

A five-coordinate ruthenium(II)–porphyrin–carbene complex: [bis(3-trifluoromethylphenyl)methylene- κ C](5,10,15,20-tetra-*p*-tolylporphyrinato- κ^4 N)ruthenium(II)

Satoko Wada, Hidetaka Yuge and Takeshi Ken Miyamoto*

Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa 228-8555, Japan
Correspondence e-mail: orgnmtl@kitasato-u.ac.jp

Received 7 July 2003

Accepted 28 July 2003

Online 16 August 2003

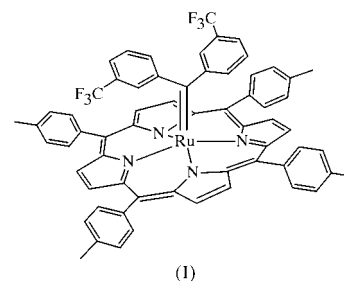
The stable title trifluoromethyl-substituted carbenyl metalloporphyrin, $[\text{Ru}(\text{C}_{15}\text{H}_8\text{F}_6)(\text{C}_{48}\text{H}_{36}\text{N}_4)]$, has a five-coordinate Ru atom which is displaced from the porphyrin N_4 plane towards the axial carbene ligand by 0.230 (3) Å. The Ru–C(carbene) bond coincides with a crystallographic twofold axis and its length of 1.841 (6) Å is notably shorter than the value of 1.868 (3) Å in the pyridine adduct.

Comment

Carbenyl metalloporphyrin chemistry has been developed since the first synthesis of $[(\text{tpp})\text{Fe}(\text{CCl}_2)]$ (where H_2tpp is 5,10,15,20-tetraphenylporphyrin; Mansuy *et al.*, 1977). Ruthenium(II)–porphyrin–carbene complexes have been reported as effective catalysts for the production of alkenes from ethyl diazoacetate (Collman *et al.*, 1993). In order to investigate the catalytic mechanism, it seems important to isolate a five-coordinate ruthenium(II) porphyrin complex, as well as a six-coordinate adduct with a Lewis base. Recently, we studied the structural details of methanol- or pyridine-ligated six-coordinate ruthenium(II)–porphyrin–carbene complexes obtained from CH_2Cl_2 solution containing the relevant Lewis bases (Kawai *et al.*, 2002; Harada *et al.*, 2003). The title compound, $[\text{Ru}(\text{tp})\{\text{C}(3\text{-CF}_3\text{C}_6\text{H}_4)_2\}]$ (where H_2tp is 5,10,15,20-tetra-*p*-tolylporphyrin), (I), having a trifluoromethyl-substituted carbene ligand to facilitate examination by ^{19}F NMR spectroscopy in solution, has been crystallized from CH_2Cl_2 –hexane and is herein compared with its pyridine adduct $[\text{Ru}(\text{tp})\{\text{C}(3\text{-CF}_3\text{C}_6\text{H}_4)_2\}(\text{pyridine})]$, (II) (Harada *et al.*, 2003).

The molecular structure of (I) features a square-pyramidal five-coordinate Ru atom, as shown in Fig. 1, in contrast with the octahedral six-coordinate Ru atom in (II). In (I), the Ru–C25 bond coincides with a crystallographic twofold axis so that

the two 3- CF_3 groups of the carbene ligand adopt an *anti* conformation, resulting in a face-to-face arrangement with the porphyrin plane. The Ru=C bond length of 1.841 (6) Å in (I) is notably shorter than the value of 1.868 (3) Å in (II). Based on UV–vis and ^1H NMR spectroscopy, Galardon *et al.* (1998) described how excessive addition of pyridine to a ruthenium(II)–porphyrin–carbene complex caused dissociation of the carbene ligand. Destabilization of the Ru=C bond by the pyridine ligand seems consistent with the longer Ru=C bond length in (II), due to the *trans* influence of the pyridine ligand.



