1-Acetonitrile-3-chloro-1,2-(μ-3,5-dinitrobenzo-ato-κ²O,O′)-1-(triphenylphosphine-κP)-closo-1-ruthenaundecaborane

Qing-Liang Guo, Jian-Min Dou,* Li-Bin Wu, Da-Cheng Li and Da-Qi Wang

School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, People's Republic of China

Correspondence e-mail: jmdou@lctu.edu.cn

The title cluster, $[Ru(C_7H_{11}B_{10}ClN_2O_6)(C_2H_3N)(C_{18}H_{15}P)]$ or $[1,2-\{3,5-(NO_2)_2(C_6H_3)COO\}-1-(PPh_3)-1-(CH_3CN)-3-Cl-1-RuB_{10}H_8]$, has an iso-closo 11-vertex RuB_{10} core geometry with the metal occupying the unique six-connected apical position, giving the characteristic 11-vertex iso-closo $[MB_{10}]$ metalloborane 1:2:4:2:2 stack. The ruthenium centre has three exo-polyhedral ligands: one triphenylphosphine, one aceto-nitrile and one 3,5-dinitrobenzoate, which is coordinated through Ru—O and B—O bonds, resulting in an exocyclic five-membered Ru/O/C/O/B ring.

Comment

Boron polyhedral clusters have attracted much attention owing to their unique molecular architecture and many useful applications (Plesek, 1992; Grimes, 2004; Saxena et al., 1993, 1997). The first two closo 11-vertex ruthenaboranes with exo-polyhedral metal-to-cluster carboxylate ligands are structu-rally typified by the clusters $[\{(PPh_3)_2Ru\}(MeCO_2)_2(H)_2-\{(MeCO_2)RuB_{10}H_7\}]$ and $[(PPh_3)(MeCO_2)_2RuB_{10}H_7(OH)]$ (Fontaine et al., 1987). Since then, a series of such ruthena-borane clusters including carboxylate or thiocarboxylate as ligands, all with one or two Ru/O(or S)/C/O/B five-membered exo-cycles, have been synthesized by reacting $[RuCl_2(PPh_3)_3]$ and closo-$[B_{10}H_{10}]^{2-}$ with PhCOOH (Yao et al., 1995), p-MeC_6H_4COOH (Nie et al., 2000), PhCOSH (Yao, et al., 1998) and MeCOSH (Nie, et al., 1999). As a continuation of this investigation on exo-polyhedral cyclization clusters, we studied the reaction of $[RuCl_2(PPh_3)_3]$, closo-$[B_{10}H_{10}]^{2-}$ and $3,5-(NO_2)_2(C_6H_4)COOH$. The preparation and structure of the title cluster, (I), are reported here.

(I)
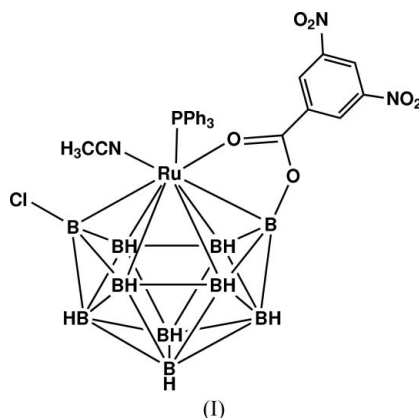
A view of the molecular structure is shown in Fig. 1. The title cluster has a closo 11-vertex $[RuB_{10}]$ polyhedral skeleton with the Ru atom occupying the unique six-connected apical position. The B atoms that bond to the metal centre have a
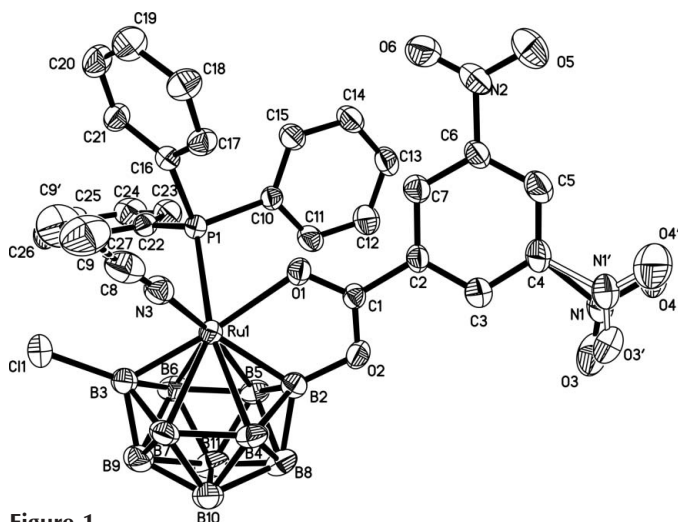
Figure 1
The structure of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

