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A 1,10-Phenanthroline-Ligated *closo*-Ruthenaundecaborane: [(C₁₂H₈N₂)Ru-B₁₀H₈(OC₂H₅)₂]

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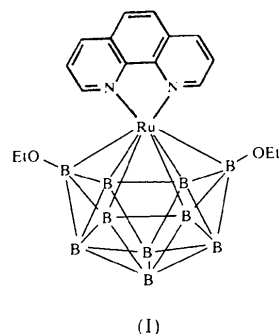
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Abstract

In the title compound, 2,3-diethoxy-1-(1,10-phenanthroline-*N,N'*)-1-ruthena-*closo*-undecaborane, [Ru(C₄H₁₈B₁₀O₂)(C₁₂H₈N₂)], the Ru atom is bound to two N atoms of the 1,10-phenanthroline (phen) ligand and six B atoms of the *closo* 11-vertex {RuB₁₀} cage. The Ru—N bond distances are 2.117 (2) and 2.128 (2) Å, and the N1—Ru1—N10 bite angle is 78.26 (8)°.

Comment

In metalloborane chemistry, ligand-exchange reactions at the metal centre of a compound present a reasonably viable way to form new metalloborane compounds (Siedle & Todd, 1976). An analysis of the literature shows that, in such processes, the leaving groups are often phosphine ligands (PPh₃ or PMe₂Ph), while the substituents could be such ligands as PMe₃ (Bown *et al.*, 1987), PMe₂Ph (Kennedy, 1986), Ph₂PCH₂PPh₂ (Elrington *et al.*, 1984), C₂S₂(CN)₂²⁻, CN⁻ (Siedle & Todd, 1976) and SCSNEt₂ (Beckett *et al.*, 1985). Siedle & Todd (1976) published the synthesis of [(phen)PdB₁₀H₁₂] via a ligand-displacement reaction, which was characterized by spectroscopic methods (Siedle & Todd, 1976). No ruthenium analogue has so far been reported. We report here the first phenligated *closo*-ruthenaborane compound, (I), the structure of which was established by X-ray diffraction.



Compound (I) (Fig. 1) contains an {RuB₁₀H₈(OC₂H₅)₂} 11-vertex metalloborane cluster, with the Ru atom lying above the boat-type face of six B atoms. Such a cluster is very similar to [(PPh₃)₂RuB₁₀H₈(OC₂H₅)₂], (II) (Crook *et al.*, 1984, 1985), and [(PMe₃)(PPh₃)RuB₁₀H₈(OC₂H₅)₂], (III) (Bown *et al.*, 1987). However, the Ru—B bond lengths in (I) [2.014 (4)–2.326 (3) Å] are shorter than those reported for both (II) [2.041 (8)–2.402 (8) Å] and (III) [2.032 (5)–2.374 (5) Å]. This indicates that the coordination of the phen ligand strengthens slightly the metal–boron bonding within the present cluster compared with the phosphines.

The bidentate phen ligand coordinates to the Ru atom with Ru—N distances of 2.117 (2) and 2.128 (2) Å. These bonds are significantly longer than the corresponding Ru—N_{phen} bond lengths in the literature, for example, 2.056 (8) and 2.082 (9) Å for [Ru(bipy)(phen)]²⁺ (Ye *et al.*, 1995), where bipy is 2,2'-bipyridine, 2.096 (5)–2.100 (5) Å for [Ru(phen)₂(py)₂]²⁺ (Bonneson *et al.*, 1983), where py is pyridine, and an average of 2.063 (4) Å for [Ru(phen)₃]²⁺ (Breu & Stoll, 1996). The relative elongation of the Ru—N bond lengths can be attributed to the influence of the {RuB₁₀} cage. In compound (I), both the N—Ru—N bite angle [78.26 (8)°]

and the geometry of the phen ligand are found to be normal when compared with those in the phen complexes mentioned above.

