metal-organic papers

Di-μ-chloro-bis[chloro(η^6-1,2,4-trimethyl-benzene)ruthenium(II)]–dichloromethane (3/2)

Bruno Therrien* and Georg Süss-Fink

Institut de Chimie, Université de Neuchâtel, Case postale 2, CH-2007 Neuchâtel, Switzerland

Correspondence e-mail:
bruno.therrien@unine.ch

Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.014 Å
H-atom completeness 72%
R factor = 0.052
wR factor = 0.136
Data-to-parameter ratio = 16.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The *meso* form of the title planar chiral dinuclear arene–ruthenium complex, [Ru$_2$Cl$_4$(C$_9$H$_{12}$)$_2$]·0.67CH$_2$Cl$_2$, is presented. There are one and a half independent dinuclear complexes and one dichloromethane molecule per asymmetric unit. The 1,2,4-trimethylbenzene ligands are involved in slipped-parallel π–π stacking interactions with neighbouring molecules, thus forming a series of one-dimensional multimers along the a axis.

Comment

1,2,4-Trimethylcyclohexadiene, accessible by standard Birch reduction, reacts with RuCl$_3$·nH$_2$O in refluxing ethanol to afford quantitatively the unsolvated title compound [(1,2,4-Me$_3$C$_6$H$_3$)RuCl(μ-Cl)]$_2$, (I) (Therrien & Süss-Fink, 2004). Coordination of 1,2,4-trimethylbenzene to the Ru atom introduces a planar chirality at the η^6-arene ligand. Thus, the dinuclear complex (I) is present as a mixture of three species, two enantiomers and a *meso* form. Crystals of the *meso* form (see scheme) were obtained as a solvate by slow evaporation of a dichloromethane solution containing the isomeric mixture of (I).

(I)
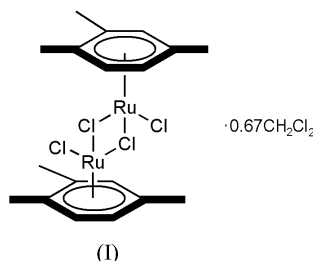
The complex crystallizes in the centrosymmetric space group $P\bar{1}$, with one and a half independent dinuclear complexes and one dichloromethane molecule per asymmetric unit. The half molecule is related by a crystallographic inversion centre to a second arene–ruthenium moiety and joined by two Cl atoms to form a second dimeric complex. The centrosymmetric dimer (A), as well as the dinuclear complex which lies in a general position (B), are shown in Fig. 1.

All Ru atoms possess a distorted octahedral geometry, surrounded by the η^6-1,2,4-trimethylbenzene ligand, a terminal Cl atom and two bridging Cl atoms. The metrical parameters around the metallic cores compare well with those of similar dinuclear η^6-arene–ruthenium [RuCl$_2$(η^6-arene)]$_2$ complexes, *viz.* arene = hexamethylbenzene (McCormick & Gleason, 1988), arene = trindane (Gupta *et al.*, 1997), arene = ethylbenzoate (Therrien *et al.*, 1998), arene = 1,2,3,4-tetrahydronaphthalene (Bown & Bennett, 1999) and arene = indane (Vieille-Petit *et al.*, 2002). In the centrosymmetric molecule (A), the two 1,2,4-trimethylbenzene rings are
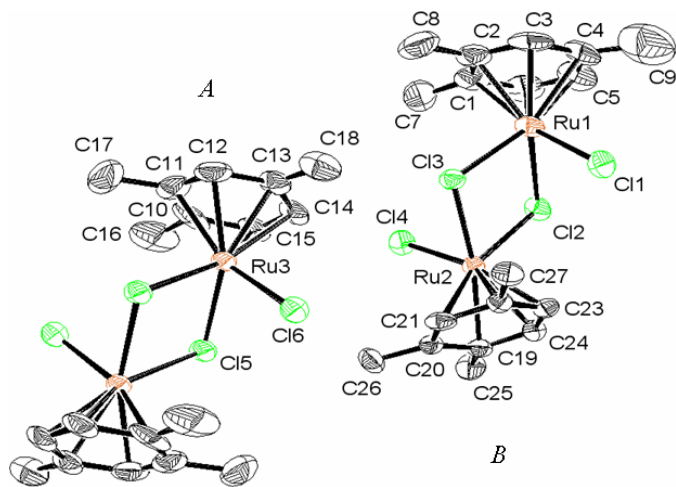
Figure 1
ORTEP-3 drawing (Farrugia, 1997) of the *meso* form of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and the dichloromethane molecule have been omitted for clarity. Unlabeled atoms in molecule A are related to labeled atoms by $(2 - x, 1 - y, 1 - z)$.
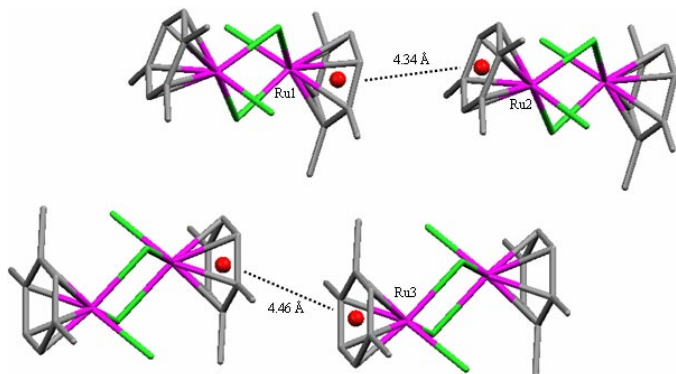