boat conformation. The Ru1—B2 and Ru1—B3 bond lengths [2.026 (5) and 2.041 (5) Å, respectively] are essentially the same as the corresponding distances found in the cluster [(PPh₃)₂(PhCO₂)RuB₁₀H₈Cl] [2.03 (1) Å for both Ru—B bonds (Yao *et al.*, 1995)]. The average length of the Ru1—B4, Ru1—B5, Ru1—B6 and Ru1—B7 bonds is 2.335 (6) Å, which is also consistent with bond lengths observed in [(PPh₃)₂(PhCO₂)RuB₁₀H₈Cl] [average 2.360 (2) Å] and [(PPh₃)(*p*-Me(C₆H₄)CO₂)₂RuB₁₀H₈] [average 2.342 (4) Å; Nie *et al.*, 2000].

The Ru atom also has three *exo*-polyhedral ligands: one triphenylphosphine, one acetonitrile molecule and one 3,5-dinitrobenzoate in which one carbonyl O atom coordinates to Ru1 and the other to B2. This results in an *exo*-polyhedral five-membered Ru/O/C/O/B ring, which is similar to that in the analogous 11-vertex *closo*-ruthenaborane [(PPh₃)₂(PhCO₂)-RuB₁₀H₈Cl] (Yao *et al.*, 1995). The distance from Ru1 to P1 is 2.5059 (12) Å, which falls in the expected range. It should be noted that the coordinated acetonitrile molecule is derived from the eluting solvent, showing that solvent can take part in these reactions. The distance from Ru1 to N3 is 2.106 (4) Å. In addition, the H atom initially bonded to B3 is replaced by a Cl atom. The bond length B3—Cl1 = 1.805 (5) Å is slightly longer than that reported in [(PPh₃)₂(PhCO₂)RuB₁₀H₈Cl] [B—Cl = 1.78 (1) Å; Yao *et al.*, 1995].

Experimental

The synthesis of the title ruthenaborane was carried out by reacting [RuCl₂(PPh₃)₃] (0.384 g, 0.4 mmol), (Et₄N)₂B₁₀H₁₀ (0.151 g, 0.4 mmol) and 3,5-(NO₂)₂PhCOOH (0.170 g, 0.8 mmol) in distilled CH₂Cl₂ in a three-necked flask under a dry N₂ atmosphere for 120 h. The solvent was concentrated to 8 ml under reduced pressure and chromatographed using CH₂Cl₂/light petroleum/acetonitrile (8:2:1) as the eluting medium to give the brown title compound at R_f = 0.75. The product was recrystallized from an *n*-pentane/CH₂Cl₂ solution.

Table 1
Selected geometric parameters (Å, °).

Ru1—B2	2.026 (5)	Ru1—B5	2.360 (5)
Ru1—B3	2.041 (5)	Ru1—B4	2.370 (5)
Ru1—N3	2.106 (4)	Ru1—P1	2.5059 (12)
Ru1—O1	2.265 (2)	Cl1—B3	1.805 (5)
Ru1—B6	2.287 (5)	O1—C1	1.240 (4)
Ru1—B7	2.325 (5)	O2—C1	1.296 (4)
B2—Ru1—B3	115.6 (2)	N3—Ru1—O1	82.77 (12)
B2—Ru1—N3	134.29 (17)	B2—Ru1—B6	84.95 (19)
B3—Ru1—N3	85.58 (18)	B3—Ru1—B6	46.64 (19)
B2—Ru1—O1	71.75 (15)	N3—Ru1—B6	131.06 (17)
B3—Ru1—O1	168.11 (17)		

Atoms C9 (CH₃CN) and N1/O3/O4 are disordered with C9′ and N1′/O3′/O4′, respectively. Site occupation factors were fixed at 0.55 for C9 and 0.45 for C9′, based on the initial refinement. Occupation factors for the disordered nitro group were refined to 0.316 (14) (N1/O3/O4) and 0.684 (14) (N1′/O3′/O4′). H atoms were included in calculated positions and refined using a riding-model approximation. [Constrained C—H bond lengths and isotropic U parameters: 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic CH; 0.96 Å and $U_{iso}(H) = U_{eq}(C)$ for CH₃; 1.10 Å and $U_{iso}(H) = 1.2U_{eq}(B)$ for BH groups.]

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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