Synthesis of Mixed-Metal (Ru−Rh) Bimetallacarboranes via *exo-nido-* and *closo*-Ruthenacarboranes. Molecular Structures of (η^4-C_8H_{12})Rh(μ-H)Ru(PPh_3)$_2$(η^5-$C_2B_9H_{11}$) and (CO)(PPh_3)Rh(μ-H)Ru(PPh_3)$_2$(η^5-$C_2B_9H_{11}$) and Their Anionic *closo*-Ruthenacarborane Precursors

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Received July 31, 1998

The reaction of *exo*-*nido*-5,6,10-[Cl(PPh_3)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$) (**1**) with [(η^4-diene)RhCl]$_2$ in EtOH or with [(CO)$_2$RhCl]$_2$ in MeOH in the presence of KOH produced novel mixed-metal bimetallacarboranes (η^4-diene)Rh(μ-H)Ru(PPh_3)$_2$(η^5-$C_2B_9H_{11}$) (**4**, diene = COD; **5**, diene = NBD) or (CO)(PPh_3)Rh(μ-H)Ru(PPh_3)$_2$(η^5-$C_2B_9H_{11}$) (**10**) along with a small amount of the mononuclear complexes *closo*-(CO)$_2$(PPh_3)Ru(η^5-$C_2B_9H_{11}$) and *closo*-(CO)(PPh_3)$_2$Ru-(η^5-$C_2B_9H_{11}$), respectively. Complexes **4** and **10** were characterized by single-crystal X-ray diffraction studies which revealed the existence of two types of bridging bonds Ru−H−Rh and B−H···Rh in these species. The bridging hydrogen atoms are asymmetrically disposed within these linkages. Several separate experiments have been carried out for the synthesis of the anionic complex [*closo*-3,3-(PPh_3)$_2$-3-H-3,1,2-$RuC_2B_9H_{11}$]$^-$, which is proposed to be the key intermediate in the reaction of **1** with [(η^4-diene)RhCl]$_2$. The reaction of (PPh_3)$_3$RuHCl with [7,8-$C_2B_9H_{12}$][Me_3NH] under reflux in THF in the presence of Et_4NCl yielded [*closo*-3,3-(PPh_3)$_2$-3-Cl-3,1,2-$RuC_2B_9H_{11}$][Et_4N] (**7**), which after reduction by $LiAlH_4$ in THF afforded [*closo*-3,3-(PPh_3)$_2$-3-H-3,1,2-$RuC_2B_9H_{11}$][Et_4N] (**8**) in poor yield. Alternatively, treatment of (PPh_3)$_3$RuHCl with Tl_2[7,8-$C_2B_9H_{11}$] in THF at ambient temperature led to **8** in 84% yield. The anionic complex **8** and the known neutral *closo*-3,3-(PPh_3)$_2$-3-Cl-3-H-3,1,2-$RuC_2B_9H_{11}$ (**6**) have been substituted for **1** in the synthesis of **4** under the same conditions. Structures of both anionic *closo*-ruthenacarboranes **7** and **8** have been confirmed by single-crystal X-ray diffraction studies. The NMR data [^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B] for the new mononuclear and binuclear ruthenacarborane complexes are discussed in detail.

Introduction

Since structural characterization of the first two bimetallic rhodacarboranes [($Ph_3PRhC_2B_9H_{11}$)]$_2$[1] and [(Et_3P)$RhC_2B_9H_{10}$]$_2$[2] demonstrated their unique nature of bonding via exopolyhedral two-electron three-center (2e,3c) B−H···M bonds supporting the Rh−Rh single bond in the dimers, the chemistry of low-nuclearity homo- and heterometallic carborane-containing clusters has been extensively studied.[3] Within this family numerous examples of homo- and mixed-metal bimetallacarboranes of the platinum group with Rh−Rh,[4−6] Rh−Ir,[5] Rh−Pt,[7] and other Rh−M fragments[5,6,8−10] have recently been synthesized and structurally characterized. All these species, however, are formally *closo*-rhodacarboranes since the dicarbollide ligand is η^5-coordinated to the rhodium atom while the latter is

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† Deceased on August 16, 1995.

(1) Baker, R. T.; King, R. E., III; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266.

(2) Behnken, P. E.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 722.

(3) For the latest reviews see: (a) Stone, F. G. A. *Adv. Organomet. Chem.* **1990**, *31*, 53. (b) Brew, S. A., Stone F. G. A. *Adv. Organomet. Chem.* **1993**, *35*, 135.

(4) Behnken, P. E.; Marder, T. B.; Baker, R. T.; Knobler, C. B.; Thompson, M. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1985**, *107*, 932.

(5) Fernandez, J. R.; Helm, G. F.; Howard, J. A. K.; Pilotti, M. U.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1747.

(6) Pilotti, M. U.; Topaloglu, I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1355.

(7) Goldberg, J. E.; Howard, J. A. K.; Muller, H.; Pilotti, M. U.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3055.

(8) Carr, N.; Gimeno, M. C.; Goldberg, J. E.; Pilotti, M. U.; Stone, F. G. A.; Topaloglu, I. *J. Chem. Soc., Dalton Trans.* **1990**, 2253.

