solvate molecules [the C(13), Cl(3), Cl(4), Cl(5) and H(19) atoms] are related by this inversion and appear to be normal. Overall, the geometry of [(η^6-hexamethylbenzene)RuCl₂]₂ is quite similar to the related

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions, and a complete table of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44574 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

osmium complex di-μ-chloro-bis[chloro(η^6-p-cymene)-osmium(II)] (Watkins & Fronczek, 1982). The bond lengths involving Ru in [(η^6-hexamethylbenzene)-RuCl$_2$]$_2$ are actually slightly longer than the corresponding Os–Cl and Os–C bond lengths found in [(η^6-p-cymene)OsCl$_2$]$_2$; Os–Cl(terminal) = 2·389 (2), Os–Cl(bridge) = 2·450 (2),   Os–p-cymene(ring centroid) = 1·637 (2) Å (Watkins & Fronczek, 1982). The hexamethylbenzene ring is essentially planar [maximum deviation from the mean plane of 0·015 (3) Å] and the distance from the ring plane to the Ru atom is 1·654 (1) Å. Each methyl group is displaced slightly [range 0·097–0·017, average 0·055 (4) Å] from the ring plane towards Ru. The C(ring)–C(methyl) distances are unremarkable except for C(3)–C(9) which appears to be slightly shortened. The C–C bonds within the ring appear to be essentially identical in length with the exception of C(2)–C(3) which is abnormally long. The Ru–C bond lengths vary somewhat, but the only significant deviation is the long Ru–C(3) bond. We suspect these anomalies are related to the dominance of the structure by the heavy Ru and Cl atoms rather than chemically significant factors. The
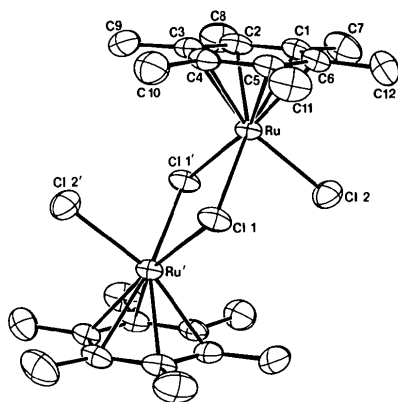
Cl-bridged Ru atoms form a planar four-membered ring with a 3·743 (1) Å separation between the Ru centers. This long distance precludes any direct Ru–Ru interaction. The Ru–ring centroid vector intersects the four membered Ru–Cl bridge plane at a 146·0 (3)° angle and the Ru–Cl(terminal) bond vector intersects this plane at an 86·1 (3)° angle. The two hexamethylbenzene ring planes are parallel as demanded crystallographically and the planes are separated by 6·408 (2) Å [6·746 (5) Å between ring centroids]. The angle between the Ru–Cl(2) vector and the Ru–ring centroid vector is 127·9 (2)°. The angles of the Ru–Cl(1) and Ru–Cl(1′) vectors with the Ru–ring centroid vector are 128·8 (2) and 129·4 (2)°, respectively.

Table 2. *Bond lengths* (Å) *and angles* (°)

Ru–Cl(1)	2·460 (1)	C(1)–C(7)	1·516 (3)
Ru–Cl(2)	2·394 (1)	C(2)–C(3)	1·457 (3)
Ru–C(1)	2·182 (2)	C(2)–C(8)	1·511 (3)
Ru–C(2)	2·179 (2)	C(3)–C(4)	1·418 (3)
Ru–C(3)	2·209 (2)	C(3)–C(9)	1·493 (4)
Ru–C(4)	2·185 (2)	C(4)–C(5)	1·428 (3)
Ru–C(5)	2·174 (2)	C(4)–C(10)	1·512 (3)
Ru–C(6)	2·189 (2)	C(5)–C(6)	1·424 (3)
C(1)–C(2)	1·420 (3)	C(5)–C(11)	1·506 (3)
C(1)–C(6)	1·431 (3)	C(6)–C(12)	1·508 (3)

Cl(1)–Ru–Cl(1′)	80·90 (2)	C(4)–C(3)–C(9)	121·1 (2)
Cl(1)–Ru–Cl(2)	87·53 (2)	C(3)–C(4)–C(5)	120·8 (2)
Ru–Cl(1)–Ru′	99·09 (2)	C(3)–C(4)–C(10)	119·1 (2)
C(2)–C(1)–C(6)	120·2 (2)	C(5)–C(4)–C(10)	120·1 (2)
C(2)–C(1)–C(7)	121·1 (2)	C(4)–C(5)–C(6)	120·0 (2)
C(6)–C(1)–C(7)	118·6 (2)	C(4)–C(5)–C(11)	120·0 (2)
C(1)–C(2)–C(3)	119·9 (2)	C(6)–C(5)–C(11)	120·0 (2)
C(1)–C(2)–C(8)	121·1 (2)	C(1)–C(6)–C(5)	120·0 (2)
C(3)–C(2)–C(8)	119·0 (2)	C(1)–C(6)–C(12)	118·7 (2)
C(2)–C(3)–C(4)	119·1 (2)	C(5)–C(6)–C(12)	121·2 (2)
C(2)–C(3)–C(9)	119·7 (2)		

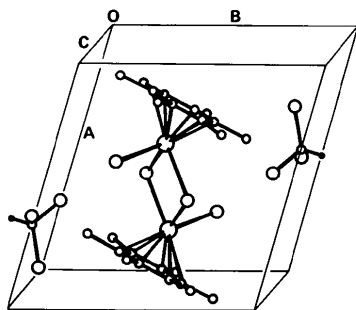Fig. 1. The molecular structure and labeling scheme for [{η^6-C$_6$(CH$_3$)$_6$}RuCl$_2$]$_2$.

Fig. 2. The unit cell. H atoms, except those on the chloroform solvate molecules, have been omitted for clarity.

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