Crystal Structure of (Cycloocta-1,5-diene)tris(hydrazine)hydrido-ruthenium(II) tetraphenylborate

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The salt $[\text{RuH}(\text{COD})(\text{H}_2\text{NNH}_2)_3][\text{BPh}_4]$ (**2**) (COD = cycloocta-1,5-diene and BPh_4 = tetraphenylborate) was prepared by reacting the polymeric species $[\{\text{Ru}(\text{COD})\text{Cl}_2\}_x]$ (**1**; $x > 2$) with hydrazine hydrate in refluxing ethanol. The obtained crystal was characterized by single-crystal X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit-cell dimensions $a = 9.7449(8)\text{\AA}$, $b = 32.881(3)\text{\AA}$, $c = 18.6962(16)\text{\AA}$, $\beta = 99.571(10)^\circ$, $V = 5907.3(9)\text{\AA}^3$ and $Z = 8$. The ruthenium has a distorted octahedral geometry with two formula units comprising two cations and two anions in the asymmetric unit.

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Our interest in the ruthenium(II) complexes with chelating phosphine ligands stem from their demonstrated utility in the asymmetric hydrogenation of a wide range of substrates.¹ The title complex is therefore synthesized by modifying a literature procedure,² as a precursor to preparing a series of catalytically active phosphine and diphosphine ruthenium(II) compounds. The product was recrystallized from $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and ethanol as colourless needles. The structure of the related dimethylhydrazine complex was reported by Singleton *et al.*³ In that report, the presence of a hydride ligand in the dimethylhydrazine derivative was only inferred from the observed peak of $0.65\text{ e}\text{\AA}^{-3}$, since it could not be located from the final difference-Fourier map during analysis. However, in the present molecule, the hydrogen atoms of the Ru-H as well as those of the NH_2 and NH_2NH_2 moieties were located from a difference Fourier map and refined isotropically. The remaining

hydrogen atoms in both molecules were placed at idealized positions, and were refined using a riding model. The largest residual electron density for structure ($2.881\text{ e}\text{\AA}^{-3}$) was located close to (less than $1.0\text{ \AA}$ from) the ruthenium atom, and was most likely due to imperfect absorption corrections frequently

Fig. 1 Chemical diagram of the title compound.

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Table 1 Crystal and experimental data

Chemical formula $\text{C}_{32}\text{H}_{45}\text{BN}_6\text{Ru}$
Formula weight = 625.62
$T = 100(2)\text{K}$
Crystal system: Monoclinic Space group: $P2_1/n$
$a = 9.7449(8)\text{\AA}$
$b = 32.881(3)\text{\AA}$ $\beta = 99.571(1)^\circ$
$c = 18.6962(16)\text{\AA}$
$V = 5907.3(9)\text{\AA}^3$ $Z = 8$
$D_{\text{calc}} = 1.407\text{ (Mg/m}^3\text{)}$
Radiation: Mo K_α ($\lambda = 0.71073\text{ \AA}$)
$\mu(\text{Mo } K_\alpha) = 0.563\text{ mm}^{-1}$ $F(0\ 0\ 0) = 2624$
Crystal size = $0.24 \times 0.17 \times 0.12\text{ mm}^3$
No of reflections collected = 53876
No of independent reflections = 13001
Theta range for data collection: 1.24 to 27.08°
$R_{\text{int}} = 0.0433$
Data/restraints/parameters = $13001/0/813$
Goodness of fit on $F^2 = 1.049$
R indices [$I \geq 2\sigma(I)$]: $R1 = 0.0392$, $wR2 = 0.0909$
R indices (all data): $R1 = 0.0499$, $wR2 = 0.0984$
$\Delta\rho(\text{max}) = 2.881\text{ e}\text{\AA}^{-3}$, $\Delta\rho(\text{min})(\text{e}\text{\AA}^{-3}) = -1.848$
Measurement: Bruker SMART APEX2 CCD
Programs system: Bruker SADABS-2007
Structure determination: SHELXS-2003
CCDC deposition number: 859974