(9) (a) Pilotti, M. U.; Stone, F. G. A.; Topaloglu, I. *J. Chem. Soc., Dalton Trans.* **1991**, 1621.

(10) (a) Pilotti, M. U.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1990**, 2625. (b) Goldberg, J. E.; Stone, F. G. A. *Polyhedron.* **1992**, *11*, 2841.

10.1021/om9806592 CCC: $18.00
Publication on Web 01/28/1999

simultaneously linked to a variety of other transition metals. This is, presumably, due to the limited number of convenient platinum metal metallacarborane reagents, other than $[Et_4N][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_{11})]$[11] or a few of its derivatives,[6,8,9] which could serve as suitable precursors for the preparation of such clusters. Only recently, several reports describe the syntheses of some new bi- and polymetallacarborane systems wherein other platinum metals were ligated either by dicarbon or monocarbon *nido*-carborane cages in the η^5-mode, namely, Ru−Rh,[12] Ru−Ir,[13] Ru−Pt,[14] Ru−Ru,[14,15] Pt−Cu,[16] and Os−Os[17] clusters.

In accord with our preliminary communication,[12] we describe here convenient syntheses of novel bimetallic Ru−Rh carborane complexes, $(\eta^4\text{-diene})Rh(\mu\text{-}H)Ru(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$ (**4**, diene = COD; **5**, diene = NBD) and $(CO)(PPh_3)Rh(\mu\text{-}H)Ru(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$ (**10**) using the new useful synthon 18e *exo-nido*-5,6,10-[Cl$(PPh_3)_2$Ru]-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$ (**1**).[18] We have also developed an alternative route to mixed-metal clusters of this kind by the reaction of the appropriate organometallic reagents with neutral or anionic *closo*-ruthenacarboranes. This approach is exemplified by the synthesis of complex **4** by the reaction of *closo*-3,3-$(PPh_3)_2$-3-Cl-3-H-3,1,2-$RuC_2B_9H_{11}$ (**6**) or [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RuC_2B_9H_{11}$][Et_4N] (**8**) with $[(\eta^4\text{-COD})RhCl]_2$. Also presented are single-crystal X-ray diffraction studies of **4** and **10** which revealed the existence of both Ru−H−Rh and B−H···Rh bridging bonds in the molecules. In addition, two new anionic *closo*-ruthenacarboranes [*closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RuC_2B_9H_{11}$][Et_4N] (**7**) and **8** have also been prepared and structurally characterized.

Results and Discussion

Preliminary Considerations. It seemed probable that some *exo-nido*-metallacarboranes could serve as appropriate reagents for the selective η^5-bonding of other metal-containing moieties following the loss of a proton from the pentagonal face of the *nido*-carborane cage. Provided that the open C_2B_3 face could be retained after the removal of an "extra-hydrogen", such an anionic species, if formed, would be a dicarbollide ion of a new type with an adjacent metal center at the *exo*-position ("metalladicarbollide ion"). However, most of the known *exo-nido*-metallacarboranes of the platinum group metals, as in primarily discovered *exo-nido*-rhodacarboranes,[19] display tautomerism between *exo-nido* and *closo* structures and, therefore, it was difficult to predict which of the possible reaction pathways would be realized if such species were treated with organometallic reagents in the presence of strong base.

For an exploratory synthesis of this type we have selected one of the known *exo-nido*-ruthenacarboranes, *exo-nido*-5,6,10-[Cl$(PPh_3)_2$Ru]-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$, **1**,[18] as the starting material. Unlike other *exo-nido* species,[19,20] *exo-nido*-ruthenacarborane **1** was shown to have in the solid state three 2e,3c bridging B−H··· Ru bonds which link the ruthenium atom with the *nido*-carborane cage, and in solution it exists as an equilibrium mixture of symmetrical and unsymmetrical isomeric species, both having an *exo-nido* structure.[18] The corresponding *closo*-isomer of **1**, *closo*-3,3-$(PPh_3)_2$-3-Cl-3-H-3,1,2-$RuC_2B_9H_{11}$ (**6**), was not detected in the ^1H or $^{11}B\{^1H\}$ NMR spectra of **1** at ambient temperature. However, this *closo*-isomer could be prepared by the nonreversible rearrangement of **1** at elevated temperatures and in quantitative yield.[21] This fact suggests a high barrier for the interconversion of *exo-nido*-(**1**) and *closo*-ruthenacarborane (**6**) in solution. It seemed probable, therefore, that under basic conditions *exo-nido*-ruthenacarborane **1** could be converted to a sufficiently stable "ruthenadicarbollide ion" which would serve as a potential precursor for the syntheses of various mixed-metal carborane-containing clusters.

Synthesis and Spectroscopic Characterization of Bimetallacarboranes 4 and 5. Indeed, the reaction of **1** with μ-halide rhodium dimers $[(\eta^4\text{-COD})RhCl]_2$ (**2**) or $[(\eta^4\text{-NBD})RhCl]_2$ (**3**) in the presence of KOH in ethanol has been found to result in the formation of bimetallic complexes $(\eta^4\text{-diene})Rh(\mu\text{-}H)Ru(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$ (**4**, diene = COD; **5**, diene = NBD) in 66 and 56% yield, respectively (Scheme 1).

