

# The first metalloporphyrin dimer linked by a bridging phenylene-dicarbene ligand

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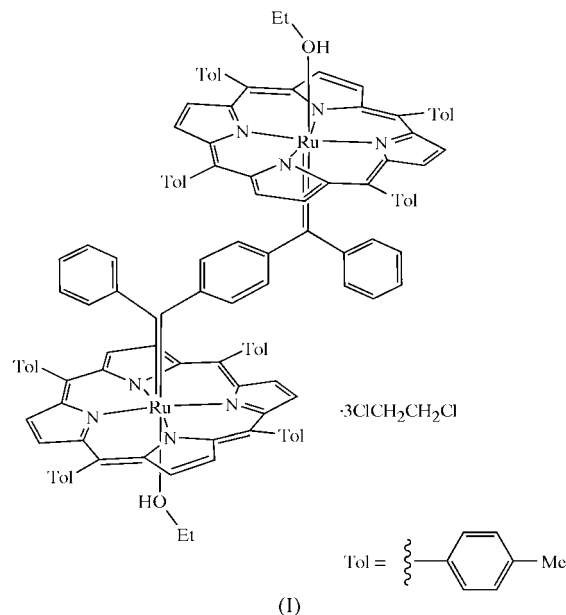
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In the first bis[ruthenium(II)–porphyrin]–dicarbene complex,  $\mu$ -[1,4-phenylenebis(phenylmethylidene- $\kappa$ C)]bis[(ethanol- $\kappa$ O)-(5,10,15,20-tetra-*p*-tolylporphyrinato- $\kappa^4$ N)ruthenium(II)] 1,2-dichloroethane trisolvate,  $[\text{Ru}_2(\text{C}_{20}\text{H}_{14})(\text{C}_{48}\text{H}_{36}\text{N}_4)_2(\text{C}_2\text{H}_6\text{O})_2] \cdot 3\text{C}_2\text{H}_4\text{Cl}_2$ , an inversion center is located at the center of the  $\mu$ -phenylene group, leading to a parallel arrangement for the pair of porphyrin ring systems. The bond lengths and angles compare favourably with literature values for ruthenium–porphyrin–monocarbene complexes; the  $\text{Ru}=\text{C}(\text{carbene})$  bond length and the  $\text{C}(\text{phenyl})-\text{C}(\text{carbene})-\text{C}(\text{phenylene})$  angle are 1.865 (3) Å and 112.3 (3)°, respectively. The  $\text{Ru}^{\text{II}}$  ion is displaced out of the  $\text{C}_{20}\text{N}_4$  porphyrin least-squares plane (by 0.2373 Å) toward the bridging ligand of the  $C_i$ -symmetry dimer. The porphyrin ring systems of the dimer thus exhibit mildly domed conformations.

## Comment

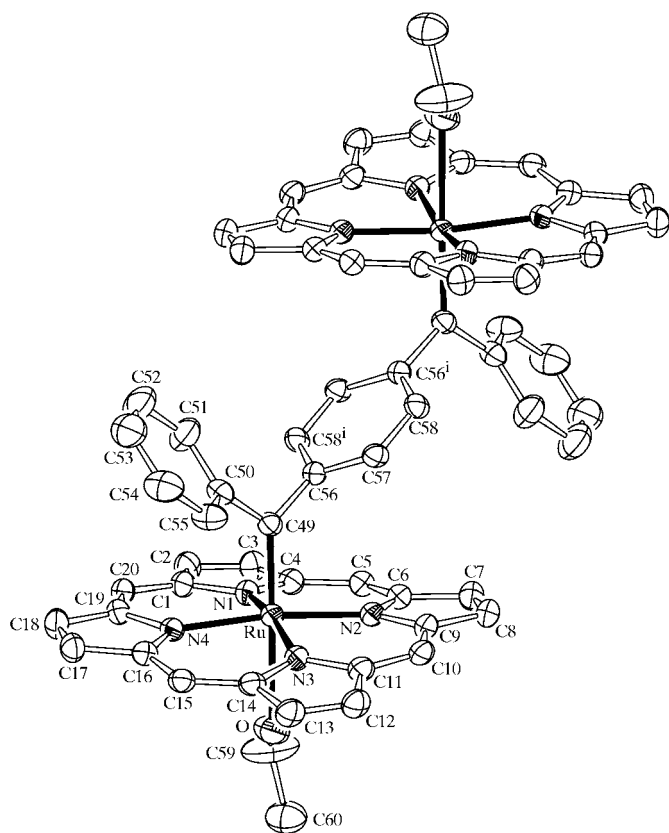
A number of ruthenium(II)–porphyrin–carbene complexes, which are fairly stable in air at room temperature, have been developed in the past decade. Our group has structurally characterized some of these compounds, namely a methanol-bonded diphenylcarbene complex  $[\text{Ru}(\text{ttp})(=\text{CPh}_2)(\text{MeOH})] \cdot \text{MeOH}$  ( $\text{H}_2\text{ttp}$  is 5,10,15,20-tetra-*p*-tolylporphyrin; Kawai *et al.*, 2002), six-coordinate pyridine adducts  $[\text{Ru}(\text{ttp})(=\text{CR}_2)(\text{py})]$  ( $R = \text{COPh}$  and *m*- $\text{C}_6\text{H}_4\text{CF}_3$ ; Harada *et al.*, 2003) and a five-coordinate complex  $[\text{Ru}(\text{ttp})\{\text{C}(\text{m}-\text{C}_6\text{H}_4\text{CF}_3)_2\}]$  (Wada *et al.*, 2003). These carbene ligands were generally prepared from ketones *via* hydrazone and diazomethylene compounds. According to analogous procedures, some  $\mu$ -phenylene-bridging dicarbene complexes have already been synthesized (Herrmann *et al.*, 1984; Werner *et al.*, 1997), but their structural features have not been reported so far. In order to investigate the structural details of the dicarbene complex, we have carried out a synthesis and structure

