*Inorg. Chem.* **1993,** *32,* 3393–3394

# Facile Conversion of the Dimeric $[\{Ph_3PRhB_{10}H_{10}CNH_2\}_2H]^-[PPN]^+$ Cluster to 16-Electron Mononuclear *closo*-Rhodacarboranes by N-Quaternization

**Igor T. Chizhevsky,**[*,†,1a] **Irina V. Pisareva,**[†] **Pavel V. Petrovskii,**[†] **Vladimir I. Bregadze,**[†] **Alexandr I. Yanovsky,**[†] **Yuri T. Struchkov,**[†] **Carolyn B. Knobler,**[‡] **and M. Frederick Hawthorne**[*,‡,1b]

Institute of Organo-Element Compounds, Russian Academy of Sciences, Vavilova Str. 28, 117813 Moscow, Russia, and Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90024-1569

*Received March 30, 1993*

Among the 11- and 12-vertex monocarbon metallacarboranes of the transition group metals[2] only a few representatives of either mono- or binuclear rhodium clusters have been previously described.[2d] Here we report a new route to the mononuclear monocarbon *closo*-rhodacarboranes *closo*-2-Br-2-($Ph_3P$)-1-($NHR^1R^2$)-2,1-$RhCB_{10}H_{10}$ [**3**, $R^1$ = H, $R^2$ = $CH_2CH{=}CHCH_3$; **4**, $R^1$ = $R^2$ = $CH_2CH{=}CHCH_3$] which are formed upon N-quaternization with alkenyl halides of the dimeric anion present in [PPN][$\{Ph_3PRhB_{10}H_{10}CNH_2\}_2H$] (**1**).[2d] Also presented are single-crystal X-ray diffraction studies of the zwitterionic cluster **4**, the first 16-electron monocarbon metallacarborane to be crystallographically characterized, as well as of the dimer [PPN]-[$(Ph_3PRhB_{10}H_{10}CNH_2)_2Br$] (**5**), which is observed as an apparent intermediate in the N-alkenylation process.

Reaction of the salt **1** (0.50 g, 0.32 mmol) with 0.20 mL (1.9 mmol) of crotyl bromide (**2**) in 25 mL of $CH_2Br_2$ at 25 °C for 24 h produced a mixture of mononuclear complexes, **3** and **4** (68% total yield), along with a small amount of an unidentified purple species (Scheme I). This mixture was separated into **3** and **4** by column chromatography on silica gel (eluent $CH_2Cl_2$) and their structures were assigned by spectroscopic and, for **4** crystallographic means. The 200.133-MHz $^1H$ NMR spectra[3] of **3** and **4** both displayed complex multiplets from $PPh_3$ ligands coordinated by rhodium atoms as well as a set of signals typical for $\sigma$-crotyl groups. The latter were attributed to the alkenylated moieties attached to the *nido*-carborane ligands in these compounds. In accord with the observation of 5:1 and 2.5:1 intensity ratios of $PPh_3$ protons to the corresponding crotyl groups' methyl protons in the $^1H$ NMR spectra of **3** and **4**, these complexes are concluded to have N-mono- and N-dialkenylated amino functions on their *nido*-carborane cages, respectively.

An X-ray diffraction study[4] of **4** proved this species to be a mononuclear *closo*-rhodacarborane with a 16-electron $Rh^{III}$ atom (Figure 1). Despite almost symmetrical bonding of the rhodium atom to the *nido*-carborane $CB_4$ open face, there is a quite noticeable folding of the $CB_4$ plane about B(3)···B(6) (8.3°) in molecule **4**. Similar and more pronounced distortion of the carbollyl ligand has been observed in [*closo*-2,2-($^tBuNC$)$_2$-1-$NMe_3$-2,1-$PdCB_{10}H_{10}$].[5] The Rh–Br distance of 2.488(1) Å observed in **4** proved to be somewhat shorter than those found in [$P(Me_2C_6H_3)_3]_3RhBr$ (2.581 Å)[6] or in [$HPPh_3$][*closo*-3-$PPh_3$-3,3-$Br_2$-3,1,2-$RhC_2B_9H_{11}$] (2.520(2) and 2.598(1) Å).[7] This is attributed to the presence of two different halogen atoms (Cl and Br) in the single crystal of **4**.[8] An important structural feature of the cluster is the existence of an intramolecular N–H···Br(Cl) hydrogen bond. Both the N···Br(Cl) and Br(Cl)···H distances of 3.074(6) and 1.92(7) Å, respectively, as well as the N–H···Br-(Cl) angle [149(5)°] are consistent with the presence of this type of interaction in the solid state of **4**.