These bimetallic complexes proved, however, to exhibit different structures from those postulated. It was evident from ^1H, ^{13}C, ^{11}B, and ^{31}P NMR data of **4** and **5** as well as from X-ray analyses of **4** (vide supra) that it was the "old" Ru atom rather than the incoming Rh that shifted to the position of the free vertex of the starting

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[11] Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1985**, *24*, 2688.

[12] Chizhevsky, I. T.; Lobanova, I. A.; Pisareva, I. V.; Zinevich, T. V.; Bregadze, V. I.; Yanovsky, A. I.; Struchkov, Yu. T.; Knobler, C. B.; Hawthorne, M. F. In *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1994; p 301.

[13] Lobanova, I. A.; Chizhevsky, I. T.; Petrovskii, P. V.; Bregadze, V. I. *Izv. Akad. Nauk, Ser. Khim.* **1996**, *1*, 250 (English translation).

[14] Anderson, S.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1995**, *14*, 3516.

[15] Lebedev, V. N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 1669.

[16] Batten, S. A.; Jeffery, J. C.; Jones, P. L.; Mullica, D. F.; Rudd, M. D.; Sappenfield, E. L.; Stone, F. G. A.; Wolf, A. *Inorg. Chem.* **1997**, *36*, 2570.

[17] Lebedev, V. N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *J. Organomet. Chem.* **1997**, *537−537*, 537.

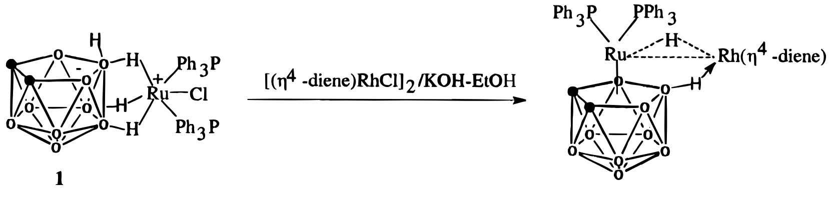
[18] Chizhevsky, I. T.; Lobanova, I. A.; Bregadze, V. I.; Petrovskii. P. V.; Antonovich, V. A.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T. *Mendeleev Commun.* **1991**, 47.

[19] (a) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979. (b) Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990. (c) Long, J. A.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3004. (d) Hewes, J. D.; Thompson, M.; Hawthorne, M. F. *Organometallics* **1985**, *4*, 13. (e) Belmont, J. A.; Soto, J.; King, R. E., III; Donaldson, A. J.; Hewes, J. D.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1989**, *111*, 7475, and references therein.

[20] (a) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687. (b) Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80. (c) Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 5757. (d) Brew, S. A.; Jeffory, J. C.; Mortimer, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1365. (e) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1281. (f) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabó, J. *Organometallics* **1994**, *13*, 2751. (g) Teixidor, F.; Viñas, C.; Casabó, J.; Romeorosa, A. M.; Rius, J.; Miravitlles, C. *Organometallics* **1994**, *13*, 914. (h) Viñas, C.; Nuñez, R.; Flores, M. A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1995**, *14*, 3952. (i) Topaloglu, I. *Synth. React. Inorg. Met.-Org. Chem.* **1996**, *26*, 1295. (j) Viñas, C.; Nuñez, R.; Flores, M. A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1996**, *15*, 3850. (k) Xie, Z.; Liu, Z.; Chiu., K.; Xue, F.; Mak, T. C. W. *Organometallics* **1997**, *16*, 2460.

[21] Chizhevsky, I. T.; Lobanova, I. A.; Bregadze, V. I.; Petrovskii, P. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T. *Organomet. Chem. U.S.S.R.* **1991**, *4*, 469 (English translation).

Scheme 1



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4, diene=C_8H_{12} (COD)
5, diene=C_7H_8 (NBD)

exo-*nido*-cluster, whereas the Rh(η^4-diene) moiety was associated with the *closo*-ruthenacarborane framework of the molecules by means of bridging Ru−H−Rh and 2e,3c B−H···Rh bonds.

The mass spectrum of both compounds **4** and **5** gave a *m*/*z* value corresponding to their molecular ion at 969 and at 953, respectively. In the mass spectrum of **4** principal fragments corresponding to $[M - (COD)]^+$, $[M - PPh_3]^+$, and $[M - (COD+PPh_3)]^+$ also were observed. The corresponding diene ligand signals revealed in the ^{1}H NMR spectra of **4** and **5** were complicated and partly overlapping multiplets with the exception of those from equivalent cyclooctadiene and norbornadiene protons of the double bonds. These appeared in the spectra as single multiplets in separate regions at 5.18 and at 4.44 ppm, respectively. This fact, coupled with the observation of only one carbon signal from the cyclooctadiene double bonds at 81.6 ppm with characteristic $J_{Rh-C} =$ 11.6 Hz in the ^{13}C NMR spectra of **4**, is in accord with the symmetrical structure of the complexes. The ^{31}P-{^{1}H} NMR spectra of both **4** and **5** showed somewhat broadened resonances (line width ca. 18−19 Hz) at 49.03 and at 49.83 ppm, respectively, as expected for the presence of equivalent PPh_3 groups at the ruthenium atom.

