

Dorothy H. Gibson, Mark S.
Mashuta* and Jose G. AndinoDepartment of Chemistry, University of
Louisville, Louisville, KY 40292, USACorrespondence e-mail:
msmashuta.xray@louisville.edu

Key indicators

Single-crystal X-ray study
 $T = 90$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
Disorder in solvent or counterion
 R factor = 0.034
 wR factor = 0.089
Data-to-parameter ratio = 11.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.***cis*-(2,2'-Bipyridyl- $\kappa^2\text{N},\text{N}'$)carbonyl(η^3 -1-methylene-
2,2':6',2''-terpyridyl- $\kappa^3\text{C}^1,\text{N},\text{N}'$)ruthenium(II)
bis(hexafluorophosphate) acetone disolvate**

The title compound, $[\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_{16}\text{H}_{13}\text{N}_3)(\text{CO})](\text{PF}_6)_2 \cdot 2\text{C}_3\text{H}_6\text{O}$, shows highly distorted octahedral geometry about the Ru atom because of the restrictions of the terdentate ligand, which includes a metallacyclic ring, and the chelating 2,2'-bipyridine ligand. The terdentate ligand is bound facially to the Ru atom.

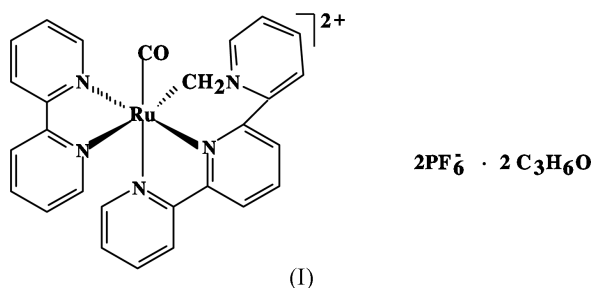
Received 10 January 2005

Accepted 14 January 2005

Online 22 January 2005

Comment

We have been investigating the chemical reactions and molecular structures of ruthenium complexes with polypyridine ligands for several years (Gibson *et al.*, 1997, 1998, 2001). In the course of these investigations, the title compound, (I), was prepared. The facial relationship of the methylene carbon (C1) and pyridyl N atoms (N3 and N4) in (I) was established prior to the ring-closure reaction resulting from intramolecular alkylation of a pendant pyridyl nitrogen (N5), which afforded the title compound. An ORTEP-3 diagram (Farrugia, 1997) of (I) (Fig. 1) illustrates the structures of the independent entities. The dication in (I) is formally related to that in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})](\text{PF}_6)_2$ (bpy is 2,2'-bipyridine and tpy is 2,2':6',2''-terpyridine) (Nagao *et al.*, 1994) since both possess bpy, CO and related terdentate ligands, but the tpy ligand in the latter compound occupies meridional sites on the Ru atom. The constraints imposed by the terdentate ligand in (I) and the chelating bpy ligand ensure that distorted octahedral geometry will result about the Ru atom. Thus, the C2–Ru1–N3 bond angle is considerably less than linear (see Table 1) as a result of the steric demands of the six-membered metallacyclic ring, and is bent away from that ring. Also, the C1–Ru1–N4 and N3–Ru1–N4 bond angles are much less than 90° .



A more closely related structure is that of *cis*- $[\text{Ru}(\eta^2\text{-tpy})(\text{bpy})(\text{CO})(\text{COOH})]\text{PF}_6$ (Gibson *et al.*, 1998), which has the two carbon ligands *cis* as in (I). In this structure, the carboxyl H atom is hydrogen bonded to the pendant pyridyl group of the tpy ligand, forming an eight-membered metallacyclic ring. The remaining ligands are arranged around the Ru atom in the same manner as in (I), with the carboxyl

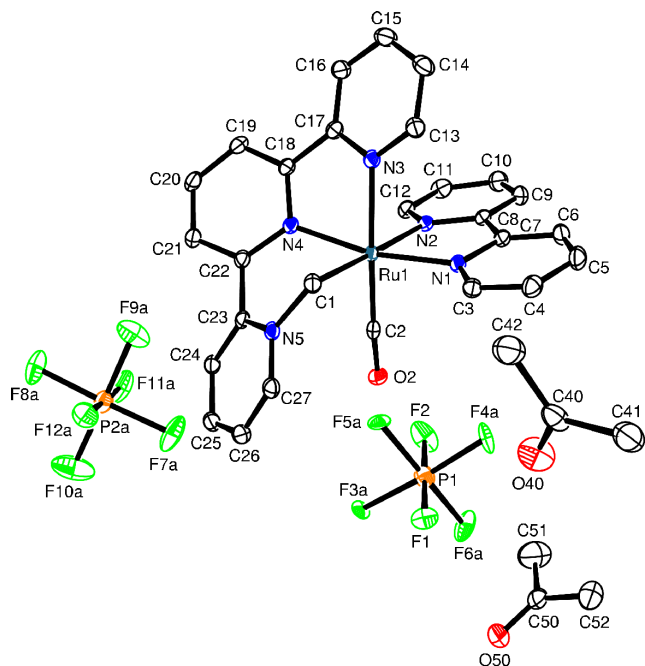


Figure 1
An ORTEP-3 view (Farrugia, 1997) of the title compound, showing 40% probability displacement ellipsoids. H atoms and one disorder component of each anion have been omitted.

carbon (C1) and atoms N3 and N4 of the tpy ligand in facial positions. The hydrogen-bonded metallacyclic ring present in the acid complex does not impose unusual geometric constraints on the Ru coordination environment, as evidenced by the C1–Ru1–N4 angle of 92.6 (2)°. However, the analogous angle in the title compound is severely contracted [77.92 (10)°], resulting from bonding limitations of the methyleneterpyridyl ligand. Other less prominent distortions involving the coordination of the Ru atom are observed in Table 1.