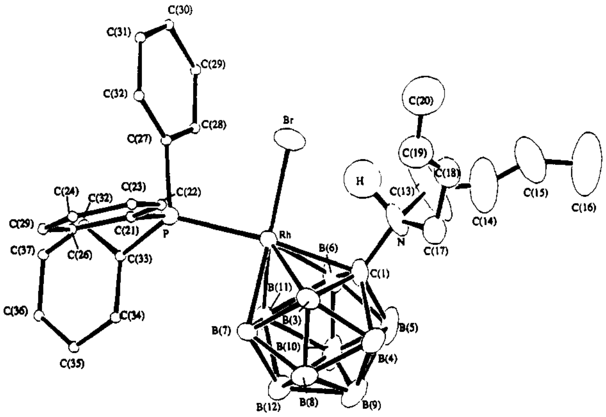

**Figure 1.** ORTEP projection of the structure of the anion of cluster **4**. Carbon atoms of the phenyl rings are depicted with a low value isotropic $\mu$ for clarity. All hydrogen atoms except H(N) have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Rh–B(3) = 2.132(5), Rh–B(6) = 2.127(6), Rh–B(7) = 2.166(4), Rh–B(11) = 2.174(5), Rh–C(1) = 2.243(5), Rh–P(1) = 2.354(1), Rh–Br(Cl) = 2.488(1), C(1)–N = 1.539(6), N–H(N) = 1.26(7), H(N)–Br(Cl) = 1.92(7), N–Br(Cl) = 3.074(6); P–Rh–Br(Cl) = 90.6(1), N–H(N)–Br(Cl) = 149(5).

When the reaction of **1** with **2** was monitored by TLC, an additional yellow band was observed which is due to an apparent intermediate, **5**. This complex was not detected in the final reaction products, but could be separated by chromatography

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[†] Russian Academy of Sciences.

[‡] University of California at Los Angeles.

(1) (a) To whom FUSSR correspondence should be directed. (b) To whom other correspondence should be directed.

(2) (a) Salentine, C. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 6382. (b) Schultz, R. V.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1979**, *18*, 2883. (c) Base, K.; Stibr, B.; Dolansky, J.; Duben, J. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2345. (d) Walker, J. A.; O'Con, C. A.; Zheng, L.; Knobler, C. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1983**, 803. (e) Quintana, W.; Ernest, R. L.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1988**, *7*, 166 and references therein.