determination of the first metalloporphyrin dimer, (I), linked by a  $\mu$ -phenylene-bridging dicarbene ligand.



As shown Fig. 1, an inversion center positioned at the centroid of the  $\mu$ -phenylene group of the centrosymmetric bis[ruthenium(II)–porphyrin]–dicarbene complex effects a parallel arrangement for the pair of porphyrin ring systems. The asymmetric unit includes one-half of the binuclear molecule and 1.5 molecules of 1,2-dichloroethane solvent. The bond lengths and angles in (I) are comparable to literature data for the ruthenium–porphyrin–monocarbene complexes reported to date (Li *et al.*, 2004). The geometry about the Ru and carbene C atoms in (I) is similar to that reported for  $[\text{Ru}(\text{ttp})(=\text{CPh}_2)(\text{MeOH})] \cdot \text{MeOH}$ , (II) (Kawai *et al.*, 2002). Moreover, the six-coordinate Ru atom is bonded by the hydroxy O atom of an ethanol ligand *trans* to the carbene C atom in each of (I) and (II). The Ru–O bond length of 2.417 (3) Å in (I) is longer than that of 2.362 (3) Å in (II). The carbene angle  $[\text{C}50-\text{C}49-\text{C}56 = 112.3 (3)^\circ]$  in (I) is very close to that of  $112.2 (3)^\circ$  in (II). The  $\text{Ru}=\text{C}(\text{carbene})$  bond length ( $\text{Ru}=\text{C}49$ ) of 1.865 (3) Å in (I) is slightly longer than that of 1.845 (3) Å in (II).

The phenyl groups of (I) are connected to the carbene donor C atoms and tilted relative to the phenylene group of the dicarbene ligand, while the phenylene group itself is oriented almost perpendicular to the carbene plane (Table 1), consistent with the phenyl group arrangements in (II). The torsion angles in (I) about the  $\text{C}(\text{carbene})-\text{C}(\text{phenyl})$  and  $\text{C}(\text{carbene})-\text{C}(\text{phenylene})$  formal single bonds are considerably larger than the corresponding angles of  $23.5 (5)^\circ$  and  $36.9 (5)^\circ$  in 1,4-dibenzoylbenzene (Kolev *et al.*, 1992), and  $30.5 (2)^\circ$  and  $39.5 (2)^\circ$  in 1,4-bis(phenylvinyl)benzene (Klokenburg *et al.*, 2003) bearing 1,4-phenylenebis(phenylmethylidene) skeletons. The tilted phenyl group in (I) seems to repel the  $\text{C}21-\text{C}27$  *p*-tolyl group of the opposite porphyrin. The dihedral angles between the porphyrin  $\text{C}_{20}\text{N}_4$  core and the *p*-tolyl groups in (I) and (II) are within their usual ranges, *viz.*

**Figure 1**

The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. The 1,2-dichloroethane solvent molecules and the *p*-tolyl groups of the porphyrinate ligands have been omitted for clarity. All H atoms and the C atoms of the minor fragment of the disordered ethanol ligand have also been omitted. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]

81.05 (13), 63.14 (16), 66.66 (13) and 79.56 (13)° in (I), and 64.80 (8), 61.31 (10), 75.19 (11) and 88.44 (14)° in (II). As the Ru<sup>II</sup> ion is displaced out of the least-squares plane toward the carbene C atom by 0.2373 (8) Å in (I), the porphyrin core is deformed in a dome conformation, with maximum and minimum deviations from the C<sub>20</sub>N<sub>4</sub> least-squares plane of 0.187 (4) and −0.301 (4) Å for atoms C8 and C13, respectively.

