Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

# A $\mu$-chloro-bridged dinuclear ruthenium complex with 9*H*-carbazole: the formation of one-dimensional linear chains of star-shaped edge-fused rings

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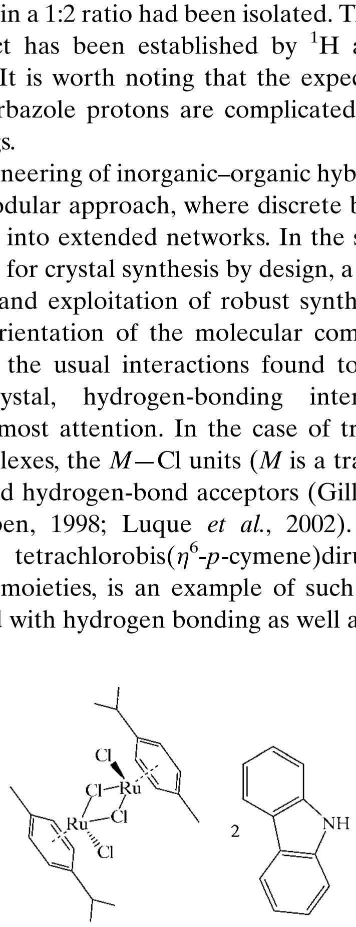
Received 19 April 2006
Accepted 31 May 2006
Online 14 July 2006

The title complex, di-$\mu$-chloro-bis[chloro($\eta^6$-*p*-cymene)ruthenium(II)]–9*H*-carbazole (1/2), $[\mathrm{Ru_2Cl_4(C_{10}H_{14})_2}]\cdot2\mathrm{C_{12}H_9N}$, is composed of one $[\mathrm{RuCl_2}(\eta^6\text{-}p\text{-cymene})]_2$ and two 9*H*-carbazole molecules. There are one-half of a dinuclear complex and one 9*H*-carbazole molecule per asymmetric unit. In the dinuclear complex, each of the two crystallographically equivalent Ru atoms is in a pseudo-tetrahedral environment, coordinated by a terminal Cl atom, two bridging Cl atoms and the aromatic hydrocarbon, which is linked in a $\eta^6$ manner; the Ru$\cdots$Ru separation is 3.688 (3) Å. The title complex has a crystallographic centre of symmetry located at the mid-point of the Ru$\cdots$Ru line. Intermolecular N—H$\cdots$Cl and $\pi$–$\pi$ stacking interactions are observed. These interactions form a four-pointed star-shaped ring and one-dimensional linear chains of edge-fused rings running parallel to the [100] direction, which stabilize the crystal packing.

## Comment

Arene–ruthenium(II) derivatives are of interest both as reagents in organic chemistry (Pigge & Coniglio, 2001) and as catalysts for a wide range of reactions, including arene hydrogenation (Boxwell *et al.*, 2002), alkene metathesis (Zaja *et al.*, 2003) and Diels–Alder reactions (Davenport *et al.*, 2004). Tetrachlorobis($\eta^6$-arene)diruthenium complexes are readily accessible compounds and are widely used as starting materials for a wide variety of materials (Bennett, 1997). As a result of their accessibility and propensity to react with nucleophiles, they are often the chosen catalyst precursors for a variety of homogeneous catalytic reactions (Soleimannejad *et al.*, 2003; Özdemir *et al.*, 2001). One of our recent interests involves ketone transfer hydrogenation reactions catalyzed by ruthenium(II) complexes in 2-propanol. In this effort, we have prepared and tested a range of pyridine–diimine complexes of ruthenium(II) (Çetinkaya *et al.*, 1999; Dayan & Çetinkaya, 2005). As part of this work, we were attempting to use carbazole as an additive in the presence of the $\mu$-chloro-bridged $[\mathrm{RuCl_2}(\eta^6\text{-}p\text{-cymene})]_2$ dimer to improve the catalytic reduction. However, gas chromatography showed that the desired secondary alcohol was not formed in a significant amount, but rather a new adduct between the *p*-cymene dimer and carbazole in a 1:2 ratio had been isolated. The formulation of the product has been established by $^1$H and $^{13}$C NMR spectroscopy. It is worth noting that the expected multiplets due to the carbazole protons are complicated because of 3-bond couplings.