On passing from compound **1** to species **4** and **5**, a significant change was observed in the high-field region of the ^{1}H NMR spectra. The spectrum of **4** showed two separate high-field resonances at −6.22 and at −14.41 ppm with a 1:1 intensity ratio, in contrast to the two sets of complex multiplets displayed in the isomeric mixture of **1**.[18] The signal at −6.22 ppm, due to its broad and quadruplet-like character, was attributed to the bridging proton of a B−H···Rh bond. Both the chemical shift and the 1:3:3:1 quadruplet multiplicity ($\Delta\delta = 21.3$ Hz) of the other sharp signal at −14.42 ppm (actually an overlapping doublet of triplets) observed in the ^{1}H NMR spectrum of **4** seem to originate from a bridging Ru−H−Rh unit rather than from any terminal metal hydride. In fact, if the terminal hydride is attached to the ruthenium atom which has two equivalent phosphine groups, an additional splitting of the hydride signal by the ^{103}Rh nucleus through a possible Ru−Rh single bond would not be expected. As previously reported for a Rh−Ir cluster $[RhIrH(\mu-\sigma{:}\eta^5\text{-}C_2B_9H_{10})(CO)_3(PPh_3)_2]$,[5] which contains a Ir−H terminal bond and at least one PPh_3 ligand at each of the metal centers, no additional splitting of this hydride resonance due to ^{1}H−^{31}P(Rh) as well as ^{1}H−^{103}Rh was observed in the ^{1}H NMR spectrum. At the same time, in the ^{1}H NMR spectrum of the bimetallic compound $[RhPt(\mu\text{-}H)(\mu\text{-}CO)(PEt_3)(\eta^5\text{-}C_2B_9H_{11})]$,[7] wherein the Rh−Pt unit is bridged by a hydrido ligand, the high-field resonance of this ligand was split by the three nonequivalent ^{31}P nuclei of the phosphine ligands attached to the different metal centers and by the ^{103}Rh nucleus as well. Additionally, examination of the ^{1}H{^{31}P} NMR spectrum of **4** revealed a doublet instead of a pseudoquartet in the same region, which was attributed to ^{1}H−^{103}Rh coupling ($J_{H-Rh} = 20.4$ Hz). The high value of this coupling constant which, at the same time, is comparable to the $\Delta\delta$ value of the undecoupled pseudoquartet at −14.42 ppm clearly confirmed the existence of a bridging hydrido ligand supporting two metal centers which might have participated in the formation of a direct metal−metal bond in **4**.

The detailed examination of the ^{31}P NMR spectra of complexes **4** and **5** gave additional useful information regarding their structures. In the selective decoupling experiment, when only protons of the PPh_3 components of **4** were decoupled, the single resonance at 49.03 ppm splits into a doublet ($J_{P-H(br)} = 19.5$ Hz). This resonance exhibits no additional long-range coupling constants, $^2J_{P-Rh}$. It should be noted that a $^2J_{P-Rh}$ coupling constant through a M−Rh single bond is usually in the range of 5−8 Hz and is more often observed for non-carborane bimetallic (M−Rh) clusters[22,23](see, however, ref 8). Thus, the observed results may be explained due either to the absence of any significant metal−metal interaction in these complexes (vide infra) or to the large line widths of the signals observed in the coupled and selective proton decoupled ^{31}P NMR spectra.

This question, however, is difficult to resolve by spectroscopy. As was shown previously,[4] in the dimeric rhodacarborane clusters $[Rh(PPh_3)(C_2B_9H_{10}\text{-}1\text{-}R)]_2$ in which a Rh−Rh bond is present, the phosphine ligands are displayed in the ^{31}P{^{1}H} NMR spectra either as a broad doublet ($^1J_{P-Rh} = 135$ Hz) along with a sharp resonance [doublet of doublets, $^1J_{P-Rh} = 172$ Hz, $^3J_{P-P}$ (possibly,$^2J_{P-Rh}$) = 5 Hz] or as the only broad doublet ($^1J_{P-Rh} = 134$ Hz) for asymmetrical (1-R═H) and symmetrical (1-R═Ph) species, respectively. The line widths of the observed signals and additional splitting due to ^{31}P−^{31}P (or, possibly, ^{31}P−^{103}Rh) long-range coupling as well as the values of $^1J_{P-Rh}$ coupling constants have been shown to depend on the preferred conformation of the phosphine rhodium moiety, and especially on whether the phosphine ligand is trans to carbon or boron atoms of the coordinating cage face. Since in **4** the phosphine ligands at the ruthenium vertex do not occupy the position trans to the carborane cage carbon atoms (see angles P−Ru−C in caption to Figure 1), the presence

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(22) (a) Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *Organometallics* **1985**, *4*, 935. (b) Delavaux, B.; Chaudret, B.; Devillers, J.; Dehan, F.; Commenges, G.; Poilblanc, R. *J. Am. Chem. Soc.* **1986**, *108*, 3703.

