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# A unique triple ruthenacarborane cluster

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In celebration of the 65<sup>th</sup> anniversary of the A. N. Nesmeyanov Institute of Organoelement  
Compounds of the Russian Academy of Sciences

Dehalogenation of [1,2-Ph<sub>2</sub>-3,3-(PPh<sub>3</sub>)<sub>2</sub>-3-Cl-*closo/pseudocloso*-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]<sup>-</sup> affords, in addition to the unusual “symbiotic” cluster [(1,2-Ph<sub>2</sub>-*pseudocloso*-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)(1',8'-Ph<sub>2</sub>-*closo*-2',1'8'-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)], a trace amount of a triple cluster species [(1,2-Ph<sub>2</sub>-*pseudocloso*-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)(1',8'-Ph<sub>2</sub>-*closo*-2',1',8'-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)(1'',8''-Ph<sub>2</sub>-*closo*-2'',1'',8''-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)], comprising three (Ph<sub>2</sub>RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>) units linked by η<sup>6</sup>-coordination of Ph rings to the Ru atoms of the adjacent cluster. The structure of the triple cluster was established by X-ray crystallography, and the potential consequences of its formation are discussed.

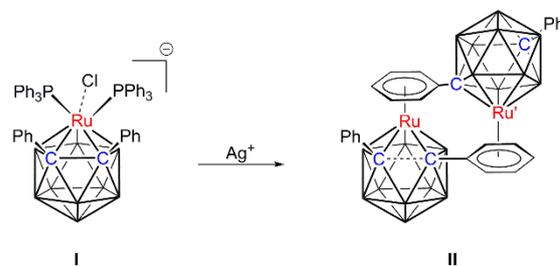
**Key words:** ruthenacarborane, triple cluster, NMR spectroscopy, X-ray diffraction.

In an attempt to prepare hypercloso metallacarboranes (species with *n* vertices but only *n* skeletal electron pairs) we recently investigated the consequences of dehalogenation of the anion [1,2-Ph<sub>2</sub>-3,3-(PPh<sub>3</sub>)<sub>2</sub>-3-Cl-*closo/pseudocloso*-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]<sup>-</sup>, **I**.<sup>1</sup> Note that this anion is prepared *in situ* and not isolated, so the *closo* or *pseudocloso* nature of its structure is unknown; the C<sub>cage</sub>H compound [3,3-(PPh<sub>3</sub>)<sub>2</sub>-3-Cl-*closo*-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]<sup>-</sup> has a *closo* structure,<sup>2</sup> but C<sub>cage</sub>Ph analogues are usually deformed into *pseudocloso* clusters by Ph...Ph contacts.<sup>3</sup> Treatment of **I** with AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> afforded a complex mixture of products which could be separated by preparative thin-layer chromatography (TLC), one of which was subsequently identified as the “symbiotic” double ruthenacarborane cluster **II** (Scheme 1).<sup>1</sup>

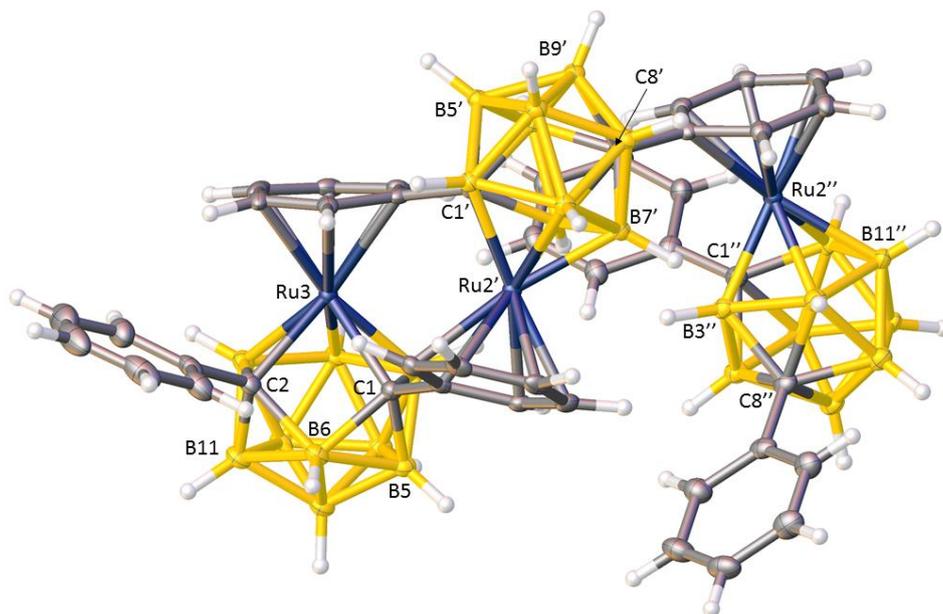
In **II** the unprimed cage adopts a 3,1,2-RuC<sub>2</sub>B<sub>9</sub> configuration but the presence of Ph rings on adjacent cage C atoms, forced to lie nearly co-planar, results in a deformed, *pseudocloso*, shape in which the C...C connectivity is considerably extended. In contrast the primed cage has undergone isomerisation to a 2,1,8-RuC<sub>2</sub>B<sub>9</sub> form and has a regular *closo* icosahedral geometry since the cage C atoms are now separated. The two

