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Key indicators

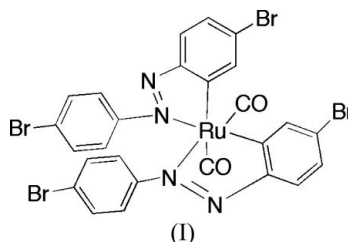
Single-crystal X-ray study
T = 200 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.031
wR factor = 0.031
Data-to-parameter ratio = 13.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

(OC-6-32)-Bis[5-bromo-2-(4-bromophenyl-diazenyl)phenyl]dicarbonylruthenium(II)

The title compound, $[\text{Ru}(\text{C}_{12}\text{H}_7\text{Br}_2\text{N}_2)_2(\text{CO})_2]$, possesses a distorted octahedral environment about the Ru atom, with two cyclometallated 4,4'-dibromoazobenzene ligands and two mutually *cis* carbonyl ligands. The donor atoms are arranged such that the N atoms are respectively *trans* to a carbonyl ligand and an aryl C atom.

Comment

The title compound, (I), has been prepared as a minor product of the reaction of $\text{Ru}_3(\text{CO})_{12}$ and 4,4'-dibromoazobenzene in refluxing *n*-octane; the major product is the cluster complex $\text{Ru}_3(\mu_3\text{-NC}_6\text{H}_4\text{Br})_2(\text{CO})_9$ (Willis *et al.*, 2005). Two strong $\nu(\text{CO})$ absorptions at 2039 and 1991 cm^{-1} in the IR spectrum of (I) are consistent with the presence of two mutually *cis* carbonyl groups. The crystal structure was investigated to ascertain the relative dispositions of the remaining C and N donor atoms of the two cyclometallated 4,4'-dibromoazobenzene ligands.



Complex (I) possesses a distorted octahedral coordination of the Ru atom and the X-ray study confirms the *cis*-disposed carbonyl ligands (Fig. 1). One N atom is *trans* to an aryl C, while the other N atom is *trans* to a carbonyl ligand, with the other aryl C *trans* to the remaining carbonyl ligand.

For ruthenium complexes of this type, *i.e.* with *cis* monodentate ligands and two *N,C*-cyclometallated ligands, three different arrangements of the cyclometallated donor atoms are possible. Compound (I) and the analogue containing azobenzene residues, $\text{Ru}(\text{C}_6\text{H}_4\text{N}=\text{NPh})_2(\text{CO})_2$ (II) (Bruce *et al.*, 1987), adopt the same configuration; the only difference in Ru-containing bond lengths between the two structures is the Ru–N bond *trans* to the carbonyl ligand [2.135 (3) \AA in (II) and 2.103 (6) \AA in (I)].

Experimental

$\text{Ru}_3(\text{CO})_{12}$ (200 mg, 0.31 mmol) was added to a solution of 4,4'-dibromoazobenzene (210 mg, 0.62 mmol) in *n*-octane (30 ml), and the mixture heated at reflux for 4 h. The resulting brown solution was taken to dryness on a rotary evaporator, and the residue dissolved in

Received 23 November 2005

Accepted 9 December 2005

Online 16 December 2005

a minimum of CH_2Cl_2 (ca 3 ml) and applied to preparative thin-layer chromatography plates. Elution with CH_2Cl_2 /petrol ether (1:9 v/v) gave four bands and a heavy baseline: band 1 was yellow ($R_F = 0.4$); band 2 was orange ($R_F = 0.52$); band 3 was yellow ($R_F = 0.21$); band 4 ($R_F = 0.10$) was yellow. The contents of band 3 were identified as $\text{Ru}(\text{CO})_2(\text{C}_{12}\text{H}_7\text{Br}_2\text{N}_2)_2$, (I) (10 mg, 4%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2039 s, 1991 s cm^{-1} . Crystals were obtained by liquid diffusion of methanol into a dichloromethane solution.