## Experimental

The dicarbene precursor, *viz.* 1,4-bis(diazobenzyl)benzene, was prepared according to the method of Murray & Trozzolo (1961). A solution of [Ru(tp)(CO)] (144 mg, 180 μmol) and 1,4-bis(diazobenzyl)benzene (23 mg, 74 μmol) in *n*-octane (50 ml) was refluxed under a nitrogen atmosphere for 3 h. After removal of the volatiles *in vacuo*, the residue was chromatographed on a silica-gel column with a CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane mixture (2:1 *v/v*). An intense red band was collected and evaporated to dryness. Recrystallization from a 1,2-dichloroethane/ethanol solution gave air-stable dark-red crystals of (I) (yield 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.79 (s, 4H), 2.52 (s, 24H), 2.84 (*d*, *J* = 7.2 Hz, 4H), 6.19 (*t*, *J* = 7.8 Hz, 4H), 6.54 (*t*, *J* = 7.2 Hz, 2H), 7.09–7.16 (*m*, 16H), 7.27 (*d*, *J* = 8.1 Hz, 8H), 7.64 (*d*, *J* = 6.4 Hz, 8H), 7.91 (s, 16H). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) 397 (5.34), 427 (5.15), 532 (4.38). An analogous dicarbene complex, [[Ru(tp)]<sub>2</sub>·{C(=CCF<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)}], was successfully synthesized in 50% yield,

starting from [Ru(tp)(CO)] and 1,4-bis(2,2,2-trifluorodiazoethyl)benzene. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.85 (s, 4H), 2.61 (s, 24H), 7.26 (*d*, *J* = 6.9 Hz, 8H), 7.36 (*d*, *J* = 6.9 Hz, 8H), 7.44 (*d*, *J* = 6.9 Hz, 8H), 7.74 (*d*, *J* = 6.9 Hz, 8H), 8.22 (s, 16H). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 470 MHz): δ −66.09 (s). UV–vis (C<sub>6</sub>H<sub>6</sub>): λ<sub>max</sub> (log ε) 401 (5.38), 533 (4.16). Unfortunately, crystals suitable for X-ray diffraction have not yet been obtained in spite of our best efforts.

## Crystal data

[Ru<sub>2</sub>(C<sub>20</sub>H<sub>14</sub>)(C<sub>48</sub>H<sub>36</sub>N<sub>4</sub>)<sub>2</sub>·  
(C<sub>2</sub>H<sub>6</sub>O)<sub>2</sub>]·3C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>  
*M*<sub>r</sub> = 2183.06  
Triclinic, *P* $\bar{1}$   
*a* = 14.786 (4) Å  
*b* = 15.816 (4) Å  
*c* = 13.879 (3) Å  
 $\alpha$  = 98.15 (2)°  
 $\beta$  = 109.047 (19)°

$\gamma$  = 114.12 (2)°  
*V* = 2653.8 (14) Å<sup>3</sup>  
*Z* = 1  
*D*<sub>x</sub> = 1.366 Mg m<sup>−3</sup>  
Mo *K*α radiation  
 $\mu$  = 0.49 mm<sup>−1</sup>  
*T* = 296 (2) K  
Prism, dark red  
0.50 × 0.45 × 0.18 mm

## Data collection

Rigaku AFC-7R diffractometer  
 $\omega/2\theta$  scans  
Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)  
*T*<sub>min</sub> = 0.791, *T*<sub>max</sub> = 0.917  
12659 measured reflections  
12189 independent reflections

7914 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.023  
 $\theta_{\text{max}}$  = 27.5°  
3 standard reflections  
every 150 reflections  
intensity decay: none

