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mark.humphrey@anu.edu.au**Key indicators**Single-crystal X-ray study  
*T* = 200 K  
Mean  $\sigma(\text{C}-\text{C})$  = 0.005 Å  
*R* factor = 0.025  
*wR* factor = 0.030  
Data-to-parameter ratio = 13.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Bis( $\mu_3$ -4-bromophenylimido)tris(tricarbonylruthenium)(2 *Ru—Ru*)**

The title compound,  $[\text{Ru}_3(\mu_3\text{-NC}_6\text{H}_4\text{Br})_2(\text{CO})_9]$ , is a V-shaped triruthenium cluster, each side of the V being face-capped by a 4-bromophenylimide ligand. Each Ru atom is also ligated by three terminal carbonyl ligands. There are two molecules in the asymmetric unit with minor conformational differences.

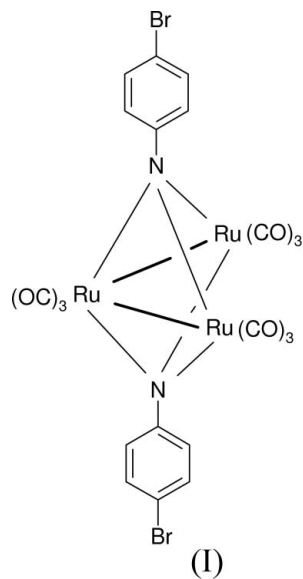
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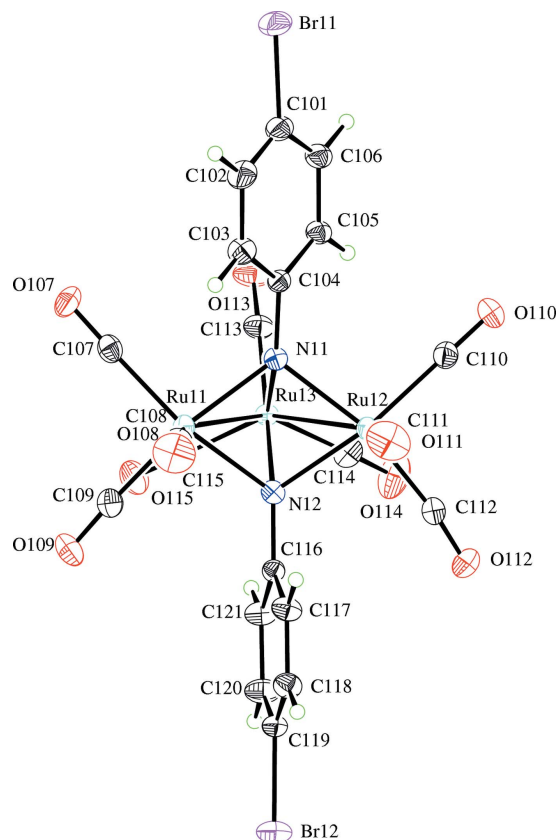
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**Comment**

Azobenzene undergoes  $\text{N}=\text{N}$  bond cleavage upon reaction with  $[\text{Ru}_3(\text{CO})_{12}]$  (Bruce *et al.*, 1986), providing access to cluster-stabilized phenylimide ligands. Carbonyl ligands on the bis(phenylimido)triruthenium cluster product can be displaced by mono- or bidentate phosphines (Bruce *et al.*, 1987). We have now examined the reaction of 4,4'-dibromoazobenzene with  $[\text{Ru}_3(\text{CO})_{12}]$ , and have structurally characterized the product, (I).



The asymmetric unit of (I) consists of two molecules of  $[\text{Ru}_3(\mu_3\text{-NC}_6\text{H}_4\text{Br})_2(\text{CO})_9]$  which are chemically identical but have minor conformational differences. In both molecules, one *Ru—Ru* bond of the triangular precursor has been cleaved, and the resultant V-shaped triruthenium cluster core is face-capped on each side by a 4-bromophenylimide ligand resulting from  $\text{N}=\text{N}$  cleavage of the substituted azobenzene precursor. Three carbonyl ligands at each Ru atom complete the coordination (Table 1, Fig. 1). Comparison of the bond distances and angles in (I) with those of the phenylimido-containing analogue  $[\text{Ru}_3(\mu_3\text{-NC}_6\text{H}_5)_2(\text{CO})_9]$  (Bruce *et al.*, 1986) reveals that core distances and angles are essentially the same.



**Figure 1**  
A view of one molecule of (I), with displacement ellipsoids drawn at the 30% probability level (arbitrary spheres for the H atoms). The second molecule (not shown) is almost identical.

