



## The First *exo-nido*-Ruthenacarborane Clusters. Synthesis and Molecular Structure of 5,6,10-[Cl(Ph<sub>3</sub>P)<sub>2</sub>Ru]-5,6,10- $\mu$ -(H)<sub>3</sub>-10-H-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>

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Novel *exo-nido*-ruthenacarboranes, 5,6,10-[Cl(Ph<sub>3</sub>P)<sub>2</sub>Ru]-5,6,10- $\mu$ -(H)<sub>3</sub>-10-H-7,8-R<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>6</sub> (**1**; R = H, structurally characterized by an X-ray diffraction study, and **2**; R = Me) have been prepared by reaction of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and [*nido*-7,8-R<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> K<sup>+</sup> in diethyl ether–tetrahydrofuran; in the solid state clusters **1** and **2** contain tridentate *nido*-carborane ligands bound to the Ru<sup>II</sup> atom through three Ru–H–B bridging hydrogen bonds, whereas in solution they exist as an equilibrium mixture of isomeric *exo-nido*-bis(triphenylphosphine)chlorohydridoruthenacarboranes formed as a result of the cleavage of one of the Ru–H–B bonds with the formation of a new Ru–B  $\sigma$ -bond and a simultaneous hydrogen atom shift to the metal atom.

Among the variety of metallocarboranes of the platinum group metals *exo-nido*-metallocarborane clusters, wherein a metal-containing moiety is linked to a *nido*-carborane cage through two-electron, three-centre (2e, 3c) M–H–B bonds, attract considerable interest from the point of view of synthetic and structural chemistry<sup>1–4</sup> and also homogeneous catalysis.<sup>5,6</sup> Previously reported 16e<sup>-</sup> *exo-nido*-rhodacarboranes<sup>1,2</sup> and 18e<sup>-</sup> *exo-nido*-iridacarborane<sup>3</sup> have only two bridging M–H–B hydrogen bonds. Until now, in the metallaborane family only, there have been two examples of unprecedented clusters<sup>7,8</sup> containing boron hydride ligands coordinated to a metal atom *via*

three 2e, 3c-bridging M–H–B bonds. In the present communication we report the synthesis, structural characterization and behaviour in solution of the first *exo-nido*-ruthenacarboranes wherein the *nido*-carborane anionic ligand functions in a tridentate manner.

Unlike the reaction of (Ph<sub>3</sub>P)<sub>3</sub>RuHCl with [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> Me<sub>3</sub>NH<sup>+</sup> yielding exclusively *closo*-3,3-(Ph<sub>3</sub>P)<sub>2</sub>-3,3-H<sub>2</sub>-3,1,2-RuC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>,<sup>9</sup> the synthetic precursor of the ruthenium complex, *viz.* (Ph<sub>3</sub>P)<sub>3</sub>RuCl<sub>2</sub>,<sup>10</sup> reacts readily with K<sup>+</sup> salts of carborane monoanions [*nido*-7,8-R<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> under mild conditions [diethyl ether–tetrahydrofuran (THF), 22 °C, 2–3 h]



in  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra respectively.¶

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¶ *NMR spectral data for 1 and 2* [mixture of hydrido clusters  $\text{A} \rightleftharpoons \text{B}$ : chemical shift ( $\delta/\text{ppm}$ ), assignment, constants  $J(\text{BH})$ ,  $J^1(\text{PH})$ ,  $J^2(\text{PP})$  in Hz]. Spectra were recorded with a Bruker WM-400 spectrometer. A selective  $^1\text{H}\{^{11}\text{B}\}$  NMR study was carried out for the assignment of signals and  $J^1$  constants in the NMR spectra of **2**.

