Structure of Bis-μ_3-phenylimido-tris(tricarbonylruthenium), [Ru$_3$(C$_6$H$_5$N)$_2$(CO)$_9$]

By William Clegg, George M. Sheldrick and Dietmar Stalke

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

AND Sumit Bhaduri AND Kalpathi S. Gopalkrishnan

Alchemie Research Centre Private Limited, CAFI Site, PO Box 155, Belapur Road, Thane-400601, Maharashtra, India

Abstract. $M_r = 737.53$, orthorhombic, *Pna2*₁, $a = 19.730$ (2), $b = 9.667$ (1), $c = 13.043$ (1) Å, $U = 2487.7$ Å³, $Z = 4$, $D_x = 1.969$ Mg m⁻³, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.81$ mm⁻¹, $F(000) = 1415.8$, $T = 291$ K, $R = 0.025$ for 2164 observed reflections. The three Ru atoms form an approximately isosceles triangle, with Ru–Ru 2.710 (1) and 2.626 (1) Å, Ru···Ru 3.289 (1) Å, Ru–Ru–Ru 76.1 (1)°. All carbonyl groups are terminal. The NPh ligands are triply bridging, with Ru–N 2.052 (4) to 2.129 (6) Å, N···N 2.405 (11) Å.

Introduction. Reaction of nitrobenzene with Ru₃-(CO)₁₂ gives Ru₃(CO)₁₀(μ_3-NPh) (1) and Ru₃(CO)₉-(μ_3-NPh)₂ (2) (Sappa & Milone, 1973; Bhaduri, Gopalkrishnan, Sheldrick, Clegg & Stalke, 1983). In (1) the Ru atoms form an equilateral triangle, triply bridged on one side by CO and on the other by NPh ligands (Bhaduri *et al.*, 1983). Spectroscopic data indicate a structure of lower symmetry for (2), with no Ru₃ equilateral triangle. This is confirmed by the crystal structure determination reported here.

Experimental. Crystals obtained from *n*-hexane, mounted in capillaries, 0.15 × 0.38 × 0.42 mm. Stoe–Siemens AED diffractometer. Unit-cell parameters refined from 2θ values of 38 reflections ($20 < 2\theta < 25°$). Systematic absences: 0*kl* for $k + l$ odd, *h*0*l* for *h* odd, 00*l* for *l* odd; space group *Pna2*₁ or *Pnam* (*Pnma* reoriented), *Pna2*₁ confirmed by structure solution. 2516 reflections with $2\theta < 50°$ and all indices ≥ 0. Profile analysis (Clegg, 1981). No significant variation for three standard reflections. Semiempirical absorption corrections based on azimuthal scan data for equivalent reflections, transmission 0.379 to 0.503. 2296 unique non-extinguished reflections, 2164 with $F > 4\sigma(F)$. Ru atoms from Patterson synthesis, others from difference syntheses. Blocked-cascade refinement on *F*. $w^{-1} = \sigma^2(F)$. H atoms constrained to lie on C–C–C external bisectors with C–H = 0.96 Å, U(H)

= $1.2U_{eq}$(C). Anisotropic thermal parameters for non-H atoms. Extinction $x = 6.0$ (4) ×10⁻⁷ [$F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$]. Scattering factors from *International Tables for X-ray Crystallography* (1974). Polar axis direction determined by refinement of $\eta = +0.94$ (11) (Rogers, 1981). 316 parameters, $R = 0.025$, $wR = 0.022$, slope of normal probability plot 1.39. Δ/σ max. = 0.02, mean = 0.005. Largest peak in final difference map 0.28 e Å⁻³, largest hole −0.46 e Å⁻³. Programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles for the Ru and N atoms in Table 2.* The molecular structure is shown in Fig. 1. One of the three Ru–Ru bonds present in Ru₃(CO)₁₂ and in (1) has been broken on replacement of a further CO group by a second NPh ligand. This is in agreement with the formulation of CO as a two-electron and NPh as a four-electron donor ligand. The additional two skeletal electrons in (2) compared with (1) are Ru–Ru antibonding (Schilling & Hoffmann, 1979).