Figure 3
The molecular packing viewed almost along the *a* axis, showing the environment of multimers *A* and *B* (MERCURY; Bruno *et al.*, 2002). Dichloromethane molecules have been omitted for clarity.

Figure 2
The two π-stacking interactions involved in the crystalline packing (MERCURY; Bruno *et al.*, 2002).

Figure 4
The hydrogen-bonded network between two dinuclear complexes and two dichloromethane molecules (MERCURY; Bruno *et al.*, 2002).

parallel as demanded crystallographically; however, in molecule *B* the angle between the two rings is 10.5 (2)°. The Ru⋯Ru distances of 3.728 (1) (molecule *A*) and 3.695 (1) Å (molecule *B*) are too long to be considered as metal–metal single bonds.

The geometry and packing arrangement in the crystal structure is quite interesting. Two independent slipped-parallel π-stacking interactions are observed, involving the benzene rings of both molecules. These interactions are shown in Fig. 2. The distance observed between the π–π interacting systems (centroid–centroid = 4.46 and 4.34 Å) are slightly longer than the theoretical value calculated for this stacking mode (Tsuzuki *et al.*, 2002). The π-stacking interacting systems form a series of one-dimensional supramolecular multimers along the *a* axis (see Fig. 3). The supramolecular chains, which are formed by *A* and *B* molecules, respectively, possess different environments. The *A* multimer is surrounded by four rows of *B* multimers, whereas the *B* multimer is surrounded by *A* and *B* multimers, as well as dichloromethane molecules. The solvent molecules are found in the void left between chains of *B* multimer. Indeed, the solvent interacts with a terminal Cl
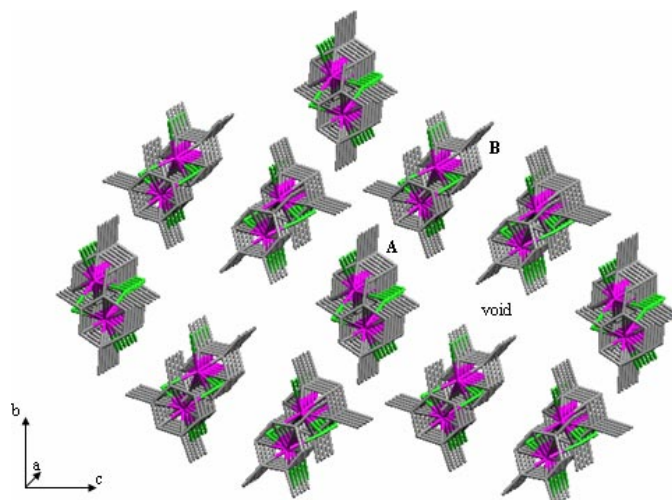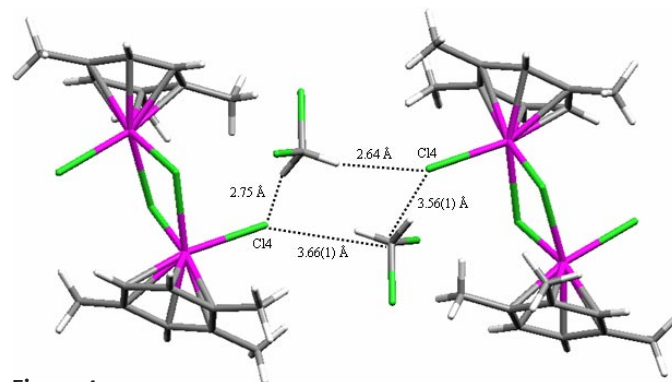
atom of molecule *B*. Two dichloromethane molecules form a weak hydrogen-bonded network with two dinuclear complexes, see Fig. 4. The Cl—C distances of the hydrogen bonds are, respectively, 3.66 (1) and 3.56 (1) Å, with C—H⋯Cl angles of 156.6 and 158.9°. The total distance between the two Cl atoms is 5.981 (4) Å.