ruthenacarborane clusters are symbiotically linked, with one Ph group from each cage η<sup>6</sup>-bonded to the Ru atom of the other cage, having displaced the two PPh<sub>3</sub> ligands.

Scheme 1



Compound **1**, a minor co-product to **II**, has also now been isolated from the reaction and completely characterised. Compound **1** is an orange solid formed in trace amounts. Its <sup>1</sup>H NMR spectrum features a large number of multiplets in the aromatic region, most integrating for 1 or 2 H atoms, to a total of 30 H atoms. Many of these are at relatively low frequency (δ < 6.5 ppm) consistent with η-bonding to a metal atom. The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **1** is relatively uninformative because of the large number of overlapping resonances, but in total integrates for 27 B atoms implying that the molecule contains three RuC<sub>2</sub>B<sub>9</sub> units.



**Fig. 1.** Molecular structure of the triple ruthenacarborane [(1,2-Ph<sub>2</sub>-pseudocloso-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)(1',8'-Ph<sub>2</sub>-closo-2',1',8'-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)(1'',8''-Ph<sub>2</sub>-closo-2'',1'',8''-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)], compound **1**, showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level except for H atoms.

The structure of compound **1** was elucidated by a crystallographic study, and Fig. 1 provides a perspective view of one molecule. Compound **1** is a triple cluster of three {RuPh<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>} units linked by  $\eta^6$ -ligation of Ph rings on one cluster to the Ru atom of an adjacent cluster. The unprimed cage (left cage in Fig. 1) has a pseudocloso 3,1,2-RuC<sub>2</sub>B<sub>9</sub> structure in which the Ph rings on C1 and C2 push against each other as a result of being forced to be close to co-planarity by the  $\eta^6$ -Ph on Ru3. This opening of the C1–C2 connectivity pulls the Ru3 and B6 atoms closer together and the Ru3C1B6C2 unit can be considered effectively as a square. The C1...C2 distance is 2.492(3) Å and the Ru3...B6 distance is 2.946(3) Å, both typical for species with this deformation.<sup>3</sup>

The Ph ring on C1 of the unprimed cluster is  $\eta^6$ -ligated to Ru2' of the primed cluster (middle cage in Fig. 1) which has a *closo*-2,1,8-RuC<sub>2</sub>B<sub>9</sub> structure, having undergone a 3,1,2- to 2,1,8-isomerisation. There is a complementary  $\eta^6$ -ligation of the Ph ring on C1' to Ru3, and thus the combination of unprimed and primed clusters constitutes the symbiotic double cluster **II** that we have previously reported.<sup>1</sup>

However, in **1** there is a further  $\eta^6$ -ligation, from the Ph ring on C8' to Ru2'' of a third

cluster (right cage in Fig. 1), thus establishing **1** as a unique triple ruthenacarborane species. The double primed cage is also of *closo*-2,1,8-RuC<sub>2</sub>B<sub>9</sub> structure and its Ph rings are non-ligating.

We believe that the symbiotic double cluster **II** and the triple cluster **1** result from the inherent instability of the transient hypercloso species [3,3-(PPh<sub>3</sub>)<sub>2</sub>-hypercloso-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] afforded on dehalogenation of **I**. In the presence of a source of 6 $\pi$  electrons (the Ph rings of another hypercloso molecule in the case of **II** and **1**) the two PPh<sub>3</sub> ligands are displaced and the cluster reverts to a normal *closo* skeletal electron count with (*n*+1) skeletal electron pairs. However, the structure established for the triple cluster **1** suggests two important consequences. Firstly, there is no reason in principle why further {RuPh<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>} units could not be added since both the unprimed and double primed cages of **1** have available Ph rings, perhaps suggesting the possibility of quadruple, quintuple, etc clusters which conceivable could be either chains or cycles. Secondly, it is possible that *any* source of 6 $\pi$  electrons could displace the phosphine ligands of a transient hypercloso P<sub>2</sub>RuC<sub>2</sub>B<sub>9</sub> species to afford a wide range of

ruthenacarboranes with interesting structural properties and potential applications. Current studies are directed towards realising these possibilities.

