Synthesis and Characterization of a Dimeric Hydridorhodacarbaborane Anion Derived from the *nido*-Monocarbaborane, $B_{10}H_{12}CNH_3$

John A. Walker, Conrad A. O'Con, Limin Zheng, Carolyn B. Knobler, and M. Frederick Hawthorne *

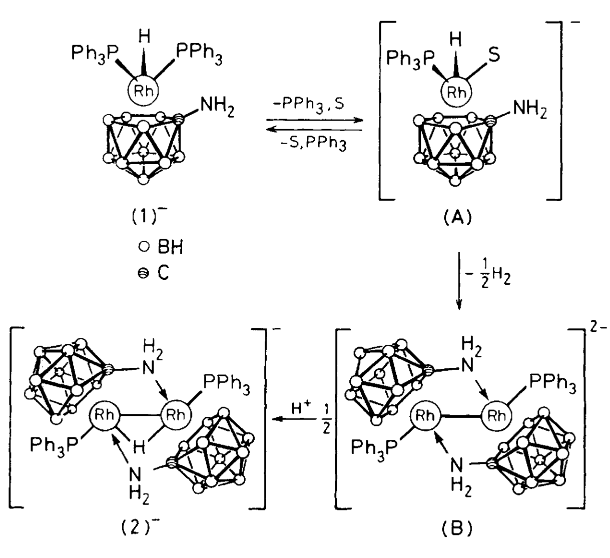
Department of Chemistry, University of California, Los Angeles, California 90024, U.S.A.

The reaction of $RhCl(PPh_3)_3$ with *nido*-$B_{10}H_{12}CNH_3$ in the presence of Bu^n_4NOH produced $[Bu^n_4N]$[*closo*-2,2-$(Ph_3P)_2$-2-H-1-(NH_2)-2,1-$RhCB_{10}H_{10}$], which upon heating in methanol produced a new orange compound confirmed by an *X*-ray diffraction study to be the $[Bu^n_4N]^+$ salt of an -NH_2-bridged Rh–H–Rh dimer anion.

The synthesis of catalytically active hydridorhodacarboranes *via* formal oxidative addition of the *nido*-carbaborane anions 7,8-,[1] 7,9-,[1a] and 2,9-[1b]$C_2B_9H_{12}$ to $RhCl(PPh_3)_3$ has been previously described. We now report the extension of this reaction to the *nido*-carbaborane anions derived from the *nido*-monocarbaborane, $B_{10}H_{12}CNH_3$.[2]

Treatment of $RhCl(PPh_3)_3$ with an equimolar quantity of *nido*-$B_{10}H_{12}CNH_3$ and three molar equivalents of potassium hydroxide in methanol produced a yellow solution of K[*closo*-2,2-$(PPh_3)_2$-2-H-1-(NH_2)-2,1-$RhCB_{10}H_{10}$], K(**1**). Metathesis of this salt with Bu^n_4NBr or $(Ph_3P)_2NCl$ produced a bright yellow precipitate of the respective salt of $(\mathbf{1})^-$ (80% yield). The i.r. spectrum (Nujol mull) of the $Bu^n_4N^+$ salt displayed a medium intensity band at 2050 cm^{-1} assigned to ν_{RhH}. The 200 MHz ^1H n.m.r. spectrum of freshly prepared $[^2H_6]$acetone solutions of this salt displayed a six-line hydride resonance at δ −10.28 consistent with the hydride ligand being coupled to ^{103}Rh and two equivalent ^{31}P nuclei. Additionally, the observation of a four-line rhodium hydride resonance at δ −9.75 indicates that one triphenylphosphine ligand dissociates from $(\mathbf{1})^-$ in solution. In accord with this observation, the 81.02 MHz $^{31}P\{^1H\}$ n.m.r. spectrum of freshly prepared $[^2H_6]$acetone–acetone (1 : 10) solutions of $[Bu^n_4N]$(**1**) displays two doublets centred at 35.3 ($J_{Rh\text{-}P}$ 139 Hz) and 34.2 p.p.m. ($J_{Rh\text{-}P}$ = 112 Hz) and a singlet at −4.22 p.p.m. The singlet is assigned to unco-ordinated triphenylphosphine and the lower-field doublet is assigned to $[Bu^n_4N]$(**1**). The higher-field doublet is assigned to the monotriphenylphosphine species observed in the ^1H n.m.r. spectrum of this salt.