Crystal data

$[\text{Ru}(\text{C}_{12}\text{H}_7\text{Br}_2\text{N}_2)_2(\text{CO})_2]$	$Z = 2$
$M_r = 835.11$	$D_x = 2.065 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.7137$ (4) Å	Cell parameters from 28902 reflections
$b = 11.5618$ (4) Å	$\theta = 3\text{--}27^\circ$
$c = 11.7896$ (5) Å	$\mu = 6.57 \text{ mm}^{-1}$
$\alpha = 78.7678$ (19)°	$T = 200 \text{ K}$
$\beta = 73.2924$ (18)°	Block, red
$\gamma = 75.651$ (2)°	$0.45 \times 0.31 \times 0.26 \text{ mm}$
$V = 1343.03$ (9) Å ³	

Data collection

Nonius KappaCCD diffractometer	6138 independent reflections
φ and ω scans	4348 reflections with $I > 3\sigma(I)$
Absorption correction: Gaussian integration (Coppens, 1970) implemented in MAXUS (Mackay <i>et al.</i> , 2000)	$R_{\text{int}} = 0.05$
$T_{\text{min}} = 0.171$, $T_{\text{max}} = 0.295$	$\theta_{\text{max}} = 27.5^\circ$
28902 measured reflections	$h = -13 \rightarrow 13$
	$k = -14 \rightarrow 14$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2 / [3.3T_0(x) - 2.25T_1(x) + 2.27T_2(x)]$
$R[F^2 > 3\sigma(F^2)] = 0.031$	where T_i are Chebychev polynomials and $x = F_o/F_{\text{max}}$ (Prince, 1982; Watkin, 1994)
$wR[F^2 > 3\sigma(F^2)] = 0.031$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.16$	$\Delta\rho_{\text{max}} = 0.58 \text{ e } \text{Å}^{-3}$
4348 reflections	$\Delta\rho_{\text{min}} = -1.19 \text{ e } \text{Å}^{-3}$
334 parameters	

Table 1

Selected geometric parameters (Å, °).

Ru1–N11	2.178 (3)	Ru1–C2	1.877 (4)
Ru1–N21	2.135 (3)	Ru1–C112	2.096 (3)
Ru1–C1	1.938 (4)	Ru1–C212	2.040 (4)
N11–Ru1–N21	94.09 (11)	C1–Ru1–C112	174.36 (14)
N11–Ru1–C1	102.07 (14)	C2–Ru1–C112	92.04 (14)
N21–Ru1–C1	92.61 (13)	N11–Ru1–C212	163.85 (12)
N11–Ru1–C2	95.27 (13)	N21–Ru1–C212	76.44 (12)
N21–Ru1–C2	167.61 (13)	C1–Ru1–C212	91.53 (15)
C1–Ru1–C2	93.36 (15)	C2–Ru1–C212	92.55 (14)
N11–Ru1–C112	75.79 (12)	C112–Ru1–C212	89.85 (13)
N21–Ru1–C112	82.40 (12)		

H atoms were included at idealized positions and made to ride on their parent atoms, with $\text{C–H} = 1.00 \text{ Å}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The deepest hole is located 0.63 Å from atom Br21.

Data collection: COLLECT (Nonius, 1997); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduc-

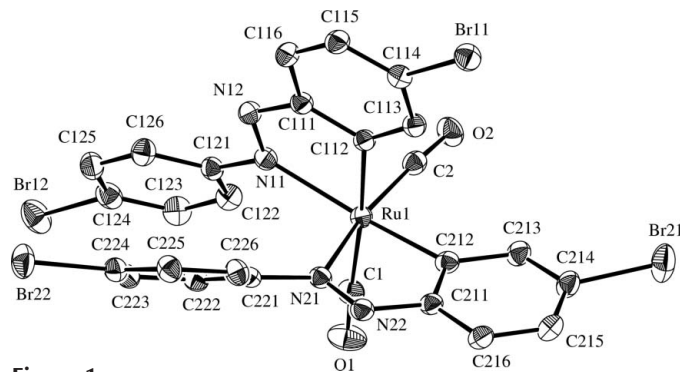


Figure 1

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

tion: DENZO/SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: ORTEPII (Johnson, 1976) in TEXSAN (Molecular Structure Corporation, 1997); software used to prepare material for publication: CRYSTALS.

We thank the Australian Research Council (ARC) for financial support and Johnson–Matthey Technology Centre for the generous loan of ruthenium salts. MGH holds an ARC Australian Professorial Fellowship. WKM thanks the University of Baghdad for a period of study leave, and the Australian Department of Education, Science and Training for an Endeavour Fellowship.

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