Experimental

In a Schlenk flask, 0.050 g of [Ru(η^2 -tpy)(bpy)(CO)(CH₂OH)]PF₆ [isomer 4b in Gibson *et al.* (2001)] was dissolved in CH₂Cl₂ (25 ml) under nitrogen. HBF₄ etherate (10 ml) was then injected into the flask through a septum and the mixture was stirred for 30 min, then evaporated to dryness. The residue was dissolved in acetone (20 ml) and a saturated solution of NH₄PF₆ (5 ml) was added. The solution was concentrated to one third of its original volume, resulting in precipitation of a red solid. Crystallization from acetone afforded orange block-shaped crystals.

Crystal data

[Ru(C₁₀H₈N₂)(C₁₆H₁₃N₃)-
(CO)](PF₆)₂·2C₃H₆O
M_r = 938.65
Triclinic, P1̄
a = 12.0293 (15) Å
b = 13.1788 (17) Å
c = 13.8881 (18) Å
α = 68.211 (2)°
β = 72.262 (2)°
γ = 67.135 (2)°
V = 1850.4 (4) Å³

Z = 2
D_x = 1.685 Mg m⁻³
Mo Kα radiation
Cell parameters from 6669
reflections
θ = 2.2–25.1°
μ = 0.61 mm⁻¹
T = 90 (2) K
Block, orange
0.23 × 0.19 × 0.15 mm

Data collection

Bruker SMART APEX CCD
diffractometer
ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)
T_{min} = 0.852, T_{max} = 0.909
13720 measured reflections

6536 independent reflections
6284 reflections with I > 2σ(I)
R_{int} = 0.013
θ_{max} = 25.1°
h = -14 → 13
k = -15 → 15
l = -16 → 16

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.034
wR(F²) = 0.089
S = 1.04
6536 reflections
572 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.042P)²
+ 2.9426P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.01
Δρ_{max} = 2.02 e Å⁻³
Δρ_{min} = -0.90 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ru1–N1	2.079 (2)	Ru1–C1	2.108 (3)
Ru1–N2	2.141 (2)	Ru1–C2	1.846 (3)
Ru1–N3	2.145 (2)	O2–C2	1.153 (3)
Ru1–N4	2.048 (2)	N5–C1	1.510 (3)
N1–Ru1–N2	77.12 (9)	N3–Ru1–C1	98.77 (10)
N1–Ru1–N4	167.70 (9)	N3–Ru1–C2	171.23 (10)
N2–Ru1–N3	80.53 (8)	N4–Ru1–C1	77.92 (10)
N3–Ru1–N4	76.52 (9)	C1–Ru1–C2	89.16 (11)
N1–Ru1–C1	104.65 (10)	Ru1–C1–N5	107.35 (16)
N2–Ru1–C1	178.13 (10)	Ru1–C2–O2	176.5 (2)

One of the hexafluorophosphate anions was modeled with a spinning-top disorder using two four-atom groups of half-occupancy F atoms (F3a–F6a and F3b–F6b) in addition to the two full-occupancy F atoms (F1 and F2). The second hexafluorophosphate anion has a slipped tumbling disorder that was modeled with one 80% occupancy (P2a/F7a–F12a) and one 20% occupancy (P2b/F7b–F12b) set of restrained P and F atoms. The ratio for the anion disorder was fixed at 80:20% after being determined from unstable refinement of the F-atom occupancies. H atoms were positioned geometrically (C–H = 0.95–0.99 Å) and refined using a riding model. Methylene H atoms were included as fixed contributions with U_{iso}(H) = 1.2U_{eq}(C), while methyl groups of the acetone molecules were allowed to ride (the torsion angle which defines its orientation was allowed to refine) on the attached C atom, and these atoms were assigned U_{iso}(H) = 1.5U_{eq}(C). Aromatic H atoms were assigned U_{iso}(H) = 1.2U_{eq}(C). The maximum residual electron density was 1.97 Å⁻³ from atom F9a.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS90 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXTL.

Support of this work by the National Science Foundation (grant No. 0203131 to DHG) is gratefully acknowledged. The X-ray equipment was purchased through a grant from the Kentucky Research Challenge Trust.

References

Bruker (2001). SHELXTL. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

- Bruker (2002). *SAINT* (Version 6.36) and *SMART* (Version 5.628). Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gibson, D. H., Andino, J. G., Bhamidi, S., Sleadd, B. A. & Mashuta, M. S. (2001). *Organometallics*, **23**, 4956–4964.
- Gibson, D. H., Sleadd, B. A., Mashuta, M. S. & Richardson, J. F. (1997). *Organometallics*, **19**, 4421–4427.
- Gibson, D. H., Sleadd, B. A., Mashuta, M. S. & Richardson, J. F. (1998). *Acta Cryst.* **C54**, 1584–1586.
- Nagao, H., Muzukawa, T. & Tanaka, K. (1994). *Inorg. Chem.* **33**, 3415–3420.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1996). *SADABS*. Version 2.03 University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.