(23) Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *J. Organomet. Chem.* **1986**, *317*, 69.

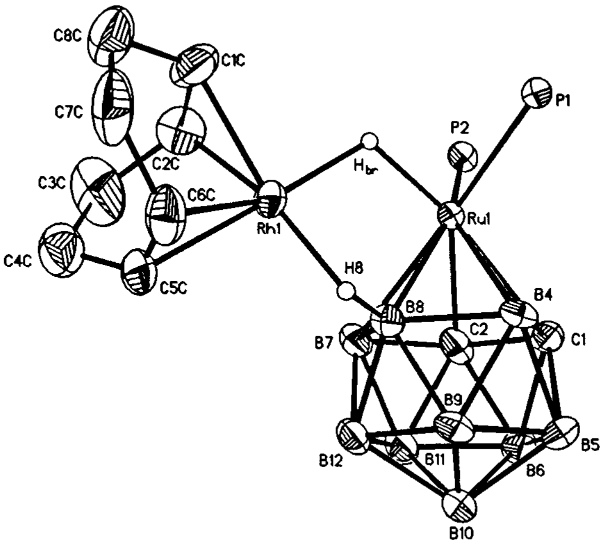


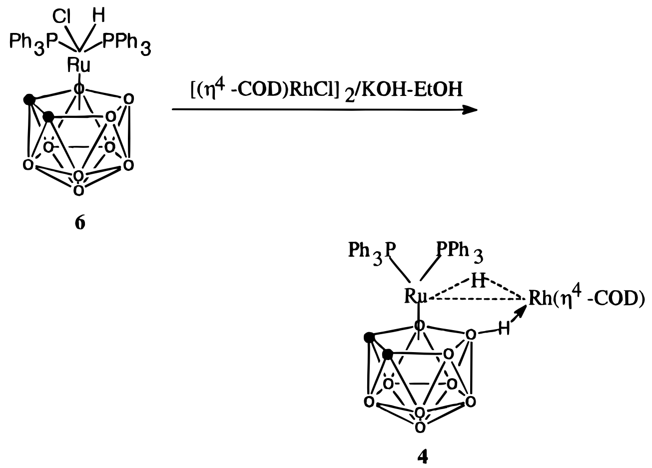
Figure 1. Molecular structure of **4**, showing 50% probability ellipsoids for the non-hydrogen atoms. Ph groups and carborane and COD hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−P(1), 2.337(3); Ru(1)−P(2), 2.368(3); Ru(1)−C(1), 2.264(9); Ru(1)−C(2), 2.220(11); Ru(1)−B(4), 2.273(11); Ru(1)−B(7), 2.307(13); Ru(1)−B(8), 2.341(11); Ru(1)−H(br), 1.6(1); B(8)−H(8), 1.03; Ru(1)···Rh(1), 2.889(1); Rh(1)−H(br), 2.0(1); Rh(1)...H(8), 1.86; Rh(1)−C(12M), 2.021; Rh(1)−C(56M), 1.993 [C(12M) and C(56M) are midpoints of the double bonds C(1)=C(2) and C(5)=C(6) in COD]; C(1C)−C(2C), 1.40(3); C(5C)−C(6C), 1.39(2); P(1)−Ru(1)−C(1), 105.0(3); P(1)−Ru(1)−C(2), 146.6(3); P(2)−Ru(1)−C(1), 103.5(3); P(2)−Ru(1)−C(2), 85.9(3); P(1)−Ru(1)−P(2), 96.1(1); Ru(1)−H(br)−Rh(1), 108(5); Rh(1)−H(8)−B(8), 105.

of long-range coupling, $^2J_{P-Rh}$ (through a possible Ru−Rh bond) or $^3J_{P-Rh}$ (through the Ru−H−Rh bridge) in the $^{31}P\{^1H\}$ NMR spectra of **4**, may not be expected due to the fact that efficient coupling of ^{31}P nuclei is affected by the quadrupole moment of the boron nuclei.

An alternative synthetic route to the above-mentioned mixed-metal cluster **4** involves the treatment of the known *closo*-3,3-$(PPh_3)_2$-3-Cl-3-H-3,1,2-$RuC_2B_9H_{11}$ (**6**)[21,24] with the dimeric μ-halide complex **2** in ethanol in the presence of KOH. However, the yield of pure bimetallic complex **4** proved to be relatively low (39%) even when the reaction was carried out under reflux conditions.

It is noteworthy that NMR monitoring of the reaction of **1** or **6** with KOH in ethanol-d_6 revealed in the ^1H and ^{31}P NMR spectra a sharp triplet at −9.98 ppm ($J_{H-P} = 33$ Hz) and one singlet at 60 ppm, respectively, as expected for a terminal hydride at the Ru center ligated by two equivalent PPh_3 ligands. Such sets of signals were tentatively attributed to an anionic complex [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RuC_2B_9H_{11}$]$^-$ which might be expected as the key intermediate in the formation of the mixed-metal complexes **4** or **5** in the first step (base treatment of **1** or **6**) of the corresponding reactions. According to the concept of a Lewis acid−Lewis base interaction,[25] this anionic hydrido complex can act as the "hydride donor" to the coordinatively unsaturated "acceptors" [(η^4-diene)RhCl]$_2$ or [(η^4-diene)RhOEt]$_2$. The latter species, by analogy with the known examples,[26] might have been formed "in situ" from starting materials **2** and **3** in ethanol under the base treatment.