### Experimental

**Synthesis:** Details of the synthesis of the symbiotic double cluster **II** have already been published,<sup>1</sup> and the triple cluster **1** was subsequently isolated from the same reaction, as an orange solid in trace amounts, by thin-layer chromatography on silica (eluent CH<sub>2</sub>Cl<sub>2</sub>:40-60 petroleum ether, 1:1, R<sub>f</sub> = 0.33). NMR spectra at 400.1 MHz (1H) or 128.4 MHz (<sup>13</sup>C) were recorded on a Bruker ADVANCEIII-400 spectrometer from a CD<sub>2</sub>Cl<sub>2</sub> solution at room temperature. <sup>1</sup>H NMR, δ 7.71-7.67 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.63-7.60 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.43 (t, 2H, C<sub>6</sub>H<sub>5</sub>), 7.36-6.99 (overlapping resonances, 10H, C<sub>6</sub>H<sub>5</sub>), 6.85-6.82 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 6.72-6.67 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 6.25-6.21 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 6.11-6.07 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 6.02-5.98 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 5.94-5.91 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 5.89-5.85 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 5.83-5.78 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 5.76-5.73 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 5.67-5.63 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 5.01-4.96 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 4.72-4.67 (m, 1H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR, δ 29.8 (1B), 17.9 (1B), 13.2 (1B), 4.3 to -11.5 (overlapping resonances with maxima at 1.4, -0.6, -2.1, and -8.1, 15B), -12.7 (1B), -13.8 to -24.0 (overlapping resonances with maxima at -15.1, -16.7, -19.3 and -22.9, 8B).

**Diffraction study:** Single crystals of 1·2CH<sub>2</sub>Cl<sub>2</sub> were afforded by slow diffusion between a CH<sub>2</sub>Cl<sub>2</sub> solution of the compounds and 40-60 petroleum ether at -20 °C, and intensity data were collected at 100 K on a Rigaku 007-HF diffractometer equipped with Cu-K<sub>α</sub> X-radiation (λ = 1.54178 Å). Using OLEX2<sup>4</sup> the structure was solved using SHELXT<sup>5</sup> and refined by full-matrix least-squares using SHELXL.<sup>6</sup> There are two disordered molecules of CH<sub>2</sub>Cl<sub>2</sub> of solvation, one of which could be modelled but one which was impossible to model, and the intensity contribution from the latter was removed using the BYPASS procedure.<sup>7</sup> H atoms bound to B were allowed positional refinement but H atoms in the phenyl rings were constrained to idealised geometries with C-H 0.95 Å (free Ph) or 1.00 Å (η-Ph). H atom displacement

parameters were set to 1.2×U<sub>eq</sub> of the bound B or C atom. Further details appear in Table 1. The structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC 1971848) and can be obtained, free of charge, on application to <http://www.ccdc.cam.ac.uk>.

**Table 1.** Crystallographic parameters and data collection and refinement statistics for compound 1.

Parameter	Value
Molecular formula	C <sub>44</sub> H <sub>61</sub> B <sub>27</sub> Cl <sub>4</sub> Ru <sub>3</sub>
Molecular weight	1326.8
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell parameters	
<i>a</i> /Å	13.33989(10)
<i>b</i> /Å	13.53839(7)
<i>c</i> /Å	15.12453(9)
α/deg	84.5284(5)
β/deg	87.0673(6)
γ/deg	83.1449(3)
<i>U</i> /Å <sup>3</sup>	2697.41(3)
<i>Z</i>	2
<i>d</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.634
Absorption coefficient, μ/mm <sup>-1</sup>	8.319
<i>F</i> (000)	1320.0
2θ range/deg	6.60-136.48
<i>h</i> , <i>k</i> , <i>l</i> ranges	-15 ≤ <i>h</i> ≤ 15 -16 ≤ <i>k</i> ≤ 16 -18 ≤ <i>l</i> ≤ 18
Number of reflections	
measured	92481
( <i>R</i> <sub>int</sub> )	0.0415
unique	9843
used in refinement	9843
Number of refined parameters	767
GOOF	1.035
Final values of	
<i>R</i> <sub>1</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0228
<i>R</i> <sub>1</sub> [all data]	0.0237
<i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0598
<i>wR</i> <sub>2</sub> [all data]	0.0603
Residual electron density	
max./e Å <sup>-3</sup>	0.44
min./e Å <sup>-3</sup>	-0.72

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