Crystal engineering of inorganic–organic hybrid materials is based on a modular approach, where discrete building blocks are connected into extended networks. In the search for reliable strategies for crystal synthesis by design, a key goal is the identification and exploitation of robust synthons to control the relative orientation of the molecular component of the solid. Among the usual interactions found to assemble the molecular crystal, hydrogen-bonding interactions have attracted the most attention. In the case of transition metal chloride complexes, the *M*—Cl units (*M* is a transition metal) can act as good hydrogen-bond acceptors (Gillon *et al.*, 2000; Lewis & Orpen, 1998; Luque *et al.*, 2002). Complex (I), composed of tetrachlorobis($\eta^6$-*p*-cymene)diruthenium and 9*H*-carbazole moieties, is an example of such an inorganic–organic hybrid with hydrogen bonding as well as $\pi$–$\pi$ stacking interactions.



(I)

The asymmetric unit of (I) contains one-half of the dimeric $[\mathrm{RuCl_2}(\eta^6\text{-}p\text{-cymene})]_2$ molecule and one 9*H*-carbazole molecule. As shown in Fig. 1, the structure of the *p*-cymene dimer contains a dimetallocyclic $\mathrm{Ru_2Cl_2}$ core with a crystallographic centre of inversion at the mid-point of the Ru1$\cdots$Ru1$^{\mathrm{i}}$ line [symmetry code: (i) $-x+1, -y+1, -z$]. The Ru1/Cl1/Ru1$^{\mathrm{i}}$/Cl1$^{\mathrm{i}}$ ring is strictly planar because of the inversion centre. The environment around the each Ru$^{\mathrm{II}}$ atom is made up of a terminal Cl atom, two bridging Cl atoms and the hydrocarbon linked through its $\pi$ cloud in a typical organometallic $\eta^6$ manner (see Fig. 1). The rotational orientation of the arene is such that the tripodal ligands are staggered with respect to the arene C atoms, *i.e.* when viewed along the arene centroid–Ru bond axis, the ligands eclipse the arene C—C bonds rather than the C atoms.

The Ru atom adopts a pseudo-octahedral coordination geometry, with the arene formally occupying three facial coordination sites. However, the geometry around the metal

DOI: 10.1107/S0108270106020543

atom may be regarded as a tetrahedron with considerable trigonal distortion, considering the linkage to the hydrocarbon as a single bond. Defining $X$ as the centroid of the aromatic ring, the Ru—$X$ distance is 1.647 (4) Å and the Cl1—Ru1—$X$, Cl1$^i$—Ru1—$X$ and Cl2—Ru1—$X$ angles are 128.06 (9), 128.61 (10) and 129.73 (9)°, respectively. Many ruthenium–arene complexes have been characterized crystallographically (Aitali *et al.*, 2000; Bown & Bennett, 1999; Feher *et al.*, 2000; Soleimannejad *et al.*, 2005). The Ru–arene distances in these complexes are in the range 1.640–1.671 Å. The Ru–arene distance for (I) is at the lower end of this range. The Cl1—Ru1—Cl2, Cl1—Ru1—Cl1$^i$ and Cl1$^i$—Ru1—Cl2 bond angles [mean 84.82 (4)°] are smaller than the ideal tetrahedral angle (109.47°), which is compensated for by the opening of the $X$—Ru—$L$ ($L$ is Cl1, Cl1$^i$ or Cl2) angles [mean 128.80 (10)°]. While there are substantial differences in the C—C [1.398 (5)–1.423 (5) Å] and C—Ru [2.150 (4)–2.193 (3) Å] distances for the arene ring, there is no evidence of the alternating C—C bonds observed in some ruthenium–arene complexes (Begley *et al.*, 1991). Note that the longest Ru—C bond (Ru1—C4; see Table 1) is *trans* with respect to atoms Cl1 and Cl2, as a result of the strong *trans* influence of this group.