(3) Characterization data for **3** and **4** are as follows. **3**: IR ($CH_2Cl_2$, $cm^{-1}$) 3206 ($\nu_{N-H}$), 2526 ($\nu_{B-H}$); $^1H$ NMR [200.133 MHz, $CD_2Cl_2$, $J$ (Hz)] 8.02 (s br, 2H, $NH_2$), 7.46 (m, 15H, Ph), 6.14 (dqt, 1H, $J_{AB}$ = 14, $J_q$ = 6.5, $J_t$ = 0.9, MeCH=), 5.62 (dqt, 1H, $J_{AB}$ = 14, $J_t$ = 7.3, $J_q$ = 1.65, =$CH_2CH$), 3.97 (d br, 2H, $J_d$ = 7.1, $CH_2$), 1.76 (dd, 3H, $J_{Me-CH}$ = 6.5, $J_d$ = 1.65, $CH_3$); $^{31}P\{^1H\}$ NMR [81.01 MHz, $CD_2Cl_2$, $J$ (Hz)] 32.90 (d, $J_{Rh-P}$ = 152). Anal. Calcd for $C_{23}H_{34}B_{10}BrNPRh$: C, 42.72; H, 5.26; B, 16.71. Found: C, 42.56; H, 5.60; B, 16.53. **5**: IR (Nujol mull, $cm^{-1}$) 2537 ($\nu_{B-H}$); $^1H$ NMR (200.133 MHz, $CD_2Cl_2$) 10.10, 9.80 (s br, 1H, NH), 7.47 (m, 15H, Ph), 5.85 (dq, 2H, $J_{AB}$ = 15.2, $J_q$ = 6.4, MeCH=), 5.64 (dm, 2H, $J_{AB}$ = 15.2, $CH_2CH$=), 4.18 (dm, 2H, $J_{AB}$ = 13.2, $CH_AH_B$), 3.88 (dt, 2H, $J_{AB}$ = 13.2, $J_t$ = 5.8, $CH_AH_B$), 1.77 (d, 6H, $J_{Me-CH}$ = 6.4, Me); $^{31}P\{^1H\}$ NMR (81.01 MHz, $CD_2Cl_2$) 33.36 (d, $J_{Rh-P}$ = 157). Anal. Calcd for $C_{27}H_{40}B_{10}BrNPRh$: C, 46.29; H, 5.71; B, 15.43; P, 4.43. Found: C, 45.99; H, 5.91; B, 15.17; P, 4.41.

(4) Crystal data for **4** ($C_{27}H_{40}B_{10}Br_{0.75}Cl_{0.25}NPRh$): space group $P\bar{1}$ with $a$ = 9.725(2) Å, $b$ = 10.134(2) Å, $c$ = 16.879(3) Å, $\alpha$ = 80.79(2)°, $\beta$ = 88.46(2)°, $\gamma$ = 78.31(2)°, $V$ = 1607.9(2) Å$^3$, $d_{calcd}$ = 1.424 g cm$^{-3}$ and $Z$ = 2. Data were collected on a Siemens P3/Pc diffractometer at −125 °C using the $\theta$–$2\theta$ scan mode and Mo K$\alpha$ radiation to a maximum $2\theta$ = 54°. The structure was solved by direct methods. A number of least-squares refinements with different Br:Cl ratios were performed; best discrepancy factors were obtained for a Br:Cl ratio equal to 3:1. Final values are $R$ = 0.0467, $R_w$ = 0.0564 for 5134 independent reflections with $I > 3\sigma(I)$.

(5) Carroll, W. E.; Green, M.; Stone, F. G. A.; Welch, A. *J. Chem. Soc., Dalton Trans.* **1975**, 2263.

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(7) Zheng, L.; Baker, R. T.; Knobler, C. B.; Walker, J. A.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3350.

(8) Complexes **3** and **4** were originally prepared using $CH_2Cl_2$ as a solvent and some halide exchange in the intermediate **5** (vide infra) probably led to the mixture of chloride and bromide ligands observed in compound **4**.

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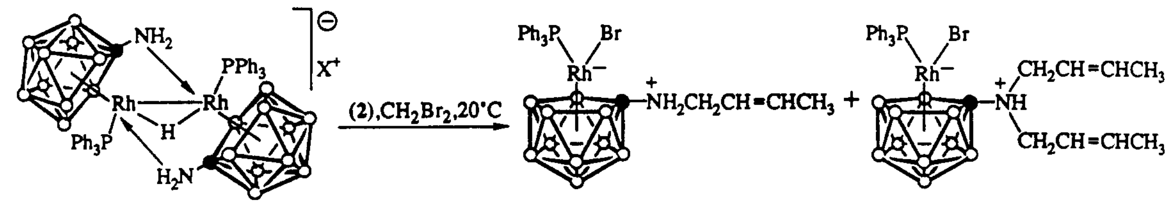
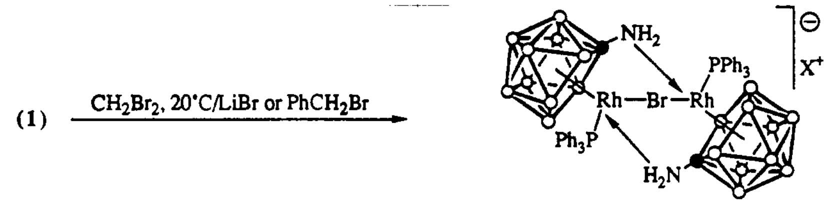
**Scheme I**