Heating a solution of $[Bu^n_4N]$(**1**) in methanol at reflux temperature for short periods produced a new ionic orange species $[Bu^n_4N]$(**2**). The same species was directly produced in high yield from the reaction of *nido*-$B_{10}H_{12}CNH_3$, $RhCl(PPh_3)_3$, and Bu^n_4NOH in refluxing methanol and $[Et_3NH]$(**2**) is produced in high yield from *nido*-$B_{10}H_{12}CNH_3$, $RhCl(PPh_3)_3$, and triethylamine in refluxing methanol. Elemental analyses and osmometric molecular weight measurements on $[Et_3NH]$(**2**) established a Rh : P : B : N ratio of 1 : 1 : 10 : 1.5 and that this species was probably dimeric. The 81.02 MHz $^{31}P\{^1H\}$ n.m.r. spectrum of $[^2H_6]$acetone solutions of $[Et_3NH]$(**2**) displayed one doublet centred at 40.3 p.p.m. ($J_{Rh\text{-}P}$ 140 Hz). The 200 MHz ^1H n.m.r. spectrum of $[^2H_6]$acetone solutions of this salt displayed a five-line rhodium hydride resonance at δ −9.84 which upon ^{31}P decoupling collapsed to a triplet. These data are consistent with the hydride ligand being coupled to two equivalent ^{103}Rh nuclei and two equivalent ^{31}P nuclei. As a bridging hydride ligand in $[Et_3NH]$(**2**) was indicated from the ^1H n.m.r. spectrum of this salt it was of interest to establish the exact co-ordination geometry of this species by *X*-ray crystallography since hydride ligands bridging two transition metals have been heretofore unobserved in metallacarbaborane chemistry.



Scheme 1

The poor solubility of $[Et_3NH]$(**2**) frustrated attempts to grow single crystals of this salt. The $[Bu^n_4N]^+$ salt of $(\mathbf{2})^-$ was more soluble in organic solvents which allowed red single crystals of $[Bu^n_4N]$(**2**) to be grown from CH_2Cl_2–pentane.

Crystal data: M = 1308.659 {calcd. for $[(C_4H_9)_4N][P(Ph_3)RhCB_{10}H_{10}NH_2)_2H]$. $1/2CH_2Cl_2$}, triclinic, space

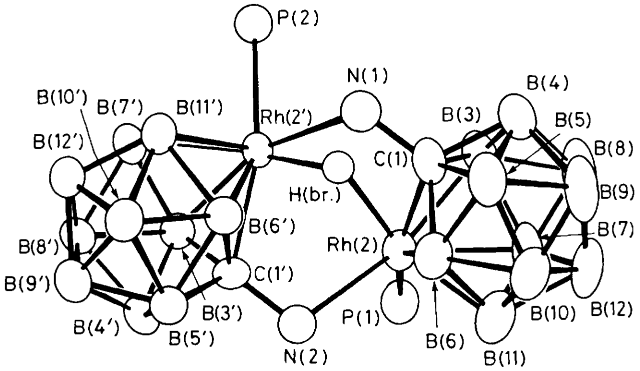


Figure 1. An ORTEP projection of the structure of the anion (**2**). Thermal ellipsoids are shown at 50% probability. Phenyl groups and all hydrogen atoms except the bridging hydride have been omitted for clarity. Some distances are Rh(2)–B(3) 2.125(10), Rh(2)–B(6) 2.231(10), Rh(2)–B(7) 2.206(10), Rh(2)–B(11) 2.265(10), Rh(2)–C(1) 2.189(9), Rh(2′)–B(3′) 2.163(9), Rh(2′)–B(6′) 2.205(9), Rh(2′)–B(7′) 2.212(9), Rh(2′)–B(11′) 2.2551(9), Rh(2′)–C(1′) 2.178(7) Å. Some angles are P(1)–Rh(2)–H(Br) 83(2), N(2)–Rh(2)–H(Br) 94(2), B(11)–Rh(2)–H(Br) 164(2), N(2)–Rh(2)–P(1) 93.8(2), P(1)–Rh(2)–Rh(2′) 112.80(6), P(2)–Rh(2′)–H(Br) 84(2), N(1)–Rh(2′)–H(Br) 83(2), B(11′)–Rh(2′)–H(Br) 174(2), N(1)–Rh(2′)–P(2) 88.4(2), P(2)–Rh(2′)–Rh(2) 117.24(6)°

group $P\bar{1}$, $a = 13.767(3)$, $b = 14.618(3)$, $c = 17.672(4)$ Å, $\alpha = 95.65(2)$, $\beta = 94.52(2)$, $\gamma = 98.73(1)°$, $U = 3482(1)$ Å,^{3} $Z = 2$; $D_c = 1.25$ g cm^{-3}; $D_m = 1.27$ g cm^{-3}; (flotation in aq. KI); R is currently 0.063 for 8122 unique reflections having $I > 3\sigma(I)$ (Syntex $P\bar{1}$ four-circle diffractometer, Mo-K_α radiation, $\lambda = 0.7107$ Å).†