Scheme 2



Taking into account this possible pathway leading to the formation of mixed-metal bimetallacarboranes **4** and **5**, and in an attempt to clarify the nature of the possible intermediate species, we have developed a convenient synthetic procedure for the preparation of two new anionic *closo*-ruthenacarboranes, [*closo*-3,3-$(PPh_3)_2$-3-R-3,1,2-$RuC_2B_9H_{11}$][Et_4N] (**7**, R = Cl; **8**, R = H). Within the family of mononuclear *closo*-ruthenacarboranes very little has been written about the chemistry of anionic species of the above type.[12] Recently the synthesis of several new anionic complexes related to **7** that are derived from *closo*-$(CO)_3Ru(\eta^5$-7,8-$C_2B_9H_{11})$ and the studies of their reactivity have been reported by Stone and co-workers.[14]

Unlike the known reaction of $(PPh_3)_3RuHCl$ with [Me_3NH][7,8-$C_2B_9H_{12}$] in boiling ethanol, which yielded a neutral *closo*-3,3-$(PPh_3)_2$-3,3-H_2-3,1,2-$RuC_2B_9H_{11}$,[24] the same reagents when refluxed in THF in the presence of Et_4NCl gave the anionic compound **7** in 68% yield.

The ^1H NMR spectrum of **7** displayed a slightly broadened resonance for the cage CH groups at 2.9 ppm as well as a phenyl multiplet at 7.3 ppm, while in the high-field region of the spectrum up to δ −17 ppm no other signals were found. In addition, the diagnostic resonances for the ethyl groups originating from the [NEt_4]$^+$ counterpart were present in the spectrum, thus evidencing the anionic structure of complex **7**. In the 160.46 MHz ^{11}B NMR spectrum there were partly overlapping doublets consistent with the symmetrical cage structure of **7**. The $^{31}P\{^1H\}$ spectrum of **7** consisted of only a single resonance at 39.7 ppm due to two equivalent phosphorus groups attached to the ruthenium atom. Complex **7** was further characterized by X-ray diffraction study (vide supra).

The reduction of the anionic *closo*-ruthenacarborane **7** was next studied (Scheme 4). The treatment of **7** by $LiAlH_4$ in THF overnight at room temperature afforded a new complex, **8**, which, by spectroscopy, has been shown to retain the anionic *closo* structure. Taking into account that the yield of **8** was relatively low (13%),

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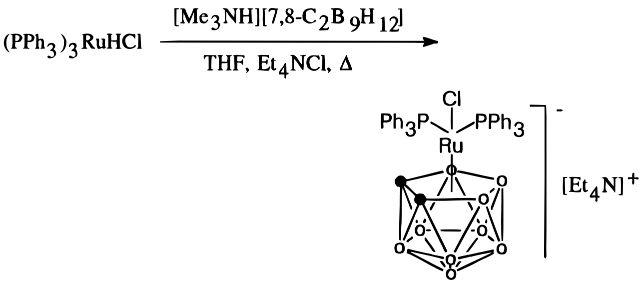
(24) Wong, E. H. S.; Hawthorne M. F. *Inorg. Chem.* **1978**, *17*, 2863.

(25) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

(26) (a) Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985**, *68*, 101. (b) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659, and references therein.

Scheme 3



7

partly due to its decomposition during the reaction process, we have also developed an alternative one-pot synthesis of **8** employing available $Tl_2[7,8-C_2B_9H_{11}]$.[27] Thus, the reaction of $(PPh_3)_3RuHCl·PhCH_3$ with 1 molar equiv of $Tl_2[7,8-C_2B_9H_{11}]$ in THF at room temperature followed by treatment with Et_4NCl afforded complex **8** in 84% yield. This reaction is most likely a metathesis process during which a Tl-salt of **8** and TlCl should be produced with subsequent loss of a triphenylphosphine molecule. In this work, however, no attempts were made to isolate and characterize this intermediate Tl-salt in the solid state.

The ^1H and $^{31}P\{^1H\}$ NMR spectrum of **8** in acetone-d_6 revealed resonances that proved to be very close to those found earlier for the apparent intermediate generated from **1** or **6** in ethanolic solution of KOH (vide infra): a high-field triplet at −9.87 ($J_{H-P} = 34$ Hz) due to the terminal metal hydride and a singlet phosphorus resonance at 61.6 ppm, respectively. The IR spectrum of **8** contained a strong band at 2488 cm^{-1} and a moderate band at 1943 cm^{-1}, which were ascribed to the B−H and Ru−H stretching absorption, respectively. The negative-ion FAB mass spectrum of **8** revealed a clear signal with $m/z = 758.5$ corresponding to a molecular ion of $[(PPh_3)_2HRuC_2B_9H_{11}]^-$. An X-ray diffraction study of **8** also confirmed its anionic *closo* structure (vide supra). As suggested, this species readily reacted with the μ-halide dimeric complex **2** at 20 °C in ethanol in the presence of KOH to produce cluster **4** in 61% yield (Scheme 5).