The angles about carbene atom C25 in (I) [$\text{C}26\text{—C}25\text{—C}26^i = 116.1(5)^\circ$ and $\text{Ru—C}25\text{—C}26 = 121.9(3)^\circ$; symmetry code: (i) $y, x, -z$] are close to the value of 120° for an ideal sp^2 configuration. The porphyrin ring is in a distorted saddle conformation, as reported for two other five-coordinate ruthenium(II)–porphyrin–carbene complexes, *viz.* $[\text{Ru}(\text{P}^*)(\text{CPh}_2)]\text{—}2\text{CH}_2\text{Cl}_2$, (III), and $[\text{Ru}(\text{P}^*)\{\text{C}(\text{Ph})\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2\}]\text{—}3\text{CH}_2\text{Cl}_2$, (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]. In (I), the largest deviations from the C_{20}N_4 least-squares plane are $-0.118(6)$ and $0.060(5)$ Å for atoms C3 and C7, respectively. The Ru atom is displaced out of the N_4 least-squares plane by 0.230 (3) Å toward the carbene ligand, and this is larger than the deviations of 0.19 and 0.22 Å in (III) and (IV), respectively.

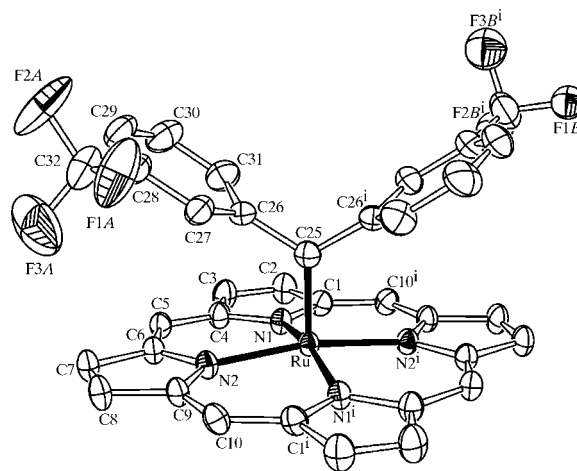


Figure 1

The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. Only one orientation of each disordered CF_3 group is drawn. H atoms and *p*-tolyl groups have been omitted for clarity. [Symmetry code: (i) $y, x, -z$.]

Experimental

The preparation of [(ttp)Ru(CO)] and the diaza compound $N_2=C(3-CF_3C_6H_4)_2$ were carried out according to the procedure of Collman *et al.* (1984) and the modified method for $N_2=CPh_2$ (Smith & Howard, 1955), respectively. A solution of [(ttp)Ru(CO)] (0.50 g, 0.63 mmol) and a small excess of $N_2=C(3-CF_3C_6H_4)_2$ in CH_2Cl_2 (50 ml) was refluxed under a nitrogen atmosphere for 3 h. After removal of the solvent by rotary evaporation, the residue was chromatographed on a silica-gel column with toluene. A dark-red band was collected and evaporated to dryness. Recrystallization from a CH_2Cl_2 -hexane solution gave air-stable dark-purple crystals of (I) (yield: 89%). Analysis found: C 70.35, H 4.03, N 5.09%; calculated for $C_{63}H_{44}F_6N_4Ru$: C 70.58, H 4.14, N 5.23%. 1H NMR (CD_2Cl_2 , 500 MHz, δ , p.p.m.): 2.66 (s, 12H), 3.04 (d, 2H), 3.27 (s, 2H), 6.30 (t, 2H), 6.73 (d, 2H), 7.49 (d, 4H), 7.52 (d, 4H), 7.71 (d, 4H), 7.90 (d, 4H), 8.41 (s, 8H). ^{19}F NMR (CD_2Cl_2 , 470 MHz, δ , p.p.m.): -62.88 (s). UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 398 (4.98), 427 sh (4.66), 537 (3.93).