The structure was solved by the heavy-atom method. The 6 phenyl groups were treated as rigid C_6 hexagons with C–C = 1.39 and C–H = 1.0 Å. Peaks corresponding to Cl of CH_2Cl_2 were found on a difference map. These cannot be at full occupancy because they are near a centre of symmetry at 0, 1/2, 0. A rigid tetrahedron at half-occupancy, with C–Cl = 1.772 Å, has been included in the refinement. All hydrogen atoms, with the exception of those of the cation and the solvate, including the hydrogen bridging the two metal atoms, were located on difference maps. In the final least-squares cycle, based on F, 473 parameters were refined, including positional and anisotropic thermal parameters for 2 Rh, 2 P, 20 B, and 18 C (those of the icosahedra and those in the cation), positional and isotropic thermal parameters for 3 N, positional parameters for the bridging H, group parameters for the seven groups described above and isotropic thermal parameters for carbon atoms included in phenyl groups. The final least-squares cycle converged at $R = 0.063$ and $R_w = 0.084$; $w = 1/\sigma^2(F_o)$. The 'goodness-of-fit' was 2.366 as defined by $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ with N_o (number of observations) = 8122 and N_v (number of variables) = 473. On a final difference map, the highest peak was 2 e Å^{-3}; all peaks > 0.9 Å were located within 1.5 Å of Cl or within 1.0 Å of another rigid group or of the cation. Of the 36 hydrogen atoms of the cation, only 11 were located and included in the structure factor calculations.

The structure of **(2)**$^-$ is shown in Figure 1. Each Rh is symmetrically bonded to all five atoms of a CB_4 pentagonal face at distances ranging from 2.12 to 2.26 Å, and also to P of a single triphenylphosphine ligand [2.367(3) and 2.356(2) Å], and interacts with the other monocarbollide ligand *via* the NH_2 group on C [2.221(6) and 2.220(6) Å]. In addition, a single hydride atom bridges the two Rh atoms at distances of 1.92(7) and 1.90(7) Å, while the separation between the Rh atoms is 2.998(1) Å. The dimer possesses approximately 2-fold symmetry about an axis perpendicular to the Rh–Rh bond. The Rh–Rh bond length of **(2)**$^-$ can be compared with 2.763(1) Å found in the Rh^{II} dimer, $[(Ph_3P)RhC_2B_9H_{11}]_2$,[3] and 2.906(1) Å found in the Rh^{III} dimer $[(\mu\text{-H})(\mu\text{-Cl})\{(\eta\text{-}C_5Me_5\text{-}RhCl\}_2]$.[4] The Rh–H–Rh distances cited above compare with 1.805(4) and 1.812(3) Å found in $\{HRh[P(OPr^i)_3]_2\}_2$.[5]

The exact mode of formation of **(2)**$^-$ from **(1)**$^-$ was not determined but probably follows the pathway indicated in Scheme 1. The spectroscopically observable intermediate (A) is unstable with respect to bimolecular reductive elimination of molecular hydrogen forming the undetected dimeric intermediate (B). Similar dimer formation from the putative monometallic 16-electron rhodium hydride species 3-(Ph_3P)-3-H-1-(Bu^n)-3,1,2-$RhC_2B_9H_{11}$ has been previously reported.[6] In the present case, dimer formation is further promoted by the presence of the nucleophilic amino substituents on the carbaborane ligand. The dinegative intermediate (B) then abstracts a proton from the solvent yielding the observed monoanion **(2)**$^-$. The proposed protonation of B constitutes a formal two-electron oxidation of the dinuclear Rh^{II} species to the dinuclear Rh^{III} product and **(2)**$^-$ is the first isolated dimeric rhodacarbaborane with rhodium in the +3 oxidation state.

Other rhodacarbaboranes derived from *nido*-$B_{10}H_{12}CNMe_3$, *nido*-$B_{10}H_{12}CH^-$, and *nido*-$CB_9PH_{11}{}^-$ have been isolated and characterized, some of which exhibit catalytic activity comparable to that of 3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$. The results of these studies will be presented elsewhere.[7]

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.