Lowering of the symmetry of the central part of the molecule from C_{3v} in (1) to essentially C_{2v} in (2) renders the Ru–N bonds no longer all equivalent. The bonds to the central Ru(1) atom are longer than those to Ru(2) and Ru(3), the NPh ligands being displaced from positions above and below the centroid of the Ru₃ triangle towards its longest edge. The mean Ru–N bond length of 2.085 (30) Å is barely longer than in (1) [2.055 (5) Å]; this, together with the opening up of the Ru₃ triangle compared with (1), brings the N atoms sufficiently close [2.405 (11) Å] for some direct N–N interaction to be likely. An alternative description of the

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles for the ligands have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39200 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

The equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U
Ru(1)	1352 (1)	1549 (1)	5000	39 (1)
Ru(2)	2127 (1)	2473 (1)	3427 (1)	41 (1)
Ru(3)	1142 (1)	−269 (1)	3537 (1)	45 (1)
C(11)	1511 (4)	387 (7)	6153 (5)	58 (2)
O(11)	1601 (3)	−342 (6)	6819 (4)	98 (2)
C(12)	462 (4)	2003 (8)	5469 (5)	78 (3)
O(12)	−72 (3)	2233 (8)	5758 (5)	135 (4)
C(13)	1765 (4)	3152 (7)	5590 (5)	60 (2)
O(13)	1976 (3)	4056 (5)	6029 (5)	100 (3)
C(21)	2388 (3)	2079 (6)	2076 (4)	50 (2)
O(21)	2537 (3)	1837 (5)	1258 (4)	78 (2)
C(22)	3055 (4)	2889 (7)	3825 (5)	58 (2)
O(22)	3596 (3)	3132 (7)	4023 (4)	96 (3)
C(23)	2013 (3)	4404 (7)	3080 (5)	58 (2)
O(23)	1979 (3)	5526 (4)	2843 (4)	88 (2)
C(31)	184 (3)	−544 (6)	3393 (7)	72 (3)
O(31)	−379 (2)	−710 (6)	3323 (7)	113 (3)
C(32)	1349 (4)	−915 (8)	2186 (6)	74 (3)
O(32)	1483 (3)	−1318 (8)	1394 (4)	122 (3)
C(33)	1234 (3)	−2041 (7)	4181 (5)	60 (2)
O(33)	1259 (3)	−3083 (5)	4596 (4)	87 (2)
N(4)	2060 (2)	529 (4)	4051 (3)	39 (1)
C(41)	2645 (3)	−259 (6)	4326 (4)	44 (2)
C(42)	2818 (3)	−1431 (6)	3774 (5)	58 (2)
C(43)	3387 (4)	−2207 (8)	4034 (6)	80 (3)
C(44)	3783 (3)	−1798 (8)	4822 (7)	84 (3)
C(45)	3629 (4)	−631 (7)	5388 (5)	73 (3)
C(46)	3052 (3)	120 (6)	5149 (5)	54 (2)
N(5)	1124 (2)	1876 (4)	3423 (4)	47 (1)
C(51)	597 (3)	2710 (7)	3017 (5)	60 (2)
C(52)	419 (4)	3966 (7)	3464 (8)	89 (3)
C(53)	−91 (5)	4764 (11)	3050 (8)	135 (5)
C(54)	−441 (5)	4285 (11)	2198 (9)	150 (6)
C(55)	−280 (4)	3083 (10)	1749 (7)	123 (5)
C(56)	243 (3)	2267 (9)	2157 (6)	85 (3)

Table 2. Selected bond lengths (Å) and angles (°)

