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## Key indicators

Single-crystal X-ray study  
*T* = 200 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
*R* factor = 0.024  
*wR* factor = 0.028  
Data-to-parameter ratio = 12.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.(OC-6-13)-Bis[5-bromo-2-(4-bromophenyl-diazenyl)phenyl]dicarbonylruthenium(II) with mutually *trans* *N*-donor atoms

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 mutually *trans* and the aryl C atoms are *trans* to carbonyl ligands.

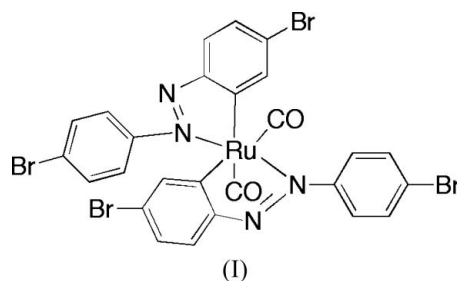
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## Comment

The title compound (I) has been prepared as a minor product from 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 2047 and 1984  $\text{cm}^{-1}$  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.



The complex possesses a distorted octahedral coordination at the Ru atom and the X-ray study confirms the *cis*-disposed carbonyl ligands (Fig. 1). The N atoms of the cyclometallated azobenzene ligands are mutually *trans*, and the aryl C atoms are *trans* to the carbonyl ligands.

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. An analogue containing azobenzene residues  $\text{Ru}(\text{C}_6\text{H}_4\text{N}=\text{NPh})_2(\text{CO})_2$  (Bruce *et al.*, 1987) and a further minor product from the present reaction (Willis *et al.*, 2006) possess one configuration, in which 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. The second possibility, in which each of the N atoms is *trans* to a carbonyl ligand, is seen in  $\text{Ru}(\text{C}_{13}\text{H}_8\text{N})_2(\text{CO})_2$  (Patrick *et al.*, 1983). Compound (I) has the third configuration, not previously observed for ruthenium complexes with ligands of this type.

## 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 a minimum of  $\text{CH}_2\text{Cl}_2$  (*ca* 3 ml) and applied to preparative thin-layer chromatography plates. Elution with  $\text{CH}_2\text{Cl}_2$ /petrol ether (1/9) 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 4 were identified as  $\text{Ru}(\text{CO})_2(\text{C}_{12}\text{H}_7\text{Br}_2\text{N}_2)_2$ , compound (I), (50 mg, 19%). MS (secondary ion,  $\text{Cs}^+$ ):  $837 - 28n$  ( $[M - n\text{CO}]^+$ ,  $n = 0-2$ ). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2047 s, 1984 s  $\text{cm}^{-1}$ . Crystals were obtained by liquid diffusion of methanol into a dichloromethane solution.

### Crystal data

$[\text{Ru}(\text{C}_{12}\text{H}_7\text{Br}_2\text{N}_2)_2(\text{CO})_2]$	$D_x = 2.115 \text{ Mg m}^{-3}$
$M_r = 835.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 32959 reflections
$a = 13.5277$ (2) Å	$\theta = 3-27^\circ$
$b = 12.4006$ (3) Å	$\mu = 6.73 \text{ mm}^{-1}$
$c = 15.6585$ (2) Å	$T = 200 \text{ K}$
$\beta = 93.176$ (1)°	Block, orange
$V = 2622.70$ (8) Å <sup>3</sup>	$0.38 \times 0.21 \times 0.14 \text{ mm}$
$Z = 4$	

### Data collection

Nonius KappaCCD diffractometer	4200 reflections with $I > 3\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.05$
Absorption correction: integration (Coppens, 1970)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.192$ , $T_{\text{max}} = 0.497$	$h = -17 \rightarrow 17$
49588 measured reflections	$k = -16 \rightarrow 16$
5998 independent reflections	$l = -20 \rightarrow 20$

### Refinement

Refinement on $F^2$	$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2 / [1.39T_o(x) - 0.108T_1(x) + 0.987T_2(x)]$
$R[F^2 > 3\sigma(F^2)] = 0.025$	where $T_i$ are Chebychev polynomials and $x = F_c/F_{\text{max}}$ (Prince, 1982; Watkin, 1994)
$wR[F^2 > 3\sigma(F^2)] = 0.028$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.95 \text{ e \AA}^{-3}$
4200 reflections	$\Delta\rho_{\text{min}} = -0.75 \text{ e \AA}^{-3}$
334 parameters	

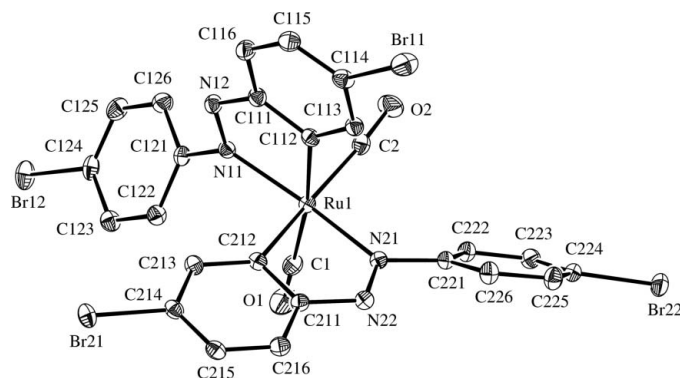
**Table 1**

Selected geometric parameters (Å, °).

Ru1–N11	2.071 (2)	Ru1–C2	1.956 (3)
Ru1–N21	2.086 (2)	Ru1–C112	2.090 (3)
Ru1–C1	1.957 (3)	Ru1–C212	2.093 (3)
N11–Ru1–N21	165.18 (10)	C1–Ru1–C112	172.86 (12)
N11–Ru1–C1	97.02 (12)	C2–Ru1–C112	85.23 (12)
N21–Ru1–C1	91.87 (12)	N11–Ru1–C212	91.05 (11)
N11–Ru1–C2	92.13 (11)	N21–Ru1–C212	76.88 (11)
N21–Ru1–C2	98.29 (12)	C1–Ru1–C212	91.21 (13)
C1–Ru1–C2	98.38 (14)	C2–Ru1–C212	169.44 (13)
N11–Ru1–C112	76.62 (11)	C112–Ru1–C212	85.72 (11)
N21–Ru1–C112	93.71 (11)		

H atoms were included at idealized positions and made to ride on their parent atoms, with  $\text{C–H} = 1.00 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

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: ORTEPIII (Johnson, 1976) in TEXSAN (Molecular Structure Corporation, 1997); software used to prepare material for publication: CRYSTALS.

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