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The *trans* influence of the pyridine ligand on ruthenium(II)–porphyrin–carbene complexes

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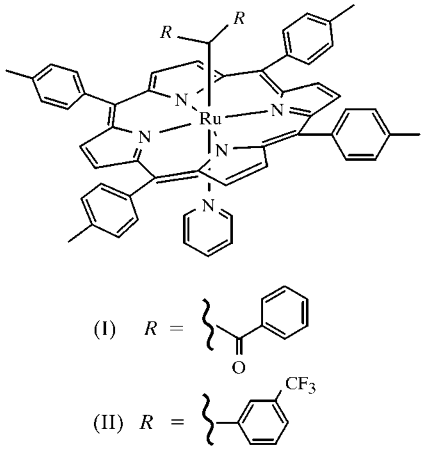
In the two ruthenium(II)–porphyrin–carbene complexes (dibenzoylcarbenyl-κC)(pyridine-κN)(5,10,15,20-tetra-*p*-tolylporphyrinato-κ^4N)ruthenium(II), $[Ru(C_{15}H_{10}O_2)(C_5H_5N)(C_{48}H_{36}N_4)]$, (I), and (pyridine-$\kappa N$)(5,10,15,20-tetra-*p*-tolylporphyrinato-κ^4N)[bis(3-trifluoromethylphenyl)carbenyl-κC]ruthenium(II), $[Ru(C_{15}H_8F_6)(C_5H_5N)(C_{48}H_{36}N_4)]$, (II), the pyridine ligand coordinates to the octahedral Ru atom *trans* with respect to the carbene ligand. The C(carbene)—Ru—N(pyridine) bonds in (I) coincide with a crystallographic twofold axis. The Ru—C bond lengths of 1.877 (8) and 1.868 (3) Å in (I) and (II), respectively, are slightly longer than those of other ruthenium(II)–porphyrin–carbene complexes, owing to the *trans* influence of the pyridine ligands.

Comment

Ruthenium(II)–porphyrin–carbene complexes have been reported as effective catalysts for the production of olefins or cyclopropanes from diazo compounds (Che & Huang, 2002). Assuming that the catalytic reaction would take place *trans* with respect to the carbene ligand, ligand-exchange reactions should play an important role in the study of such catalytic reactions. A large amount of Lewis base, PPh_3, pyridine or CO causes dissociation of the carbene ligand, and the exchange reaction of the axial ligand *trans* to the carbene has been examined using UV–vis spectroscopy in CH_2Cl_2 solution (Galardon *et al.*, 1998). We have synthesized two (porphyrinato)ruthenium(II)–carbene complexes coordinated by a pyridine ligand, [Ru(ttp){C(COPh)$_2$}(py)], (I) and [Ru(ttp){C(3-$C_6H_4CF_3$)$_2$}(py)], (II) (where H_2ttp is 5,10,15,20-tetra-*p*-tolylporphyrin and py is pyridine), and have investigated the *trans* influence of the axial ligands on their molecular structures in the crystalline state.

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. The geometry about the Ru atoms is distorted octahedral in both complexes, and the equatorial Ru—N(porphyrin) bond lengths in (I) and (II) are as expected for ruthenium(II)–porphyrin complexes. The Ru—C bond length in (II) is longer than that in the five-coordinate derivative [Ru(ttp){C(3-$C_6H_4CF_3$)$_2$}] [1.842 (6) Å; Wada *et al.*, 2003]. Compared with analogous ruthenium(II) tetra-*p*-tolylporphyrin and tetraphenylporphyrin (H_2tpp) carbene complexes, the Ru—C bond *trans* to the *N*-donor ligand in (I) and (II) is obviously longer than that *trans* to an *O*-donor; an Ru—C bond length of 1.829 (9) Å was observed in [Ru(tpp){C(CO$_2$Et)$_2$}(CH$_3$OH)]·H$_2$O (Galardon *et al.*, 1998), and a value of 1.845 (3) Å was observed in [Ru(ttp)(CPh$_2$)(CH$_3$OH)]·CH$_3$OH (Kawai *et al.*, 2002). Thus, the *N*-donor ligand seems to have a larger *trans* influence than the *O*-donor ligand in ruthenium(II)–porphyrin–carbene complexes. In addition, the Ru—N bond *trans* to the carbene in (I) and (II) is much longer than that *trans* to a carbonyl group; an Ru—N distance of 2.193 (4) Å was observed in [Ru(tpp)(CO)(py)]·1.5(toluene) (Little & Ibers, 1973). Therefore, the *trans*