Bond	Length		Bond	Length
Ru(1)–Ru(2)	2·710 (1)		Ru(1)–Ru(3)	2·626 (1)
Ru(1)–C(11)	1·903 (6)		Ru(1)–C(12)	1·912 (7)
Ru(1)–C(13)	1·912 (6)		Ru(1)–N(4)	2·110 (4)
Ru(1)–N(5)	2·129 (6)		Ru(2)–C(21)	1·876 (6)
Ru(2)–C(22)	1·945 (7)		Ru(2)–C(23)	1·933 (6)
Ru(2)–N(4)	2·052 (4)		Ru(2)–N(5)	2·061 (4)
Ru(3)–C(31)	1·918 (6)		Ru(3)–C(32)	1·914 (7)
Ru(3)–C(33)	1·917 (7)		Ru(3)–N(4)	2·080 (4)
Ru(3)–N(5)	2·079 (4)		N(4)–C(41)	1·429 (7)
N(5)–C(51)	1·418 (8)			

| Angle	Value		Angle	Value
Ru(2)–Ru(1)–Ru(3)	76·1 (1)		Ru(2)–Ru(1)–C(11)	134·5 (2)
Ru(3)–Ru(1)–C(11)	101·8 (2)		Ru(2)–Ru(1)–C(12)	133·2 (2)
Ru(3)–Ru(1)–C(12)	104·0 (2)		C(11)–Ru(1)–C(12)	91·9 (3)
Ru(2)–Ru(1)–C(13)	78·3 (2)		Ru(3)–Ru(1)–C(13)	154·4 (2)
C(11)–Ru(1)–C(13)	95·2 (3)		C(12)–Ru(1)–C(13)	94·4 (3)
Ru(2)–Ru(1)–N(4)	48·5 (1)		Ru(3)–Ru(1)–N(4)	50·7 (1)
C(11)–Ru(1)–N(4)	94·5 (2)		C(12)–Ru(1)–N(4)	154·6 (3)
C(13)–Ru(1)–N(4)	109·4 (2)		Ru(2)–Ru(1)–N(5)	48·6 (1)
Ru(3)–Ru(1)–N(5)	50·5 (1)		C(11)–Ru(1)–N(5)	152·4 (2)
C(12)–Ru(1)–N(5)	94·6 (2)		C(13)–Ru(1)–N(5)	111·0 (2)
N(4)–Ru(1)–N(5)	69·1 (2)		Ru(1)–Ru(2)–C(21)	143·1 (2)
Ru(1)–Ru(2)–C(22)	113·4 (2)		C(21)–Ru(2)–C(22)	92·0 (3)
Ru(1)–Ru(2)–C(23)	115·5 (2)		C(21)–Ru(2)–C(23)	90·5 (3)
C(22)–Ru(2)–C(23)	88·4 (3)		Ru(1)–Ru(2)–N(4)	50·3 (1)
C(21)–Ru(2)–N(4)	101·8 (2)		C(22)–Ru(2)–N(4)	98·2 (2)
C(23)–Ru(2)–N(4)	165·8 (2)		Ru(1)–Ru(2)–N(5)	50·8 (2)
C(21)–Ru(2)–N(5)	101·8 (2)		C(22)–Ru(2)–N(5)	164·2 (2)
C(23)–Ru(2)–N(5)	99·1 (2)		N(4)–Ru(2)–N(5)	71·5 (2)
Ru(1)–Ru(3)–C(31)	108·6 (2)		Ru(1)–Ru(3)–C(32)	148·6 (2)
C(31)–Ru(3)–C(32)	94·3 (3)		Ru(1)–Ru(3)–C(33)	105·4 (2)
C(31)–Ru(3)–C(33)	90·7 (3)		C(32)–Ru(3)–C(33)	95·3 (3)
Ru(1)–Ru(3)–N(4)	51·7 (1)		C(31)–Ru(3)–N(4)	160·3 (3)
C(32)–Ru(3)–N(4)	103·4 (2)		C(33)–Ru(3)–N(4)	96·2 (2)
Ru(1)–Ru(3)–N(5)	52·2 (2)		C(31)–Ru(3)–N(5)	96·6 (2)
C(32)–Ru(3)–N(5)	105·2 (3)		C(33)–Ru(3)–N(5)	157·6 (3)
N(4)–Ru(3)–N(5)	70·6 (2)		Ru(1)–N(4)–Ru(2)	81·2 (2)
Ru(1)–N(4)–Ru(3)	77·6 (2)		Ru(2)–N(4)–Ru(3)	105·5 (2)
Ru(1)–N(4)–C(41)	129·6 (3)		Ru(2)–N(4)–C(41)	122·4 (3)
Ru(3)–N(4)–C(41)	125·9 (3)		Ru(1)–N(5)–Ru(2)	80·6 (2)
Ru(1)–N(5)–Ru(3)	77·2 (2)		Ru(2)–N(5)–Ru(3)	105·2 (2)
Ru(1)–N(5)–C(51)	126·9 (4)		Ru(2)–N(5)–C(51)	123·1 (4)
Ru(3)–N(5)–C(51)	127·3 (4)			
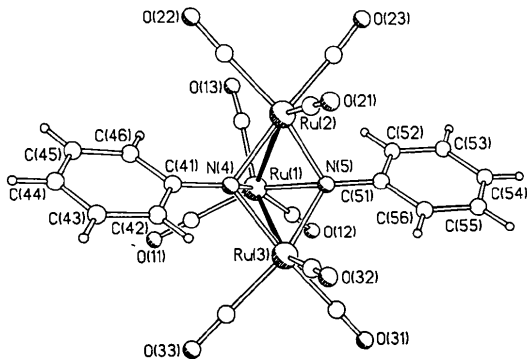
Fig. 1. Molecular structure of (2), showing the numbering scheme. Carbonyl C atoms take the same numbers as the corresponding O atoms; H atoms take the same numbers as the corresponding phenyl C atoms.

