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1,2:1,3-Bis(μ-*p*-toluato-*O*:*O*′)-1-(triphenylphosphine-*P*)-1-ruthena-*closo*-undecaborane

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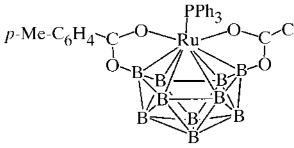
The title compound, $[(PPh_3)(p\text{-}MeC_6H_4COO)_2RuB_{10}H_8]$, contains an 11-vertex *closo*-type RuB_{10} cluster fused to two symmetric exopolyhedral Ru—O—C—O—B five-membered rings. Principal distances include Ru—B 2.010 (5)–2.392 (4) Å and Ru—O 2.218 (5) and 2.222 (2) Å.

Comment

Since the first two ruthenaboranes with exopolyhedral metal-to-cluster acetate bridges were prepared by the reaction of $[RuCl_2(PPh_3)_3]$ and *closo*-$[B_{10}H_{10}]^{2-}$ in MeCOOH/tetrahydrofuran solution (Fontaine *et al.*, 1987), a series of such carboxylato- or thiocarboxylato-bridged ruthenaborane compounds, all with one or two Ru—O(or S)—C—O—B five-membered exocycles, have been isolated by our group from similar reactions with PhCOOH, *o*-PhNHC$_6$H$_4$COOH or PhCOSH (Zheng *et al.*, 1999; Nie *et al.*, 1999). We have also demonstrated that in $[(PPh_3)(MeCOS)_2RuB_{10}H_8]$, (II) (Nie *et al.*, 1999), derived from the same reaction with MeCOSH, the existence of the two symmetric Ru—S—C(Me)—O—B cycles slightly strengthens the Ru—B bonding at the cyclized sites compared with the non-cyclized compound. To make a comparative study of the two different types of exocyclization, we report here the *p*-toluato-bridged title compound, (I), as an additional member of this class of ruthenaborane complexes.



(I)

Compound (I) (Fig. 1) displays the expected *closo* molecular architecture, with the Ru centre ligating to one P atom of the PPh$_3$ ligand, six B atoms of the borane and two O atoms of the *p*-toluato moieties. The Ru—B2 and Ru—B3 bond lengths of 2.010 (5) and 2.027 (4) Å, respectively, are essentially the same as the corresponding distances found in $[(PPh_3)(PhCOO)_2RuB_{10}H_8]$, (III) [2.014 (7) and 2.019 (7) Å; Zheng, P.-J., unpublished results], $[(PPh_3)Ru(\mu\text{-}MeCOO)_3(\mu\text{-}H)_2\text{-}RuB_{10}H_7]$, (IV) [2.047 (6) Å], and $[(PPh_3)(MeCOO)_2\text{-}RuB_{10}H_7(OH)]$, (V) [2.044 (5) Å; Fontaine *et al.*, 1987], and $[(PPh_3)_2(PhCOO)RuB_{10}H_8Cl]$, (VI) [2.03 (1) Å; Yao *et al.*, 1995], but slightly shorter than those of 2.052 (6) and 2.067 (5) Å for $[(PPh_3)(PhCOS)_2RuB_{10}H_8]$ (Yao *et al.*, 1998), and 2.037 (8) and 2.062 (8) Å for (II). All these bonds are again shorter than those [2.092 (7) and 2.103 (7) Å, respectively] in the non-cyclized compound [1-(pcym)-*isocloso*-1-RuB$_{10}$H$_{10}$] (where pcym is *p*-cymene, 1-Me-4-Pr^{i}C$_6$H$_4$; Bown *et al.*, 1990). This indicates that, despite the limited data for comparison, the formation of the two types of five-membered rings, *i.e.* Ru—O—C—O—B and Ru—S—C—O—B, in such ruthenaboranes slightly strengthens the Ru—B bonding at the cyclized sites compared with the non-cyclized cage. However, the former has a stronger effect than the latter, presumably due to the different electronegativity of O and S. Interestingly, it has also been found that, in both cases, the substituent effect of (thio)carboxylate moieties upon the relative shortening of the two Ru—B bond lengths is different. When the groups of cyclization are thiocarboxylates, an alkyl group (*i.e.* Me) has a stronger effect than an aryl group (*i.e.* Ph; Nie *et al.*, 1999), while in the cases of carboxylates (with Me *versus* Ph or *p*-tolyl), the effect is found to be contrary. This may arise from the combination of the different electronic and steric natures that the two different types of substituents impart to the system.

