

A ruthenium(II)–porphyrin–carbene complex with a weakly bonded methanol ligand

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The title diphenylcarbene porphyrin complex (diphenylcarbenyl- κC)(methanol- κO)(5,10,15,20-tetra-*p*-tolylporphyrinato- $\kappa^4 N$)ruthenium(II) methanol solvate, $[\text{Ru}(\text{C}_{13}\text{H}_{10})(\text{C}_{48}\text{H}_{36}\text{N}_4)(\text{CH}_4\text{O})]\cdot\text{CH}_4\text{O}$, has a six-coordinate Ru atom with a methanol molecule as the second axial ligand. The carbene fragment is slightly distorted from an ideal sp^2 configuration, with a C(phenyl)–C(carbene)–C(phenyl) angle of 112.2 (3)°. The Ru–C bond length of 1.845 (3) Å is comparable with other carbene complexes. The two phenyl rings of the carbene ligand are perpendicular to the carbene plane. Methanol solvate molecules link the methanol ligands of adjacent porphyrin complexes *via* hydrogen bonds.

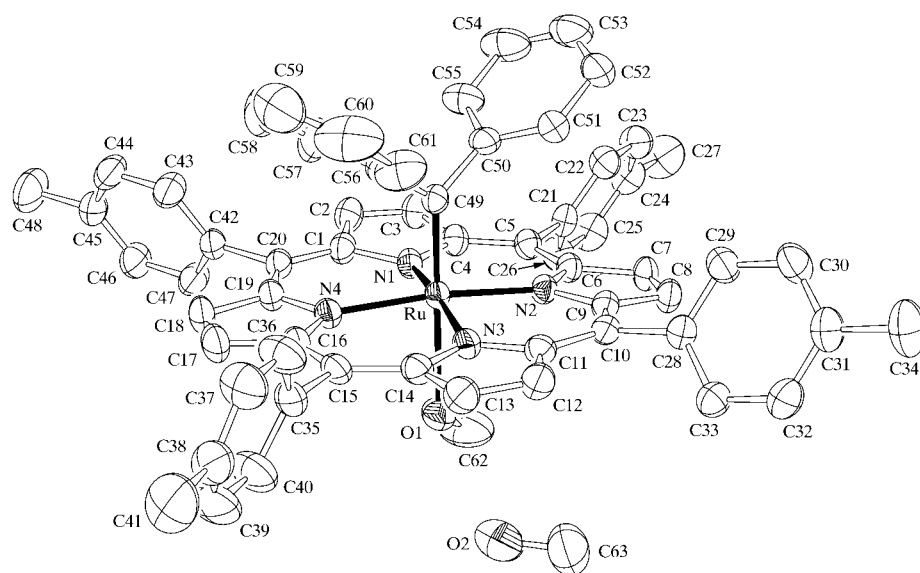
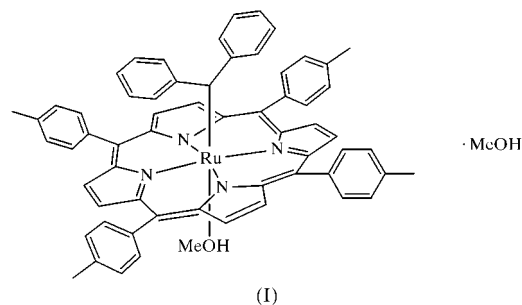