(1), X = $(Ph_3P)_2N$ (3) (4)

**Scheme II**



(5)

when the reaction was interrupted after 2.5 h and the products isolated. The $^1$H and $^{31}$P{$^1$H} NMR spectra as well as the IR spectrum of **5**[9] proved to be very similar to those of dimer **1**. The $^1$H NMR spectrum of **5**, however, revealed no hydride resonances in the region upfield of $\delta$ 1 ppm. This suggested that the bridging hydrido ligand in cluster **1** was replaced by bromide in forming **5**. Analytical data confirmed the presence of the bromine atom in **5**.[9] The exact geometry of the PPN salt of **5** was then elucidated by X-ray crystallography[10] (Figure 2).

Molecule **5** consists of two equivalent 14e$^-$ Rh(PPh$_3$)($\eta^5$-B$_{10}$H$_{10}$-CNH$_2$) fragments joined by a symmetrically bridging Rh–Br–Rh bond [Rh–Br, 2.584(3) and 2.590(3) Å] which is further supported by interaction between the Rh atom of each of the fragments and the NH$_2$ group located in the other carbollide ligand. Unlike structure **1**, dimeric cluster **5** contains no direct Rh–Rh bond. Both the separation between the rhodium atoms of 3.595(2) Å and the Rh–Br–Rh angle of 88.0° observed in **5** compare well with the corresponding values found in $\mu$-halogen rhodium complexes in which no metal–metal interaction is present.[11] Thus, cluster **5** is an anionic dimer wherein each Rh$^{III}$ atom possesses an 18-electron configuration.

Cluster **5** can be directly obtained as the principal product (76% yield) by reaction of **1** with CH$_2$Br$_2$ (20 °C, 72 h) or in the presence of excess LiBr or PhCH$_2$Br. As expected, the reaction of **5** with an excess of crotyl bromide in CH$_2$Br$_2$ at 20° for 36 h resulted in the formation of compounds **3** and **4** in 62% and 12% yield, respectively. The course of this process depends upon the quantity of crotyl bromide used in the reaction. Treatment of **5** by 1.5 molar equiv of **2** for 24 h under the same conditions afforded only the sterically less hindered complex **3**.