structural core in this case is as an Ru_3N_2 trigonal-bipyramidal cluster, with Ru(1) and the two N atoms occupying the equatorial sites.

The two phenyl rings are essentially perpendicular to the Ru_3 plane [dihedral angles 95 (1) and 93 (1)°]. They are approximately parallel to each other [dihedral angle 9 (1)°], and to the Ru(1)–Ru(3) bond [angles between plane normals and bond are both 91 (1)°]. The considerable lengthening of Ru(1)–Ru(2) compared

with Ru(1)–Ru(3) is presumably due to this orientation of the NPh ligands, and to the asymmetrical arrangement of the three CO ligands of Ru(1) relative to Ru(2) and Ru(3). A similar carbonyl arrangement is observed in $(MeN)_2Fe_3(CO)_9$ (Doedens, 1969), without an additional asymmetry due to the nitrene ligands, and in this case the difference in Fe—Fe bond lengths is rather smaller (0·05 Å).

The internal geometry of the phenyl rings is normal, and all carbonyl groups are essentially linear [minimum Ru—C—O = 172·8 (6)°] with C—O 1·124 (9)–1·145 (8) Å.

References

Bhaduri, S., Gopalkrishnan, K. S., Sheldrick, G. M., Clegg, W. & Stalke, D. (1983). J. Chem. Soc. Dalton Trans. pp. 2339–2341.

Clegg, W. (1981). Acta Cryst. A37, 22–28.

Doedens, R. J. (1969). Inorg. Chem. 8, 570–574.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.

Rogers, D. (1981). Acta Cryst. A37, 734–741.

SAPPA, E. & MILONE, L. (1973). *J. Organomet. Chem.* **61**, 383–388.

SCHILLING, B. E. R. & HOFFMANN, R. (1979). *J. Am. Chem. Soc.* **101**, 3456–3467.

SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

Structures of Two Isomers of Dichlorobis(2-phenylazopyridine)ruthenium(II), [RuCl₂(C₁₁H₉N₃)₂]

BY ALPANA SEAL AND SIDDHARTHA RAY

X-ray Crystallography Laboratory, Department of Magnetism, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