Figure 1

The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

Comment

Ruthenium–carbene complexes have attracted much attention in recent years as catalysts of the cyclopropanation of olefins (Trost *et al.*, 2001). Some ruthenium–porphyrin–carbene complexes have been reported as effective catalysts because of their higher stereoselectivity and turnover numbers. However, ruthenium–porphyrin–carbene complexes are so unstable that, since the initial investigation by Collman *et al.* (1985), they have only been characterized using UV–visible or NMR spectroscopy. The first crystal structure of a ruthenium(II)–porphyrin–carbene complex, *viz.* $[\text{Ru}(\text{tpp})\{\text{C}(\text{CO}_2\text{Et})_2\}(\text{CH}_3\text{OH})]\cdot\text{H}_2\text{O}$, (II) (H_2tpp is 5,10,15,20-tetraphenylporphyrin),



was determined by Galardon *et al.* (1998). A methanol molecule was bound to the six-coordinate Ru atom *trans* to the carbene ligand and could be replaced by other ligands, such as PPh_3 , pyridine or CO, in solution. Che *et al.* (2001) reported that ruthenium(II)–porphyrin diphenyl- or phenyl(allyloxy-carbonyl)carbene complexes, recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ in air, contained five-coordinate Ru atoms in the crystalline state. Both cases show that carbene complexes without α - and β -H atoms would be stable enough for isolation and crystallization even in air. We have synthesized a simple carbene complex, $[\text{Ru}(\text{ttp})(\text{CPh}_2)(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}$ (H_2ttp is 5,10,15,20-tetra-*p*-tolylporphyrin) (I), and here we compare its structure with those of some other ruthenium(II)–porphyrin–carbene complexes.

As shown in Fig. 1, the Ru atom is six-coordinate in (I), similar to (II), while the Ru atoms are square-pyramidally five-coordinate in $[\text{Ru}(\text{P}^*)(\text{CPh}_2)]\cdot 2\text{CH}_2\text{Cl}_2$, (III), and $[\text{Ru}(\text{P}^*)\{\text{C}(\text{Ph})\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2\}]\cdot 3\text{CH}_2\text{Cl}_2$, (IV) [H_2P^* is 5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrin} (Che *et al.*, 2001). The Ru–C(carbene) bond length in (I) is similar to that in (II) [1.829 (9) Å], and the Ru–N(porphyrin) bond lengths are also within the range previously reported for ruthenium(II)–porphyrin complexes. A methanol molecule is bonded to the Ru atom *trans* to the

carbene ligand, and is associated with two other methanol solvate molecules through hydrogen bonding. The Ru—O(methanol) bond length in (I) is significantly longer than that in (II) [2.293 (6) Å], perhaps due to these hydrogen bonds.

The carbene fragment in (I) is distorted from an ideal sp^2 configuration, as the C(phenyl)—C(carbene)—C(phenyl) angle is 112.2 (3)°, similar to that in the diphenylcarbene complex (III) [112.1 (5)°]. The two phenyl groups are oriented perpendicular to the plane of the carbene fragment, adopting a face-to-face arrangement, as observed in (III). The projection of the phenyl groups on to the porphyrin plane reveals a staggered configuration with regard to the Ru—N bonds; the N2—Ru—C49—C50 and N4—Ru—C49—C56 torsion angles are 27.1 (3) and 26.4 (3)°, respectively. Because of steric repulsion between the porphyrin group and the phenyl groups of the carbene ligand, the porphyrin system in (I) is slightly distorted into a saddle conformation, whereas those of (III) and (IV) in the square-pyramidal configuration are severely distorted. The largest deviations from the $C_{20}N_4$ least-squares plane in (I) are -0.187 (4) and 0.180 (3) Å for atoms C2 and C7, respectively. The Ru atom is slightly out of this least-squares plane by 0.1139 (7) Å towards the carbene ligand, close to the value of 0.12 Å in (II), but less than the values of 0.19 and 0.22 Å in (III) and (IV), respectively.

Experimental

The title compound was prepared according to the procedure of Galardon *et al.* (1998). A CH_2Cl_2 solution containing equimolar amounts of $[Ru(ttp)(CO)(CH_3OH)]$ and the diaza compound $N_2=CPh_2$ was refluxed under N_2 for 3 h. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with toluene as eluant. The compound is stable in air at room temperature. Crystals of (I) suitable for X-ray diffraction were prepared by recrystallization from CH_2Cl_2/CH_3OH .