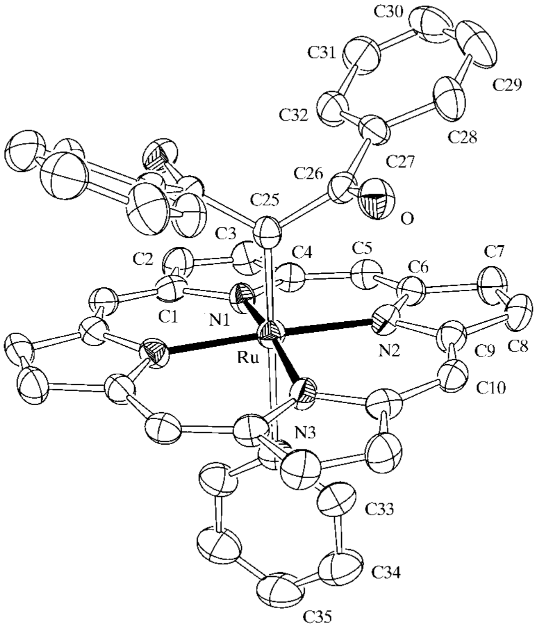


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. H atoms and *p*-tolyl groups have been omitted for clarity.

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influence of the carbene ligand is apparently stronger than that of the carbonyl ligand for (porphyrinato)ruthenium(II) complexes. The Ru—C—C angle about the carbene C atom in (I) is closer to 120° than in (II). The pairs of benzoyl [in (I)] and 3-trifluoromethylphenyl [in (II)] groups assume a face-to-face arrangement in an *anti* conformation.

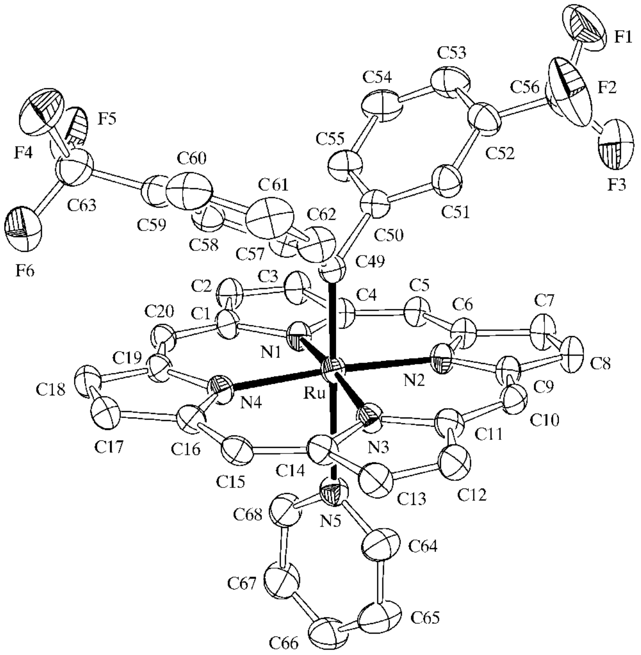

Figure 2

The molecular structure of (II), showing displacement ellipsoids at the 30% probability level. H atoms and *p*-tolyl groups have been omitted for clarity.

The porphyrin rings in these two compounds are slightly distorted into saddle conformations. The largest deviations from the $C_{20}N_4$ least-squares planes are −0.235 (6) and 0.194 (6) Å at C3 and C8, respectively, in (I), and 0.148 (3) and −0.107 (3) Å at C10 and C13, respectively, in (II). The Ru atoms are displaced out of the least-squares planes toward the carbene ligands by 0.1460 (17) and 0.0603 (6) Å in (I) and (II), respectively. The Ru displacement in (II) is the smallest among the ruthenium(II)–porphyrin–carbene complexes reported to date.

Experimental

For (I), a solution of [Ru(ttp)(CO)(EtOH)] in tetrahydrofuran was irradiated with a 100 W high-pressure mercury lamp under N_2 for 6 h. An equimolar quantity of $N_2{=}C(COPh)_2$ was added and the resulting solution refluxed for 6 h. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel and eluted with CH_2Cl_2–hexane (2:1), affording [Ru(ttp){C(COPh)$_2$}], (I′). Addition of an excess amount of pyridine to a CH_2Cl_2 solution of (I′) and subsequent evaporation gave compound (I) as a dark-red solid. Compound (II) was prepared according to a procedure similar to that of Kawai *et al.* (2002); the detailed procedure will be published elsewhere (Wada *et al.*, 2003). Crystals of (I) and (II) were prepared by recrystallization from CH_2Cl_2–cyclohexane (1:1) and CH_2Cl_2–pyridine (1:1) solutions, respectively.