Experimental

The title compound was prepared according to a published method (Therrien & Süss-Fink, 2004). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a dichloromethane solution.

Crystal data

$C_{18}H_{24}Cl_4Ru_2 \cdot 0.67CH_2Cl_2$	$Z = 3$
$M_r = 640.93$	$D_x = 1.886$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.9388$ (11) Å	Cell parameters from 7734
$b = 12.3703$ (13) Å	reflections
$c = 14.4034$ (17) Å	$\theta = 2.1–25.8°$
$\alpha = 97.105$ (13)°	$\mu = 1.97$ mm^{-1}
$\beta = 90.644$ (13)°	$T = 153$ (2) K
$\gamma = 105.358$ (12)°	Plate, orange
$V = 1692.7$ (3) Å^3	$0.57 \times 0.36 \times 0.14$ mm

Stoe IPDS diffractometer	3899 reflections with $I > 2\sigma(I)$
φ scans	$R_{int} = 0.062$
Absorption correction: multi-scan	$\theta_{max} = 25.8°$
(Blessing, 1995)	$h = -12 \rightarrow 12$
$T_{min} = 0.463$, $T_{max} = 0.759$	$k = -14 \rightarrow 14$
12013 measured reflections	$l = -17 \rightarrow 17$
6090 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0745P)^2]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} < 0.001$
6090 reflections	$\Delta\rho_{max} = 1.61$ e Å^{-3}
361 parameters	$\Delta\rho_{min} = -1.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—Ru1	2.384 (2)	Cl4—Ru2	2.398 (2)
Cl2—Ru1	2.446 (2)	Cl5—Ru3^i	2.4404 (18)
Cl2—Ru2	2.4461 (17)	Cl5—Ru3	2.449 (2)
Cl3—Ru1	2.4380 (17)	Cl6—Ru3	2.396 (2)
Cl3—Ru2	2.4423 (18)		
Ru1—Cl2—Ru2	98.13 (6)	Cl4—Ru2—Cl3	86.82 (7)
Ru1—Cl3—Ru2	98.44 (6)	Cl4—Ru2—Cl2	86.97 (7)
Ru3^i—Cl5—Ru3	99.36 (7)	Cl3—Ru2—Cl2	81.01 (6)
Cl1—Ru1—Cl3	87.82 (7)	Cl6—Ru3—Cl5	87.15 (7)
Cl1—Ru1—Cl2	86.79 (7)	Cl5^i—Ru3—Cl5	80.64 (7)
Cl3—Ru1—Cl2	81.11 (6)		

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

H atoms were included in calculated positions (C—H = 0.93–0.97 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTE-GRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bown, M. & Bennett, M. A. (1999). *Acta Cryst.* C**55**, 852–854.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gupta, H. K., Lock, P. E., Hughes, D. W. & McGlinchey, M. J. (1997). *Organometallics*, **16**, 4355–4361.
McCormick, F. B. & Gleason, W. B. (1988). *Acta Cryst.* C**44**, 603–605.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. Release 97-2. University of Göttingen, Germany.
Stoe & Cie (2000). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.
Therrien, B., Ward, T. R., Pilkington, M., Hoffmann, C., Gilardoni, F. & Weber, J. (1998). *Organometallics*, **17**, 330–337.
Therrien, B. & Süss-Fink, G. (2004). *Inorg. Chim. Acta*, **357**, 219–224.
Tsuzuki, S., Honda, K., Uchimura, T., Mikami, M. & Tanabe, K. (2002) *J. Am. Chem. Soc.* **124**, 104–112.
Vieille-Petit, L., Therrien, B. & Süss-Fink, G. (2002). *Acta Cryst.* E**58**, m656–m657.