Refinement

Refinement on F
$R = 0.031$
$wR = 0.030$
$S = 1.748$
2924 reflections
235 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00004|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—Cl1	2.295 (1)	Pd1—N1	2.017 (3)
Pd1—O1	1.990 (2)	Pd1—N2	2.051 (2)
Cl1—Pd1—O1	176.24 (8)	O1—Pd1—N1	84.1 (1)
Cl1—Pd1—N1	94.65 (8)	O1—Pd1—N2	93.2 (1)
Cl1—Pd1—N2	88.16 (8)	N1—Pd1—N2	176.7 (1)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H23···O1^{i}	0.87	1.77	2.604 (3)	160
N1—H4···Cl1^{ii}	1.04	2.31	3.285 (3)	156
N2—H18···O2	0.95	2.41	2.776 (3)	103

Symmetry codes: (i) $y, x-1, 2-z$; (ii) $x-y, -y, \frac{5}{3}-z$.

All H atoms were located by difference Fourier syntheses.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1045). Services for accessing these data are described at the back of the journal.

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Di-μ-bromo-bis[bromo(η^6-*para*-cymene)ruthenium(II)] benzene solvate and di-μ-iodo-bis[(η^6-*para*-cymene)iodoruthenium(II)] toluene solvate

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Abstract

The homologous title molecules, [$Ru_2Br_4(C_{10}H_{14})_2$]·C_6H_6, (1), and [$Ru_2I_4(C_{10}H_{14})_2$]·C_7H_8, (2), consist of arene–ruthenium moieties [Ru-to-ring distances of 1.655 (2) Å in (1) and 1.673 (3) Å in (2)] with a terminal halogen ligand [Ru—Br 2.548 (1) Å in (1) and Ru—I 2.726 (1) Å in (2)], held together by two symmetrical halogen bridges [Ru—Br 2.575 (1) Å in (1) and Ru—I 2.736 (1) Å in (2)]. The arene rings are planar and parallel to each other, and the terminal halogen ligands are coordinated to ruthenium *trans* with respect to each other. Both molecules possess C_i symmetry.

Comment

The title compounds, $(\eta^6\text{-}p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_2\text{Ru}_2(\mu\text{-}X)_2X_2$ [(1) X = Br; (2) X = I], were first obtained from the reaction of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_2\text{Ru}_2(\mu\text{-OH})_3][\text{BPh}_4]$ with HBr and HI, respectively (Gould *et al.*, 1984), while the chloro analogue, $(\eta^6\text{-}p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_2\text{Ru}_2(\text{Cl})_2\text{Cl}_2$, was first reported as a product of the reaction of hydrated ruthenium(III) chloride with α-phellandrene (Bennett & Smith, 1974). The benzene complexes $(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2(\mu\text{-}X)_2X_2$ have been known for even longer (Zelonka & Baird, 1972), the chloro derivative having been reported first, erroneously as a polymer (Winkaus & Singer, 1967). Surprisingly, structural information is available only for chloro derivatives of the hexamethylbenzene, ethylbenzoate and trindane analogues, *i.e.* $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ (McCormick & Gleason, 1988), $(\eta^6\text{-C}_6\text{H}_6\text{CO}_2\text{Et})_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ (Therrien *et al.*, 1998) and $(\eta\text{-}^6\text{C}_{15}\text{H}_8)_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ (Gupta *et al.*, 1997). As

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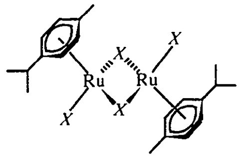
(1) and (2) are easily accessible in high yield from $(\eta^6\text{-}p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ with NaBr and KI, respectively, giving high quality crystals, we decided to undertake a single-crystal X-ray structure analysis of these simple compounds.