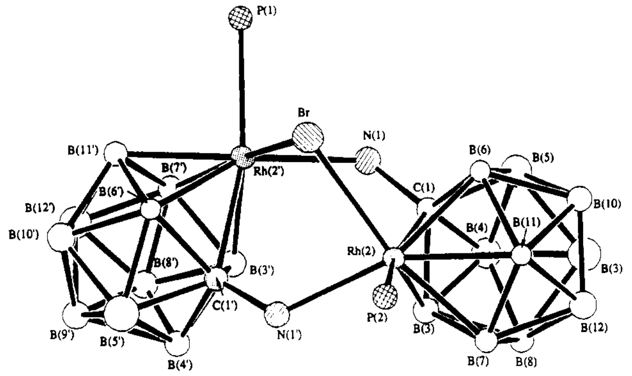


**Figure 2.** ORTEP projection of the anion of cluster **5**. All hydrogen atoms, phenyl groups and the cation of the salt (PPN) have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Rh(2)–B(3,6,7,11) and Rh(2′)–B(3′,6′,7′,11′) distances range from 2.14(3) to 2.22(2), Rh(2)–C(1) = 2.17(2), Rh(2′)–C(1′) = 2.16(2), Rh(2)–P(2) = 2.356(6), Rh(2′)–P(1) = 2.368(6), Rh(2)–Br = 2.584(3), Rh(2′)–Br = 2.590(3), Rh(2)–N(1′) = 2.260(16), Rh(2′)–N(1) = 2.265(16), Rh(2)···Rh(2′) = 3.595(2), C(1)–N(1) = 1.48(3), C(1′)–N(1′) = 1.54(3); Rh(2)–Br–Rh(2′) = 88.0(1), Rh(2)–C(1)–N(1) = 114.5(13), P(1)–Rh(2)–N(1) = 89.3(4).

We are currently extending our studies to related halogenated clusters based on monocarbon carboranes and plan to study the reactivity of the compounds obtained.

**Acknowledgment.** This research was supported in part by National Science Foundation Grant CHE-91-11437. I.T.C. thanks the National Science Foundation for support and the Institute of Organo-Element Compounds of the Russian Academy of Sciences for sabbatical leave.

**Supplementary Material Available:** Tables of crystallographic data collection parameters, atom coordinates, bond distances and angles, and anisotropic parameters and ORTEP figures for **4** and **5**, respectively (26 pages). Ordering information is given on any current masthead page.

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(9) Characterization data for **5**: IR (KBr, cm$^{-1}$) 3312, 3252 ($\nu_{N-H}$), 2516 ($\nu_{B-H}$); $^{31}$P{$^1$H} NMR (81.01 MHz, CD$_2$Cl$_2$) 31.28 (d, $J_{Rh-P}$ = 131), 23.20 (s); $^1$H NMR (200.133 MHz, CD$_2$Cl$_2$, −40 °C) 7.92–7.3 (m, 60H, Ph), 4.66 (br d, 2H, $J_{H-H}$ = 8.9, NH$_A$H$_B$), 3.69 (br d, 2H, $J_{H-H}$ = 9.0, NH$_A$H$_B$). Anal. Calcd for $C_{74}H_{84}B_{20}BrN_3P_4Rh_2$: C, 54.15; H, 5.12; B, 13.17; Br, 4.88. Found: C, 55.02; H, 5.30; B, 13.27; Br, 5.12. [Compare to **2**: IR (KBr, cm$^{-1}$) 3316, 3265 ($\nu_{N-H}$), 2508 ($\nu_{B-H}$); $^{31}$P{$^1$H} NMR (81.02 MHz, CH$_2$Cl$_2$) 35.19 (d, $J_{Rh-P}$ = 140), 22.60 (s); $^1$H NMR (200.133 MHz, CD$_2$Cl$_2$, −40 °C) 7.90–7.56 (m, 60H, Ph), 5.82 (br d, 2H, $J_{H-H}$ = 9.2, NH$_A$H$_B$), 3.57 (br s, 2H, NH$_A$H$_B$), −9.90 (quintet, $J_{av}$ = 17.6, H$_{br}$.]

(10) Crystal data for **5**: space group $P\bar{1}$ with $a$ = 15.652(2) Å, $b$ = 15.669(3) Å, $c$ = 21.224(4) Å, $\alpha$ = 75.615(9)°, $\beta$ = 74.596(9)°, $\gamma$ = 72.819(9)°, $V$ = 4712 Å$^3$, $d_{calcd}$ = 1.38 g cm$^{-3}$ and $Z$ = 2. Data were collected on a Picker FACS-1 diffractometer at −117 °C in the $\theta$–2$\theta$ scan mode using Mo K$\alpha$ radiation, to a maximum 2$\theta$ = 35°. The structure was solved by direct methods. The final discrepancy index was $R$ = 0.062, $R_w$ = 0.082 for 3619 independent reflections with $I > 3\sigma(I)$.

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