**1**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  7.6–6.9 (m,  $\text{Ph}_{\text{A,B}}$ ), 2.0 (s, br,  $\text{CH}_{\text{A,B}}^{\text{extra}}$ ), –1.2 (q,  $\text{H}_{\text{A,B}}^{\text{extra}}$ ,  $J = 95$ ), –3.0 (dq, br,  $\text{H}_{\text{B}}^{\text{B}^2}$ ,  $J \approx 120$ ,  $J^1 \approx 35$ ), –4.1 (m\*,  $\text{H}_{\text{A}}^{\text{A}^6}$ ), –6.1 (dq, br,  $\text{H}_{\text{B}}^{\text{B}^0}$ ,  $J \approx 90$ ,  $J^1 \approx 45$ ), –14.8 (m\*,  $\text{H}_{\text{B}}^{\text{B}^4}$ ), –16.2 (m\*,  $\text{H}_{\text{A}}^{\text{A}^4}$ ) (m\*, a quadruplet-like signal);  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 60 °C)  $\delta$  3.8 (d, br,  $\text{B}_{\text{A,B}}^{\text{A}^2}$ ,  $J \approx 160$ ), 1.1 (d, br,  $\text{B}_{\text{A,B}}^{\text{A}^4}$ ,  $J \approx 190$ ), –14.1 (d, br,  $\text{B}_{\text{A,B}}^{\text{A}^3}$ ,  $J \approx 185$ ), –20.0 (d, br,  $J = 95$ ,  $\text{B}_{\text{B}}^{\text{B}^6}$ ), –23.8 (d,  $\text{B}_{\text{A,B}}^{\text{A}^1}$  +  $\text{B}_{\text{B}}^{\text{B}^6}$ ), –25.8 (d,  $\text{B}_{\text{B}}^{\text{B}^5}$ ,  $J = 120$ ), –32.6 (d,  $\text{B}_{\text{A,B}}^{\text{A}^5}$ ,  $J = 150$ ), –41.0 (t, br,  $\text{B}_{\text{A}}^{\text{A}^0}$ ,  $J = 95$ ), –43.6 (t,  $\text{B}_{\text{B}}^{\text{B}^0}$ ,  $J = 92$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  50.8 (d,  $\text{P}^{1(2)}$ ,  $J^2 = 24$ ), 46.9 (s,  $\text{P}_{\text{A}}^{\text{A}^2}$ ), 43.3 (d, br,  $\text{P}_{\text{B}}^{\text{B}^1}$ ,  $J^2 = 25$ ).

**2**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 40 °C)  $\delta$  7.6–6.9 (m,  $\text{Ph}_{\text{A,B}}$ ), 1.39 (s, br,  $\text{Me}_{\text{A,B}}$ ), 1.37 (s,  $\text{Me}_{\text{B}}$ ), –1.3 (q,  $\text{H}_{\text{A,B}}^{\text{extra}}$ ,  $J = 88$ ), –3.25 (d, q,  $\text{H}_{\text{B}}^{\text{B}^6}$ ,  $J \approx 125$ ,  $J^1 \approx 40$ ), –4.35 (d, q,  $\text{H}_{\text{A}}^{\text{A}^6}$ ,  $J = 125$ ,  $J^1 = 38$ ), –6.35 (d, q,  $\text{H}_{\text{B}}^{\text{B}^0}$ ,  $J = 88$ ,  $J^1 = 48$ ), –15.6 (m\*,  $\text{H}_{\text{B}}^{\text{B}^4}$ ,  $J^1 = 8$ ), –16.8 (m\*,  $\text{H}_{\text{A}}^{\text{A}^4}$ ,  $J^1 = 8$ );  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 40 °C)  $\delta$  5.9 (d, br,  $\text{B}_{\text{A,B}}^{\text{A}^3}$ ,  $J \approx 180$ ), 2.8 (d, br,  $\text{B}_{\text{A,B}}^{\text{A}^2}$ ,  $J \approx 180$ ), –6.2 (d, br,  $\text{B}_{\text{A,B}}^{\text{A}^1}$ ,  $J \approx 160$ ), –20.0 (d, br,  $\text{B}_{\text{A,B}}^{\text{A}^0}$  +  $\text{B}_{\text{B}}^{\text{B}^6}$ ,  $J \approx 100$ ), –24.4 (d,  $\text{B}_{\text{B}}^{\text{B}^5}$ ,  $J = 125$ ), –26.0 (d,  $\text{B}_{\text{B}}^{\text{B}^4}$ ,  $J = 125$ ), –31.3 (d,  $\text{B}_{\text{A,B}}^{\text{A}^5}$ ,  $J = 160$ ), –41.2 (t, br,  $\text{B}_{\text{A}}^{\text{A}^0}$ ,  $J = 90$ ); –44.3 (t,  $\text{B}_{\text{B}}^{\text{B}^0}$ ,  $J = 88$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  51.3 (d,  $\text{P}_{\text{B}}^{\text{B}^2}$ ,  $J^2 = 34$ ), 47.0 (s,  $\text{P}_{\text{A}}^{\text{A}^2}$ ), 43.8 (s, br,  $\text{P}_{\text{B}}^{\text{B}^1}$ ).

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