Syntheses and Characterization of Bimetallacarborane 10. It was found that complex **1** also readily reacted with μ-halide dimer $[(CO)_2RhCl]_2$ (**9**) in the presence of KOH in methanol at ambient temperature, yelding a mixture of bimetallacarborane $(CO)(PPh_3)Rh(\mu\text{-}H)Ru(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$ (**10**) along with two mononuclear complexes, *closo*-$(CO)_2(PPh_3)Ru(\eta^5\text{-}C_2B_9H_{11})$ (**11**) and *closo*-$(CO)(PPh_3)_2Ru(\eta^5\text{-}C_2B_9H_{11})$ (**12**), as byproducts (Scheme 6). This crude mixture of complexes was successfully separated by column chromatography on florisil into **10**−**12** in 46, 3, and 5% yield, respectively.

In the IR spectrum of **10**, the ν_{CO} stretching frequency is observed at 1988 cm^{-1}, a somewhat lower frequency than the values usually observed for terminal carbonyl functions in neutral *closo*-carbonylruthenacarboranes.[14,28] The $^{13}C\{^1H\}$ spectrum of **10** showed the expected resonance for a carbonyl carbon atom at 192.2 ppm, which appears as a doublet of doublets due to splitting on ^{31}P [$J_{C-P(Rh)} = 16$ Hz] and on ^{103}Rh ($J_{C-Rh} = 73.7$ Hz) nuclei. All carbon signals of the coordinated PPh_3 groups appeared in the range 127−138 ppm and proved to be complex and partly overlapped. However, the $^{31}P\{^1H\}$ NMR spectrum of this compound unambiguously established the existence of two types of PPh_3 ligands in the molecule. Two phosphorus signals were observed in the spectrum: a singlet at 49.0 ppm and a sharp doublet at 40.3 ppm ($J_{P-Rh} = 156.4$ Hz) with 2:1 intensity ratio. These resonances were assigned to two equivalent PPh_3 groups at the Ru atom and to one PPh_3 group attached to the Rh center, respectively. The composition of **10** is also in accord with the FAB MS described in the Experimental Section.

Since the rhodium atom in cluster **10** proved to coordinate to one CO and to a PPh_3 ligand, the synthesis is evidently not stoichiometric. The required free PPh_3 molecule might have originated from the decomposition of starting complex **1.** Alternatively, PPh_3 could arise in the course of further transformation of the anionic intermediate formed by the base treatment of **1** in the presence of complex **9**, which serves as the source of carbonyl ligand. Such a pathway was confirmed by the formation of mononuclear *closo*-ruthenacarboranes **11** and **12** as byproducts of the reaction. The structures of the latter complexes are consistent with the spectroscopic and analytical data given in the Experimental Section.

X-ray Diffraction Studies of Bimetallacarborane Complexes 4 and 10. The molecular structures of **4** and **10** are shown in Figures 1 and 2, respectively. The X-ray diffraction study of **4** and **10** showed that these species should be formally regarded as *closo*-ruthenacarboranes wherein the icosahedral ruthenacarborane components are attached to the (COD)Rh or $(PPh_3)(CO)Rh$ moieties, respectively, by doubly H-bridged B−H···Rh and Ru−H−Rh linkages. The bridging hydride atoms were located in **4** and **10** from difference Fourier maps, and their positional parameters were refined. It is noteworthy that these hydrides are asymmetrically disposed within the bridging Ru−H−Rh and B−H···Rh linkages. Although the hydrogen atom positions determined by X-ray diffraction in the presence of heavy metal atoms are limited in accuracy, we found it worthwhile to compare differences in the location of the bridging hydrides in the studied species**.** Indeed, a considerable difference in the positions of both bridging hydrides is observed. The hydride H(8) atom is located 1.86 Å from the Rh atom in **4**, but in cluster **10** it is 1.53 Å, which might have occurred due to stronger structural *trans*-influence of the terminal carbonyl ligand in **10** as compared to that of the π-coordinated double bond of the COD group in **4**. It is interesting to note, however, that the bridging hydride of the Ru−H−Rh linkage has also been found to occupy a position nearer to the Rh atom in cluster **10** [Rh−H(br.) bond length of 2.0(1) and 1.58(11) Å in **4** and **10**, respectively]. Thus, the strengthening of a bridging B−H(8)···Rh interaction and the shortening of the distance between Rh and H(br) atoms on passing from **4** to **10** indicate that an overall electron-withdrawing effect exerted by substituents at the Rh atom in **10** should be considered