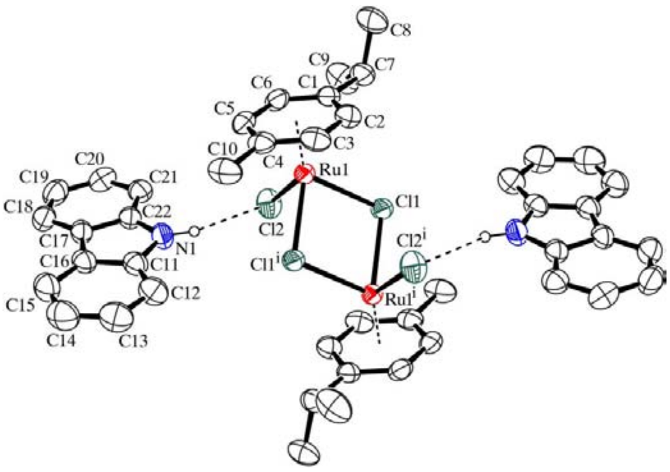


**Figure 1**
A view of complex (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, -y + 1, -z$.]

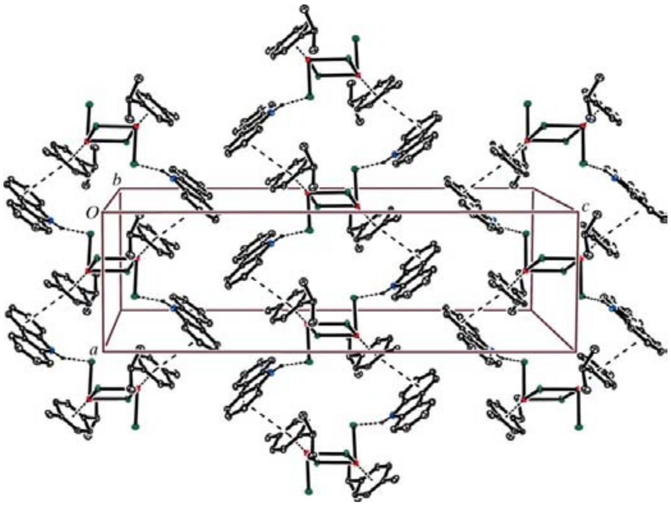


**Figure 2**
Part of the crystal structure of (I), showing the formation of one-dimensional linear chains of star-shaped edge-fused rings along [100]. For clarity, only H atoms involved in hydrogen bonding have been included.

The two terminal Cl atoms have *trans* orientations with respect to the planar $Ru_2Cl_2$ core. In the dinuclear $Ru_2Cl_2$ core, the Ru1—Cl1, Ru1—Cl1$^i$ and Ru1—Cl2 bond distances are 2.4459 (9), 2.4445 (8) and 2.3956 (10) Å, respectively, while the Ru1—Cl1—Ru1$^i$ and Cl1—Ru1—Cl1$^i$ angles are 97.92 (3) and 82.08 (3)°, respectively. The bridging and terminal Ru—Cl distances agree well with those found in other arene–ruthenium complexes possessing $\mu$-Cl ligands (McCormick & Gleason, 1988; Gupta *et al.*, 1997; Therrien *et al.*, 1998; Bown & Bennett, 1999). There is clearly no Ru—Ru bond in the dimer, the Ru···Ru distance of 3.688 (3) Å being too long to include any metal–metal interaction. The carbazole moiety in (I) is planar, the r.m.s. deviation from the plane being 0.022 Å, and the geometric parameters do not deviate from the standard values for the corresponding heterocyclic systems (Allen *et al.*, 1987).

The geometry and packing arrangement in the crystal structure are quite interesting. There are no intermolecular interactions between molecules in the $b$ or $c$ directions. In the construction of the intermolecular connections along the $a$ axis, the carbazole moieties play an active bridging role. Fig. 2 shows that the molecules are translated linearly along the $a$ axis of the unit cell at $z = 0, \frac{1}{2}$ and 1, and are related to one another by $2_1$ screw symmetry, in which the $2_1$ screw axes are along $(a, \frac{1}{2}, \frac{1}{4})$ and $(a, \frac{1}{2}, \frac{3}{4})$. There are two carbazole moieties between two adjacent dimeric molecules along the $a$ axis, and these are on a line that is perpendicular to the mid-point of the line linking the centres of inversion of each core of the two adjacent dimeric molecules along the [100] direction, and which is parallel to the [001] direction. In this arrangement, each of the two inversion-related carbazole moieties forms an N1—H1···Cl2 contact with one of the two neighbouring dimeric molecules (Table 2) and $\pi$–$\pi$ stacking interactions between the C17–C22 ring of the carbazole moiety and the arene ring of the adjacent dimeric molecule; the arene ring at $(x, y, z)$ stacks above the C17–C22 ring at $(x + 1, y, z)$, with a distance of 3.574 (6) Å between the ring centroids and a perpendicular distance between the rings of 3.387 (5) Å. This arrangement leads to a four-pointed star-shaped ring between two neighbouring dimeric molecules, translated linearly along the $a$ axis of the unit cell. Propagation of this hydrogen-bonding motif generates one-dimensional linear chains of edge-fused rings running parallel to the [100] direction (Fig. 2).