Crystal data

[Ru(C ₁₅ H ₈ F ₆)(C ₄₈ H ₃₆ N ₄)]	Mo $K\alpha$ radiation
$M_r = 1072.09$	Cell parameters from 25 reflections
Tetragonal, $P4_12_12$	$\theta = 13.4\text{--}14.8^\circ$
$a = 11.817$ (3) Å	$\mu = 0.37$ mm ⁻¹
$c = 36.608$ (4) Å	$T = 296$ (2) K
$V = 5112.0$ (19) Å ³	Prism, intense purple
$Z = 4$	$0.25 \times 0.23 \times 0.20$ mm
$D_x = 1.393$ Mg m ⁻³	

Data collection

Rigaku AFC-7R diffractometer	$h = 0 \rightarrow 15$
ω scans	$k = 0 \rightarrow 10$
6817 measured reflections	$l = -47 \rightarrow 47$
5890 independent reflections	3 standard reflections
4305 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.053$	intensity decay: none
$\theta_{max} = 27.5^\circ$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$\Delta\rho_{max} = 0.52$ e Å ⁻³
$wR(F^2) = 0.142$	$\Delta\rho_{min} = -0.75$ e Å ⁻³
$S = 1.02$	Absolute structure: Flack (1983),
5890 reflections	2333 Friedel pairs
348 parameters	Flack parameter = 0.03 (5)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

Ru—N1	2.036 (4)	Ru—C25	1.841 (6)
Ru—N2	2.053 (3)		
N1—Ru—C25	97.47 (11)	N1—Ru—N2 ⁱ	89.74 (14)
N2—Ru—C25	95.47 (11)	N2—Ru—N2 ⁱ	169.1 (2)
N1—Ru—N1 ⁱ	165.1 (2)	C26—C25—C26 ⁱ	116.1 (5)
N1—Ru—N2	88.84 (14)	Ru—C25—C26	121.9 (3)

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

All H atoms were placed in geometrically idealized positions and were constrained to ride on their parent atoms, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups, or C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other H atoms. At a late stage in the refinement, rotational disorder of the CF_3 group was suggested by the rather large U_{eq} values (0.18–0.22 Å²) of the F atoms and some peaks (0.29–0.35 e Å⁻³) in the difference Fourier map. Accordingly, the CF_3 group was assumed to be disordered over two orientations. The F atoms of the major component (F1A, F2A and F3A) were refined anisotropically and those of the minor component (F1B, F2B and F3B) were treated isotropically. The occupancy factor refined to 0.846 (16) for the major component and 0.154 (16) for the minor component.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Molecular Structure Corporation and Rigaku, 2002); 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: DE1218). Services for accessing these data are described at the back of the journal.

References

- Che, C.-M., Huang, J.-S., Lee, F.-W., Li, Y., Lai, T.-S., Kwong, H.-L., Teng, P.-F., Lee, W.-S., Lo, W.-C., Peng, S.-M. & Zhou, Z.-Y. (2001). *J. Am. Chem. Soc.* **123**, 4119–4129.
- Collman, J. P., Barnes, C. E., Brothers, P. J., Collins, T. J., Ozawa, T., Gallucci, J. C. & Ibers, J. A. (1984). *J. Am. Chem. Soc.* **106**, 5151–5163.
- Collman, J. P., Rose, E. & Venburg, G. D. (1993). *J. Chem. Soc. Chem. Commun.* pp. 934–935.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Galardon, E., Le Maux, P., Toupet, L. & Simonneaux, G. (1998). *Organometallics*, **17**, 565–569.
- Harada, T., Wada, S., Yuge, H. & Miyamoto, T. K. (2003). *Acta Cryst.* **C59**, m37–m39.
- Kawai, M., Yuge, H. & Miyamoto, T. K. (2002). *Acta Cryst.* **C58**, m581–m582.
- Mansuy, D., Lange, M., Chottard, J.-C., Guerin, P., Morliere, P., Brault, D. & Rougee, M. (1977). *J. Chem. Soc. Chem. Commun.* pp. 648–649.
- Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. Version 5.1.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation and Rigaku (2002). *CrystalStructure*. Version 3.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Smith, L. I. & Howard, K. L. (1955). *Org. Synth.* **3**, 351–352.