## Experimental

[Ru<sub>3</sub>(CO)<sub>12</sub>] (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 was heated at reflux for 4 h. The resulting brown solution was evaporated to dryness on a rotary evaporator, and the residue dissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub> (*ca* 3 ml) and applied to preparative thin-layer chromatography plates. Elution with CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether (1:9) gave three bands and a heavy baseline. Band 1 was yellow ( $R_f = 0.75$ ), band 2 was orange ( $R_f = 0.52$ ) and band 3 was yellow ( $R_f = 0.21$ ). The contents of band 2 were identified as (I) (yield 12.8 mg, 0.014 mmol, 13%). Analysis: MS (secondary ion, Cs<sup>+</sup>): 895 – 28*n* ([*M* – *n*CO]<sup>+</sup>, *n* = 0–7); IR (c-C<sub>6</sub>H<sub>12</sub>, *v*, cm<sup>-1</sup>): (CO) 2097 (*w*), 2075 (*vs*), 2052 (*vs*), 2024 (*s*), 2018 (*s*), 2014 (*s*), 1991 (*m*), 1981 (*w*). Crystals suitable for X-ray diffraction study were obtained by liquid diffusion of methanol into a dichloromethane solution.

### Crystal data

[Ru<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>BrN)<sub>2</sub>(CO)<sub>9</sub>]  
 $M_r = 895.32$   
 Triclinic, *P* $\bar{1}$   
 $a = 13.0136$  (2) Å  
 $b = 14.6979$  (2) Å  
 $c = 15.8864$  (2) Å  
 $\alpha = 100.9819$  (9)°  
 $\beta = 112.3150$  (8)°  
 $\gamma = 98.9674$  (8)°  
 $V = 2671.05$  (7) Å<sup>3</sup>

$Z = 4$   
 $D_x = 2.226$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 36343 reflections  
 $\theta = 3$ –27°  
 $\mu = 4.72$  mm<sup>-1</sup>  
 $T = 200$  K  
 Plate, red  
 0.40 × 0.34 × 0.12 mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: integration via Gaussian method (Coppens, 1970) implemented in MAXUS (Mackay *et al.*, 2000)  
 $T_{\min} = 0.284$ ,  $T_{\max} = 0.624$

58882 measured reflections  
 12233 independent reflections  
 8846 reflections with  $I > 3\sigma(I)$   
 $R_{\text{int}} = 0.05$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -19 \rightarrow 19$   
 $l = -20 \rightarrow 20$

### Refinement

Refinement on  $F$   
 $R[F^2 > 2\sigma(F^2)] = 0.025$   
 $wR(F^2) = 0.030$   
 $S = 1.07$   
 8846 reflections  
 668 parameters  
 H-atom parameters constrained  
 Weighting scheme: Chebyshev polynomial (Watkin, 1994; Prince, 1982);

$w = 1/[1.71T_0(x) + 0.166T_1(x) + 1.45T_{n-1}(x)]$ ,  
 where  $x = F/F_{\max}$ ;  
 $W = w[1 - (\delta F/6\sigma F)^2]^2$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 1.03$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.01$  e Å<sup>-3</sup>  
 Extinction correction: Larson (1970), eq. 22  
 Extinction coefficient: 100 (8)

**Table 1**

Selected geometric parameters (Å, °).

Ru11···Ru12	3.2923 (3)	Ru21···Ru22	3.2879 (3)
Ru11–Ru13	2.6557 (3)	Ru21–Ru23	2.6414 (3)
Ru12–Ru13	2.6758 (3)	Ru22–Ru23	2.7064 (3)
Ru11–N11	2.069 (3)	Ru21–N21	2.088 (2)
Ru11–N12	2.069 (3)	Ru21–N22	2.085 (2)
Ru12–N11	2.061 (3)	Ru22–N21	2.058 (3)
Ru12–N12	2.072 (3)	Ru22–N22	2.065 (2)
Ru13–N11	2.156 (2)	Ru23–N21	2.109 (2)
Ru13–N12	2.113 (3)	Ru23–N22	2.129 (2)
Ru12···Ru11–Ru13	52.142 (8)	Ru22···Ru21–Ru23	52.961 (8)
Ru11···Ru12–Ru13	51.590 (8)	Ru21···Ru22–Ru23	51.173 (8)
Ru12–Ru13–Ru11	76.268 (10)	Ru22–Ru23–Ru21	75.866 (9)

H atoms were placed in idealized positions and refined as riding on their parent C atoms, with C–H = 1.00 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The largest peaks in the final difference electron-density map are located near Br and Ru atoms.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and 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.

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