## Experimental

All manipulations were performed under argon using standard Schlenk techniques. $RuCl_3{\cdot}3H_2O$ (Johnson and Mathey), carbazole (Fluka) and ethanol (Merck) were used as received. $[RuCl_2(p\text{-cymene})]_2$ was synthesized according to a published procedure (Bennett & Smith, 1974). An ethanol solution (30 ml) of carbazole

(351 mg, 2.10 mmol) was mixed with $[RuCl_2(p\text{-cymene})]_2$ (612 mg, 1.0 mmol). The reaction mixture was heated on a water bath for 3 h and was concentrated (10 ml). The product crystallized from ethanol. After filtration, the brown crystals were washed with cold ethanol (2 × 5 ml) and diethyl ether (2 × 5 ml) and dried *in vacuo* to give 515 mg (66%) of product (m.p. 440 K). $^1H$ NMR ($\delta$ in p.p.m., 400 MHz, $J$ in Hz, $CDCl_3$): 8.35 (*s*, 2H, NH), 8.06 [*d*, $J = 7.6$, 4H, Cz ArH (Cz is carbazole)], 7.48 (*d*, $J = 7.4$, 4H, Cz ArH), 7.41 (*t*, $J = 7.6$, 4H, Cz ArH), 7.23 (*t*, $J = 7.4$, 4H, Cz ArH), 5.42 (*d*, $J = 5.6$, 4H, *p*-cymene ArH), 5.28 (*d*, $J = 6$, 4H, *p*-cymene ArH), 2.89 [heptet, $J = 6.9$, 2H, $-CH(CH_3)_2$], 2.12 (*s*, 6H, $CH_3$), 1.24 [*d*, $J = 7.2$, $-CH(CH_3)_2$]; $^{13}C$ NMR ($\delta$ in p.p.m., 100 MHz, $CDCl_3$): 139.83, 125.97, 123.52, 120.46, 119.53, 111.08, 101.41, 96.95, 81.51, 80.75, 30.84, 22.34, 19.10.

### *Crystal data*

$[Ru_2Cl_4(C_{10}H_{14})_2]\cdot 2C_{12}H_9N$
$M_r = 946.77$
Orthorhombic, *Pbca*
$a = 8.1427\ (5)$ Å
$b = 18.3212\ (14)$ Å
$c = 27.303\ (3)$ Å
$V = 4073.2\ (6)$ Å$^3$
$Z = 4$
$D_x = 1.544$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 1.04$ mm$^{-1}$
$T = 296$ K
Needle, brown
0.65 × 0.31 × 0.11 mm

### *Data collection*

Stoe IPDS-2 diffractometer
$\omega$ scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min} = 0.803$, $T_{max} = 0.902$
13233 measured reflections
3964 independent reflections
2660 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 26.0°$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.073$
$S = 1.01$
3964 reflections
239 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å$^{-3}$
$\Delta\rho_{min} = -0.42$ e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00090 (8)

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

| | | | |
|---|---|---|---|
| Ru1—C2 | 2.150 (4) | N1—C11 | 1.390 (4) |
| Ru1—C6 | 2.153 (3) | C1—C6 | 1.398 (5) |
| Ru1—C5 | 2.159 (3) | C1—C2 | 1.417 (5) |
| Ru1—C3 | 2.169 (4) | C2—C3 | 1.408 (5) |
| Ru1—C1 | 2.180 (3) | C3—C4 | 1.409 (5) |
| Ru1—C4 | 2.193 (3) | C4—C5 | 1.398 (5) |
| N1—C22 | 1.373 (4) | C5—C6 | 1.423 (5) |
| | | | |
| Cl2—Ru1—Cl1$^i$ | 86.05 (4) | Cl1$^i$—Ru1—Cl1 | 82.08 (3) |
| Cl2—Ru1—Cl1 | 86.33 (4) | | |

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

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···Cl2 | 0.86 | 2.63 | 3.381 (3) | 146 |

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96, 0.98, 0.93 and 0.86 Å for $CH_3$, CH, aromatic and NH groups, respectively. The displacement parameters of the H atoms were constrained as $U_{iso}(H) = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl) of the carrier atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

This study was supported financially by the Research Centre of Ondokuz Mayıs University (project No. F-366).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3009). Services for accessing these data are described at the back of the journal.

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