Crystal data

| | |
|--|---|
| $[Ru(C_{13}H_{10})(C_{48}H_{36}N_4)(CH_4O)] \cdot CH_4O$ | $D_x = 1.295 \text{ Mg m}^{-3}$ |
| $M_r = 1000.17$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 25 reflections |
| $a = 12.4608 (12) \text{ \AA}$ | $\theta = 14.4\text{--}15.0^\circ$ |
| $b = 17.744 (2) \text{ \AA}$ | $\mu = 0.35 \text{ mm}^{-1}$ |
| $c = 23.7491 (13) \text{ \AA}$ | $T = 296 (2) \text{ K}$ |
| $\beta = 102.428 (6)^\circ$ | Prism, dark red |
| $V = 5128.0 (8) \text{ \AA}^3$ | $0.28 \times 0.14 \times 0.13 \text{ mm}$ |
| $Z = 4$ | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-------------|-------------|-------------|
| Ru—N1 | 2.051 (3) | Ru—N4 | 2.051 (3) |
| Ru—N2 | 2.040 (2) | Ru—C49 | 1.845 (3) |
| Ru—N3 | 2.042 (3) | Ru—O1 | 2.362 (3) |
| N1—Ru—N2 | 89.57 (11) | N4—Ru—O1 | 85.93 (10) |
| N1—Ru—N3 | 171.76 (11) | C49—Ru—N1 | 92.74 (13) |
| N1—Ru—N4 | 89.80 (11) | C49—Ru—N2 | 93.55 (13) |
| N1—Ru—O1 | 87.29 (11) | C49—Ru—N3 | 95.50 (13) |
| N2—Ru—N3 | 89.85 (11) | C49—Ru—N4 | 93.53 (12) |
| N2—Ru—N4 | 172.91 (11) | C49—Ru—O1 | 179.46 (12) |
| N2—Ru—O1 | 86.99 (10) | C50—C49—C56 | 112.2 (3) |
| N3—Ru—N4 | 89.76 (11) | Ru—C49—C50 | 123.5 (2) |
| N3—Ru—O1 | 84.47 (11) | Ru—C49—C56 | 124.2 (2) |

Table 2

Hydrogen-bonding geometry (Å, °).

| | | | | |
|---------------------------------|-------|--------------|--------------|----------------|
| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
| O1—H47 \cdots O2 ⁱ | 0.82 | 1.910 | 2.704 (5) | 163 |
| O2—H51 \cdots O1 | 0.82 | 2.204 | 2.949 (6) | 151 |

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

Data collection

| | |
|--|--------------------------|
| Rigaku AFC-7R diffractometer | $h = -16 \rightarrow 0$ |
| $\omega/2\theta$ scans | $k = 0 \rightarrow 23$ |
| 12 304 measured reflections | $l = -30 \rightarrow 30$ |
| 11 769 independent reflections | 3 standard reflections |
| 6589 reflections with $I > 2\sigma(I)$ | every 150 reflections |
| $R_{int} = 0.030$ | intensity decay: 0.9% |
| $\theta_{max} = 27.5^\circ$ | |

Refinement

| | |
|---------------------------------|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 1.1504P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.128$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.02$ | $\Delta\rho_{max} = 0.46 \text{ e \AA}^{-3}$ |
| 11 769 reflections | $\Delta\rho_{min} = -0.33 \text{ e \AA}^{-3}$ |
| 635 parameters | |
| H-atom parameters constrained | |

The positions of the methanol H atoms were refined as rotating methyl and hydroxy groups, with C—H = 0.96 Å and O—H = 0.82 Å, respectively. All remaining H atoms were placed in geometrically idealized positions, with $Csp^2-H = 0.93 \text{ \AA}$ and $Csp^3-H = 0.96 \text{ \AA}$. The isotropic displacement parameters of all the H atoms were constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C,O)$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); 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: TR1039). Services for accessing these data are described at the back of the journal.

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