Compound (I)

Crystal data

$[Ru(C_{15}H_{10}O_2)(C_5H_5N)(C_{48}H_{36}N_4)]$
M_r = 1071.21
Monoclinic, $C2/c$
a = 15.806 (2) Å
b = 16.6172 (18) Å
c = 20.644 (2) Å
β = 95.872 (10)°
V = 5393.7 (10) Å^3
Z = 4
D_x = 1.319 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.8–13.7°
μ = 0.34 mm^{-1}
T = 296 (2) K
Needle, dark red
0.20 × 0.12 × 0.10 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
6419 measured reflections
6197 independent reflections
2792 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.048
$\theta_{\rm max}$ = 27.5°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 21$
$l = -26 \rightarrow 26$
3 standard reflections every 150 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.182
S = 0.97
6197 reflections
345 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.64 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.51 e Å^{-3}

Table 1

Selected geometric parameters (Å, °) for (I).

Ru—N1	2.038 (4)	O—C26	1.228 (6)
Ru—N2	2.049 (4)	C25—C26	1.498 (6)
Ru—N3	2.329 (7)	C26—C27	1.479 (8)
Ru—C25	1.877 (8)		
N1—Ru—N1$^{\rm i}$	169.1 (2)	N1—Ru—C25	95.45 (12)
N1—Ru—N2	89.57 (15)	N2—Ru—C25	91.43 (13)
N1—Ru—N2$^{\rm i}$	90.16 (15)	N3—Ru—C25	180
N1—Ru—N3	84.55 (12)	C26—C25—C26$^{\rm i}$	116.8 (6)
N2$^{\rm i}$—Ru—N2	177.1 (3)	Ru—C25—C26	121.6 (3)
N2—Ru—N3	88.57 (13)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Compound (II)

Crystal data

$[Ru(C_{15}H_8F_6)(C_5H_5N)(C_{48}H_{36}N_4)]$
M_r = 1151.19
Monoclinic, $P2_1/c$
a = 12.4428 (17) Å
b = 17.3768 (19) Å
c = 25.1794 (17) Å
β = 99.436 (9)°
V = 5370.5 (10) Å^3
Z = 4
D_x = 1.424 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.9–15.0°
μ = 0.36 mm^{-1}
T = 296 (2) K
Prism, dark red
0.50 × 0.40 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.840, $T_{\rm max}$ = 0.930
12 882 measured reflections
12 323 independent reflections
8702 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.018
$\theta_{\rm max}$ = 27.5°
$h = 0 \rightarrow 16$
$k = -22 \rightarrow 0$
$l = -32 \rightarrow 32$
3 standard reflections every 150 reflections intensity decay: 0.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 1.7405P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.108$	$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{\min} = -0.30$ e Å^{-3}
12 323 reflections	
721 parameters	
H-atom parameters constrained	

Table 2
Selected geometric parameters (Å, °) for (II).

Ru—N1	2.049 (2)	Ru—N4	2.056 (2)
Ru—N2	2.046 (2)	Ru—N5	2.313 (2)
Ru—N3	2.052 (2)	Ru—C49	1.868 (3)
N1—Ru—N2	89.15 (8)	N4—Ru—N5	86.75 (8)
N1—Ru—N3	173.72 (8)	C49—Ru—N1	92.68 (10)
N1—Ru—N4	90.55 (8)	C49—Ru—N2	91.69 (10)
N2—Ru—N3	90.89 (8)	C49—Ru—N3	93.60 (9)
N2—Ru—N4	175.36 (8)	C49—Ru—N4	92.96 (10)
N3—Ru—N4	88.90 (8)	C49—Ru—N5	179.56 (10)
N1—Ru—N5	87.66 (8)	C50—C49—C57	112.8 (2)
N2—Ru—N5	88.60 (8)	Ru—C49—C50	125.04 (18)
N3—Ru—N5	86.06 (8)	Ru—C49—C57	122.13 (18)

All H atoms of (I) and (II) were placed in geometrically idealized positions, with Csp^2—H = 0.93 Å and Csp^3—H = 0.96 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

For both compounds, 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: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1046). Services for accessing these data are described at the back of the journal.

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