Abstract. $M_r = 538$. C_2 isomer: $P2_1/c$, $a = 8 \cdot 421$ (8), $b = 22 \cdot 88$ (2), $c = 12 \cdot 99$ (2) Å, $\beta = 116 \cdot 3$ (1)°, $V = 2243 \cdot 2$ Å^3, $Z = 4$, $F(000) = 1080$, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $\mu = 9 \cdot 4$ cm^{-1}, $D_x = 1 \cdot 59$ g cm^{-3}, $R = 0 \cdot 051$ for 3257 observed [$I > 2\sigma(I)$] reflections. C_1 isomer: $P\bar{1}$, $a = 13 \cdot 371$ (4), $b = 15 \cdot 345$ (3), $c = 13 \cdot 101$ (4) Å, $\alpha = 114 \cdot 75$ (2), $\beta = 93 \cdot 75$ (3), $\gamma = 67 \cdot 61$ (3)°, $V = 2242 \cdot 7$ Å^3, $Z = 4$, $F(000) = 1080$, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $\mu = 9 \cdot 4$ cm^{-1}, $D_x = 1 \cdot 59$ g cm^{-3}, $R = 0 \cdot 054$ for 3660 observed reflections. With reference to the pairs of Cl, N(py) and N(azo) coordinating with Ru, the C_2 isomer has a *cis–trans–cis* configuration and the C_1 isomer a *cis–cis–cis*. In both structures Ru—N(azo) distances are relatively shorter than Ru—N(py), indicating stronger bonding in the former case, caused by the considerable π-backbonding power of the azo function.

Introduction. The title compound is known to exist in three isomeric forms (Krause & Krause, 1980; Goswami, Chakravarty & Chakravorty, 1981, 1982, 1983), one of which is green and the other two are dark blue. In principle, five isomers are possible. If the co-ordinating pairs of Cl, N(py) and N(azo) are considered in that order, the configurations of these five are (Fig. 1) *trans–trans–trans* (*ttt*), *trans–cis–cis* (*tcc*), *cis–trans–cis* (*ctc*), *cis–cis–trans* (*cct*) and *cis–cis–cis* (*ccc*). Spectroscopic evidence suggested that the green isomer has the *ttt* configuration. Either the *ctc* or *cct* configuration has been indicated in the case of one blue isomer (herein referred to as the C_2 isomer, owing to the nominal twofold symmetry of the complex), while the other (the C_1 isomer) appears to be of the *ccc* variety (Goswami *et al.*, 1981, 1982, 1983).

This investigation was undertaken with two primary ends in view: (1) to establish unequivocally the structural identities of the two blue isomers; and (2) to ascertain the relative π-backbonding abilities of N(py) and N(azo) towards Ru$^{\text{II}}$.

Experimental. Specimens $0 \cdot 25 \times 0 \cdot 2 \times 0 \cdot 15$ mm (C_2 isomer) and $0 \cdot 25 \times 0 \cdot 2 \times 0 \cdot 1$ mm (C_1 isomer). CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 25 reflections (to $\theta = 15 \cdot 2°$) for measurement of lattice parameters in each case. D_m not measured since all suitable liquids available were solutions of bromides and iodides with which the crystals reacted. ω–2θ scan, $\theta_{\max} = 25°$ for C_2 isomer [25° for C_1 isomer], h −9 to 8 [−15 to 15], k 0 to 27 [−18 to 16], l 0 to 15 [0 to 15]. 3924 [7980] unique reflections measured (no merging of equivalents), 667 [832] unobserved with $I \leq 2\sigma(I)$. Max. value of decay
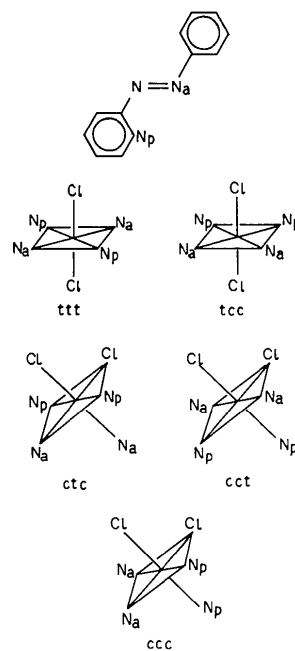

Fig. 1. The ligand and the five geometrically possible isomeric configurations of its dichloro complex with Ru.