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.048  
*wR* (*F*<sup>2</sup>) = 0.141  
*S* = 1.01  
12189 reflections  
663 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 1.3374P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
(Δ/σ)<sub>max</sub> = 0.001  
Δρ<sub>max</sub> = 0.44 e Å<sup>−3</sup>  
Δρ<sub>min</sub> = −0.63 e Å<sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ru1–N1	2.046 (3)	Ru1–N4	2.050 (3)
Ru1–N2	2.046 (3)	Ru1–C49	1.865 (3)
Ru1–N3	2.051 (3)	Ru1–O1	2.417 (3)
N1–Ru1–N2	89.84 (11)	N4–Ru1–O1	86.54 (12)
N1–Ru1–N3	168.18 (11)	C49–Ru1–N1	90.83 (13)
N1–Ru1–N4	89.90 (11)	C49–Ru1–N2	94.10 (13)
N2–Ru1–N3	89.56 (12)	C49–Ru1–N3	100.99 (13)
N2–Ru1–N4	172.57 (11)	C49–Ru1–N4	93.32 (13)
N3–Ru1–N4	89.18 (11)	C49–Ru1–O1	174.05 (13)
N1–Ru1–O1	83.22 (11)	C50–C49–C56	112.3 (3)
N2–Ru1–O1	86.05 (12)	Ru1–C49–C56	122.2 (3)
N3–Ru1–O1	84.96 (12)	Ru1–C49–C50	125.3 (2)
Ru1–C49–C50–C55	51.5 (5)	Ru1–C49–C56–C58 <sup>i</sup>	87.8 (4)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y, -z$ ; (iii)  $-x + 2, -y + 1, -z + 1$ .

At a late stage in the refinement, positional disorder of the C59/C60 ethyl group of the ethanol ligand and the C63 methylene group of the 1,2-dichloroethane solvent was suggested by their large *U*<sub>11</sub> and *U*<sub>22</sub> values. A disordered model over two sites was adopted, where the C atoms of the minor fragments (C59<sup>2</sup>, C60<sup>2</sup> and C63<sup>2</sup>) were found in a Fourier map. The displacement parameters of the major fragments (C59, C60 and C63) were refined anisotropically, and those of the minor fragments were treated isotropically. The C1–C and C–C bond lengths of the 1,2-dichloroethane solvent molecules were restrained to 1.79 (2) and 1.53 (3) Å, respectively. The site-occupancy

factors of the major fragments of the C59/C60 ethyl and C63 methylene groups converged to respective values of 0.595 (18) and 0.68 (3), and those of the minor fragments to 0.405 (18) and 0.32 (3). All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with O—H bond lengths of 0.82 Å, C—H bond lengths of 0.96, 0.97 and 0.93 Å for CH<sub>3</sub>, CH<sub>2</sub> and aromatic CH groups, respectively, and  $U_{\text{iso}}(\text{H})$  values of  $1.5U_{\text{eq}}(\text{O or methyl C})$  or  $1.2U_{\text{eq}}(\text{methylene or aromatic C})$ .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MS, 2005); 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: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MY3011). Services for accessing these data are described at the back of the journal.

## References

- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Harada, T., Wada, S., Yuge, H. & Miyamoto, T. K. (2003). *Acta Cryst.* **C59**, m37–m39.
- Herrmann, W. A., Plank, J., Kriechbaum, G. W., Ziegler, M. L., Pfisterer, H., Atwood, J. L. & Rogers, R. D. (1984). *J. Organomet. Chem.* **264**, 327–352.
- Kawai, M., Yuge, H. & Miyamoto, T. K. (2002). *Acta Cryst.* **C58**, m581–m582.
- Klokkenburg, M., Lutz, M., Spek, A. L., van der Maas, J. H. & van Walree, C. A. (2003). *Chem. Eur. J.* **9**, 3544–3554.
- Kolev, T., Preut, H., Bleckmann, P. & Juchnovski, I. (1992). *Acta Cryst.* **C48**, 1715–1717.
- Li, Y., Huang, J.-S., Xu, G.-B., Zhu, N., Zhou, Z.-Y., Che, C.-M. & Wong, K.-Y. (2004). *Chem. Eur. J.* **10**, 3486–3502.
- Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. Version 5.1.0. MSC, The Woodlands, Texas, USA.
- Murray, R. W. & Trozzolo, A. M. (1961). *J. Org. Chem.* **26**, 3109–3112.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rigaku/MS (2005). *CrystalStructure*. Version 3.7.0. Rigaku/MS Inc., The Woodlands, Texas, USA.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXL97*. University of Göttingen, Germany.
- Wada, S., Yuge, H. & Miyamoto, T. K. (2003). *Acta Cryst.* **C59**, m369–m370.
- Werner, H., Schwab, P., Bleuel, E., Mahr, N., Steinert, P. & Wolf, J. (1997). *Chem. Eur. J.* **3**, 1375–1384.