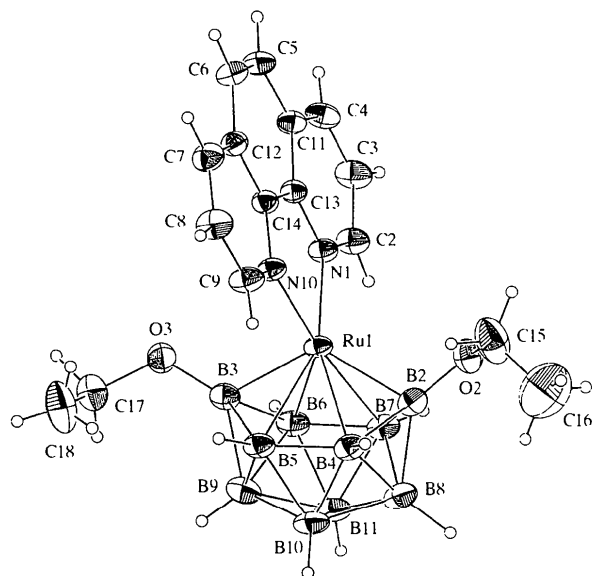


Fig. 1. ZORTEP (Zsolnai & Huttner, 1994) plot of (I) showing 30% probability displacement ellipsoids.

Experimental

The synthesis of the title compound was carried out by the reaction of compound (II) (30 mg, 0.036 mmol) with excess 1,10-phenanthroline hydrate (15 mg, 0.076 mmol) in refluxing dichloromethane for 24 h under an atmosphere of dry nitrogen. The resulting solution was reduced in volume and chromatographed using dichloromethane as the eluting medium to give the red title compound at $R_f = 0.4$ in a high yield of 92%. Crystals suitable for X-ray study were grown from an *n*-pentane–dichloromethane (3:1) solution.

Crystal data

[Ru(C ₄ H ₁₈ B ₁₀ O ₂)(C ₁₂ H ₈ N ₂)]	Mo $K\alpha$ radiation
$M_r = 487.56$	$\lambda = 0.71069 \text{ \AA}$
Monoclinic	Cell parameters from 20 reflections
$P2_1/n$	$\theta = 9.25\text{--}13.36^\circ$
$a = 9.069 (2) \text{ \AA}$	$\mu = 0.698 \text{ mm}^{-1}$
$b = 17.009 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 15.104 (2) \text{ \AA}$	Square prism
$\beta = 99.47 (2)^\circ$	$0.40 \times 0.20 \times 0.20 \text{ mm}$
$V = 2298.1 (7) \text{ \AA}^3$	Dark red
$Z = 4$	
$D_x = 1.409 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Rigaku AFC-7R diffractometer	3875 reflections with $I > 2\sigma(I)$
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ω scans

Absorption correction:

ψ scan (North *et al.*, 1968)

$T_{\min} = 0.768$, $T_{\max} = 0.873$

4844 measured reflections

4519 independent reflections

$R_{\text{int}} = 0.029$

$\theta_{\max} = 27.49^\circ$

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 22$

$l = -19 \rightarrow 19$

3 standard reflections

every 200 reflections

intensity decay: -0.09%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.086$

$S = 1.009$

4519 reflections

364 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2$

$+ 1.1701P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.006$

$\Delta\rho_{\max} = 0.670 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.458 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Ru1—B3	2.014 (4)	Ru1—B5	2.304 (3)
Ru1—B2	2.017 (3)	Ru1—B4	2.322 (3)
Ru1—N1	2.117 (2)	Ru1—B7	2.326 (3)
Ru1—N10	2.128 (2)	B2—O2	1.368 (4)
Ru1—B6	2.280 (3)	B3—O3	1.368 (4)
B3—Ru1—N1	106.54 (11)	N1—Ru1—B5	153.76 (11)
B2—Ru1—N1	116.68 (11)	N10—Ru1—B5	95.10 (10)
B3—Ru1—N10	97.19 (11)	N1—Ru1—B4	162.91 (11)
B2—Ru1—N10	126.71 (11)	N10—Ru1—B4	106.13 (10)
N1—Ru1—N10	78.26 (8)	N1—Ru1—B7	101.16 (10)
N1—Ru1—B6	96.88 (10)	N10—Ru1—B7	172.64 (11)
N10—Ru1—B6	143.92 (11)		

H atoms on B atoms were located using Fourier methods and were refined isotropically. H atoms attached to C atoms were refined isotropically except for those of the C15—C16 ethyl group, which were placed in calculated positions with C—H distances of 0.97 and 0.96 \AA .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCR electronic archives (Reference: FR1135). Services for accessing these data are described at the back of the journal.