(1) X = Br, benzene solvate
(2) X = I, toluene solvate

In the molecular structures of (1) (Fig. 1) and (2) (Fig. 2), the two metal atoms and the symmetrically bridging Br^- or I^- ions are coplanar, with average an Ru—Br distance of 2.573 (3) Å for (1) and an average Ru—I distance of 2.733 (3) Å for (2). The Ru···Ru distances are 3.854 (1) Å in (1) and 4.092 (1) Å in (2), and are too long to be considered as bonds. The two halves of the molecules are related by a crystallographic inversion center, and thus the two *p*-cymene ligands lie in parallel planes. The distance of the Ru atom from the *p*-cymene centroid in (1) is slightly shorter [1.655 (2) Å] than in (2) [1.673 (3) Å]. In similar $\text{Ru}_2\text{Cl}_4L_2$ structures [L = hexamethylbenzene (McCormick & Gleason, 1988) and trindane (Gupta *et al.*, 1997)] the corresponding ruthenium–ligand-centroid distances are even shorter, with an average distance of 1.647 (2) Å. The Ru—I terminal bond distances in (2) [2.726 (1) Å] are longer than the corresponding Ru—Br bond distances in (1) [2.547 (1) Å]. The similar position of the terminal halogen ligand in both compounds with respect to the isopropyl group of the *p*-cymene ligand can be expressed by the torsion angles Br2—Ru1—C1—C7 [31.7 (7) Å] and I2—Ru1—C1—C7 [33.2 (6) Å]. Selected bond lengths and angles for (1) and (2) are given in Tables 1 and 2, respectively.

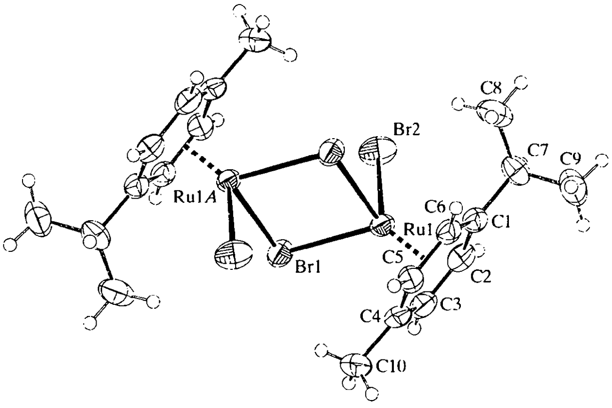


Fig. 1. The molecular structure of (1) showing the numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

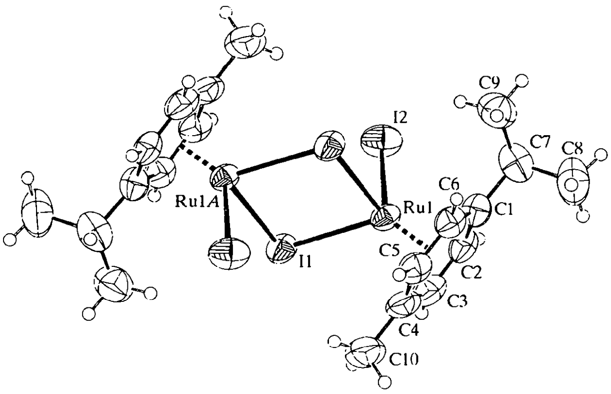


Fig. 2. The molecular structure of (2) showing the numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Experimental

A suspension of $(\eta^6\text{-}p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ (100 mg, 0.16 mmol) in water (20 ml) was stirred with silver sulfate (102 mg, 0.33 mmol) for 2 h at room temperature. After filtration, solid NaBr (168 mg, 1.63 mmol) or NaI (245 mg, 1.63 mmol) was added to the yellow solution, which was stirred for 2 h. The deep-red precipitate obtained was filtered off, washed with water (3 × 5 ml) and dried *in vacuo*. Recrystallization of (1) from chloroform/benzene gave dark-brown crystals (78 mg, 60%) and recrystallization of (2) from chloroform/toluene gave black crystals (121 mg, 76%).