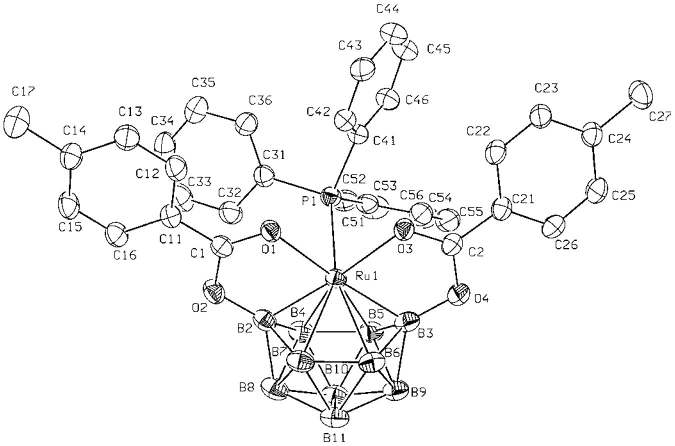


Figure 1
ORTEP-3 (Farrugia, 1996) drawing of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

In the present structure, the bond lengths of 1.245 (5) and 1.244 (4) Å for C1—O1 and C2—O3, respectively, are rather similar to the value expected for a double bond (*ca* 1.22 Å), while the distances of 1.324 (4) and 1.332 (4) Å for C1—O2 and C2—O4, respectively, are between the values expected for a single (*ca* 1.43 Å) and a double bond, suggesting a partial but unequal electron delocalization over the O—C—O system. Similar situations have also been observed in compounds (III)–(VI).

Experimental

The synthesis of the title compound was effected by the reaction of $[RuCl_2(PPh_3)_3]$ (0.38 g, 0.4 mmol) and $[NEt_4]_2B_{10}H_{10}$ (0.16 g, 0.4 mmol) with *p*-toluic acid (0.11 g, 0.8 mmol) in refluxing dichloromethane for 118 h under an atmosphere of dry nitrogen. The resulting solution was reduced in volume and chromatographed using dichloromethane/light petroleum (b.p. 333–363 K; 2:1) as the eluting medium, to give red (I) at $R_f = 0.88$. Crystals suitable for X-ray study were grown from an *n*-pentane/dichloromethane (2:1) solution.

Crystal data

$[Ru(C_{16}H_{22}B_{10}O_4)(C_{18}H_{15}P)]$
$M_r = 749.78$
Triclinic, $P\bar{1}$
$a = 11.368$ (2) Å
$b = 16.922$ (3) Å
$c = 11.092$ (2) Å
$\alpha = 103.26$ (2)°
$\beta = 117.80$ (1)°
$\gamma = 89.64$ (2)°
$V = 1824.6$ (7) Å^3
$Z = 2$
$D_x = 1.365$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 9.3$–10.8°
$\mu = 0.511$ mm^{-1}
$T = 296$ (2) K
Block, red
0.5 × 0.4 × 0.3 mm

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.78$, $T_{max} = 0.86$
7172 measured reflections
7172 independent reflections
6051 reflections with $I > 2\sigma(I)$
$\theta_{max} = 26°$
$h = 0 \rightarrow 14$
$k = -20 \rightarrow 20$
$l = -13 \rightarrow 11$
3 standard reflections every 300 reflections intensity decay: 2.6%

Table 1
Selected geometric parameters (Å, °).

Ru1—B2	2.010 (5)	Ru1—P1	2.4779 (10)
Ru1—B3	2.027 (4)	O1—C1	1.245 (5)
Ru1—O3	2.218 (5)	O2—C1	1.324 (4)
Ru1—O1	2.222 (2)	O2—B2	1.443 (5)
Ru1—B4	2.276 (5)	O3—C2	1.244 (4)
Ru1—B5	2.277 (4)	O4—C2	1.332 (4)
Ru1—B7	2.362 (4)	O4—B3	1.430 (6)
Ru1—B6	2.392 (4)		
B2—Ru1—O3	158.23 (13)	B2—Ru1—B6	85.89 (17)
B3—Ru1—O3	71.76 (16)	O3—Ru1—B6	88.96 (13)
B2—Ru1—O1	72.54 (13)	O1—Ru1—B6	115.92 (12)
B3—Ru1—O1	153.68 (14)	B2—Ru1—P1	108.75 (13)
O3—Ru1—O1	90.91 (9)	B3—Ru1—P1	114.63 (12)
O3—Ru1—B4	154.17 (14)	O3—Ru1—P1	81.60 (7)
O1—Ru1—B4	113.28 (16)	O1—Ru1—P1	80.93 (6)
O3—Ru1—B5	109.89 (13)	B4—Ru1—P1	92.97 (11)
O1—Ru1—B5	158.18 (14)	B5—Ru1—P1	95.28 (10)
O3—Ru1—B7	119.97 (13)	B7—Ru1—P1	155.45 (13)
O1—Ru1—B7	86.76 (12)	B6—Ru1—P1	160.95 (12)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.123$
$S = 1.023$
7172 reflections
483 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.8346P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 1.00$ e Å^{-3} (1.02 Å from Ru1)
$\Delta\rho_{min} = -0.87$ e Å^{-3} (1.00 Å from Ru1)

The cage H atoms were located using Fourier methods and refined isotropically, with B—H distances in the range 1.03 (4)–1.16 (4) Å. Other H atoms were treated as riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1512). Services for accessing these data are described at the back of the journal.

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