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A Hetero-Tribridged Dinuclear Molybdenum Compound $[\text{Bu}_4\text{N}][\text{Mo}_2(\text{CO})_6(\mu\text{-Cl-C}_6\text{H}_4\text{S})_2\text{Br}]^-$

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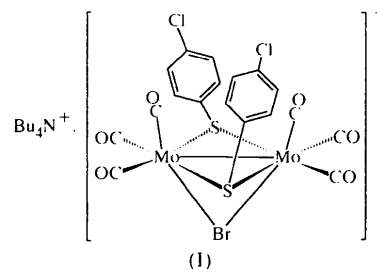
Abstract

The title compound, tetra-*n*-butylammonium μ -bromobis(μ -*p*-chlorobenzenethiolato)bis(tricarbonylmolybdenum)(*Mo*—*Mo*), $(\text{C}_{16}\text{H}_{36}\text{N})[\text{Mo}_2\text{Br}(\text{C}_6\text{H}_4\text{ClS})_2(\text{CO})_6]$, contains a Bu_4N^+ cation and an $[\text{Mo}_2(\text{CO})_6(\mu\text{-Cl-C}_6\text{H}_4\text{S})_2\text{Br}]^-$ anion. The structure of the anion can be viewed as a cofacial bi-octahedral dimer, in which two *fac*- $\text{Mo}(\text{CO})_3$ fragments are bridged by two *p*- $\text{Cl-C}_6\text{H}_4\text{S}^-$ groups and one Br^- ligand. The mean Mo — Br distance is 2.765 (2) Å and the Mo — Br — Mo angle is 62.68 (4)°.

Comment

Low-valence dinuclear molybdenum–carbonyl complexes with thiolato bridges of the type $[\text{Mo}_2(\text{CO})_8(\text{SR})_2]$ were synthesized over a decade ago (Zhuang *et al.*,

1984; Smith *et al.*, 1987) by a convenient route. These complexes were found to undergo a reversible two-electron redox reaction in a single step, accompanied by formation/cleavage of a single metal–metal bond and significant rearrangement of the Mo_2S_2 core. The axial CO ligands of these complexes can be substituted by coordinating solvent molecules such as CH_3CN to afford solvent-substituted species, *i.e.* $[\text{Mo}_2(\text{CO})_6(\text{CH}_3\text{CN})_2(\text{SR})_2]$. The structures of these complexes were subsequently determined (Zhuang *et al.*, 1989*a,b*, 1995). Herein, the title compound, $[\text{Bu}_4\text{N}][\text{Mo}_2(\text{CO})_6(\mu\text{-Cl-C}_6\text{H}_4\text{S})_2\text{Br}]^-$ (I), is taken account of as an additional member of this family.



The structure of the anion of the title compound is shown in Fig. 1. The geometry around each Mo atom is distorted octahedral, with one Br, three carbonyl C and two *p*-chlorobenzenethiolato S ligating atoms. Two *fac*- $\text{Mo}(\text{CO})_3$ fragments are bridged by two *p*- $\text{Cl-C}_6\text{H}_4\text{S}$ ligands and one Br^- ion to form a hetero-tribridged cofacial bi-octahedral structure containing an approximately planar Mo_2S_2 unit. The two chlorobenzene groups are in a *syn* configuration relative to the Mo_2S_2 plane. The fact that the Mo — Mo distance [2.8761 (14) Å] is significantly shorter than that of

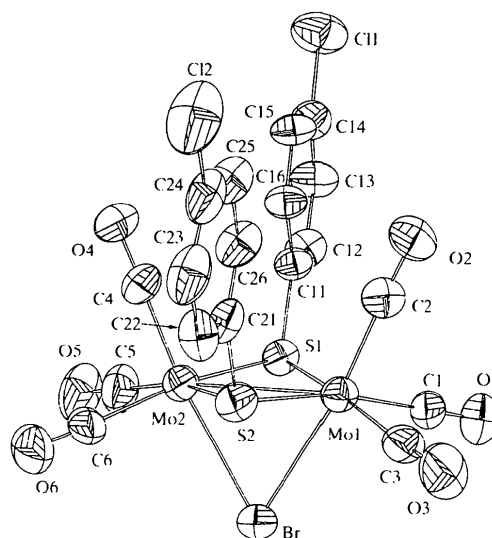


Fig. 1. View of the structure of the title complex anion with displacement ellipsoids shown at the 30% probability level.