Compound (1)

Crystal data

$[\text{Ru}_2\text{Br}_4(\text{C}_{10}\text{H}_{14})_2]\cdot\text{C}_6\text{H}_6$
M_r = 868.31
Triclinic
$P\overline{1}$
a = 8.5740 (10) Å
b = 8.7391 (10) Å
c = 9.9027 (11) Å
α = 102.879 (13)°
β = 97.367 (14)°
γ = 100.535 (14)°
V = 700.00 (14) Å^3
Z = 1
D_x = 2.060 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 5000 reflections
θ = 1.65–26.05°
μ = 6.800 mm^{-1}
T = 293 (2) K
Block
0.76 × 0.38 × 0.30 mm
Dark brown

Data collection

Stoe Image Plate diffractometer
φ oscillation scans
Absorption correction: semi-empirical (*MULABS* in *PLATON*99; Spek, 1999)
$T_{\min}$ = 0.037, $T_{\max}$ = 0.130
5433 measured reflections
2515 independent reflections

2204 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
$\theta_{\max}$ = 25.87°
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 12$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.139$
$S = 1.029$
2515 reflections
149 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1031P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.97$ e Å^{-3}
$\Delta\rho_{\min} = -2.21$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.027 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Ru1—Br1	2.5650 (8)	Ru1—Br2	2.5471 (8)
Ru1—Br1^i	2.5802 (8)	Ru1···Ru1^i	3.8539 (11)
Br1—Ru1—Br1^i	82.99 (3)	Ru1—Br1—Ru1^i	97.01 (3)
Br2—Ru1—Br1^i	88.03 (3)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Compound (2)

Crystal data

$[Ru_2I_4(C_{10}H_{14})_2]\cdot C_7H_8$
$M_r = 1070.34$
Triclinic
$P\overline{1}$
$a = 8.755$ (1) Å
$b = 9.090$ (1) Å
$c = 10.420$ (1) Å
$\alpha = 103.71$ (1)°
$\beta = 96.18$ (1)°
$\gamma = 100.12$ (1)°
$V = 783.37$ (15) Å^3
$Z = 1$
$D_x = 2.269$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 12.8$–20.5°
$\mu = 4.919$ mm^{-1}
$T = 293$ (2) K
Block
0.68 × 0.60 × 0.38 mm
Black

Data collection

Stoe AED-2 four-circle diffractometer
$\omega/2\theta$ scan
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min} = 0.063$, $T_{\max} = 0.154$
2866 measured reflections
2866 independent reflections
2603 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.48°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 10$
$l = 0 \rightarrow 12$
2 standard reflections
frequency: 60 min
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.123$
$S = 1.294$
2866 reflections
156 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 1.2754P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.13$ e Å^{-3}
$\Delta\rho_{\min} = -1.28$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.051 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Ru1—I1	2.7292 (8)	Ru1—I2	2.7256 (8)
Ru1—I1^i	2.7359 (7)	Ru1···Ru1^i	4.0918 (12)
I1—Ru1—I1^i	83.04 (2)	Ru1—I1—Ru1^i	96.96 (2)
I2—Ru1—I1	87.59 (2)		

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

In (1), one benzene molecule was found per asymmetric unit, while (2) crystallizes with one disordered molecule of toluene per asymmetric unit. The toluene disorder was modeled with three C atoms and two H atoms at population 1.0, with the methyl moiety at population 0.5. The disordered H atom at population 0.5 was not included in the model.

Data collection: *EXPOSE* (Stoe & Cie, 1997) for (1); *STADI*4 (Stoe & Cie, 1995*a*) for (2). Cell refinement: *CELL* (Stoe & Cie, 1997) for (1); *STADI*4 for (2). Data reduction: *INTEGRATE* (Stoe & Cie, 1997) for (1); *X-RED* (Stoe & Cie, 1995*b*) for (2). For both compounds, program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*99 (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1323). Services for accessing these data are described at the back of the journal.

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