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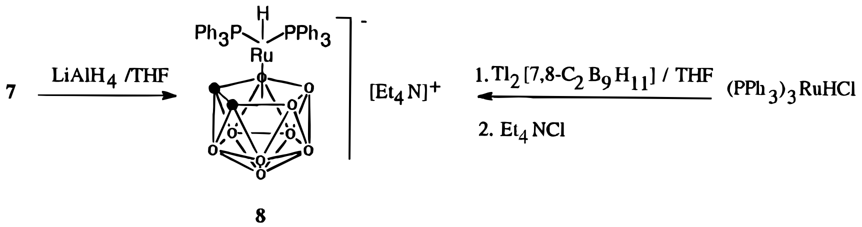
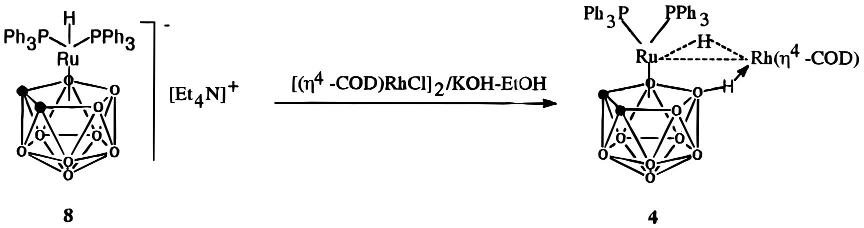
[27] (a) Spencer, J. L.; Green, M.; Stone F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178. (b) Smith, H. D.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 2312.

[28] (a) Behnken, P. E.; Hawthorne, M. F. *Inorg. Chem.* **1984**, *23*, 3420. (b) Anderson, S.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 1676.

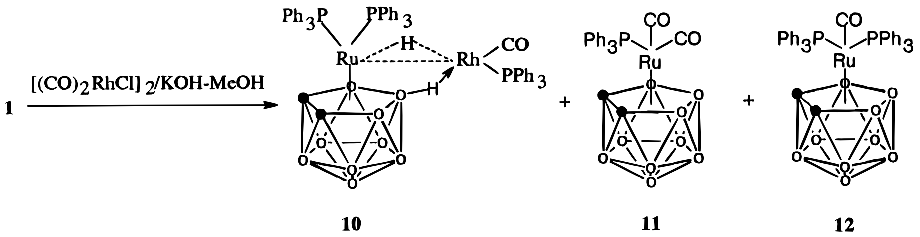
Scheme 4



Scheme 5



Scheme 6



as being responsible for the observed differences in the position of bridging hydrides within these two species. These data also suggest that the species obtained may be considered as donor−acceptor bimetallic complexes wherein the initial anionic 18e $[(PPh_3)_2HRuC_2B_9H_{11}]^-$ unit acts as a four-electron donor (through the Ru−H and B−H bonds) to a cationic 12e L_2Rh (L = CO, PPh_3, COD, or NBD) unit. There is evidence[29] that the bridging hydride ligands themselves in donor−acceptor complexes usually interact much more strongly with the more electron-deficient moiety, which, in our case, is apparently the $(CO)(PPh_3)Rh$ unit in complex **10**.

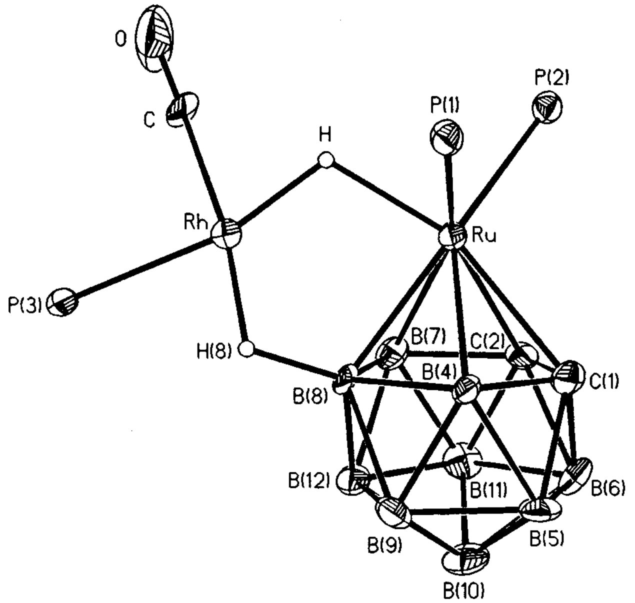


Figure 2. Molecular structure of **10**, showing 50% probability ellipsoids for the non-hydrogen atoms. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−P(1), 2.330(2); Ru−P(2), 2.367(2); Ru−C(1), 2.271(7); Ru−C(2), 2.245(7); Ru−B(4), 2.214(9); Ru−B(7), 2.279(9); Ru−B(8), 2.229(9); Ru−H(br), 1.88(11); B(8)−H(8), 1.30(12); Ru···Rh, 2.845(1); Rh−H(br), 1.58(11); Rh···H(8), 1.53(6); Rh−P(3), 2.240(2); Rh−C(O), 1.816(9); C−O, 1.118(12); P(1)−Ru−P(2), 95.9(1); Ru−H(br)−Rh(1), 110(6); Rh−H(8)−B(8), 110(6); P(3)−Rh−C(O), 91.6(3); H(8)−Rh−H(br), 116(4); P(3)−Rh−H(8), 79(2); C(O)−Rh−H(br), 72(4).

Unlike the Ru^{II} atom with a 18e configuration, the rhodium atom, which is formally Rh^I, in the complexes **4** and **10** has only a 16e shell. This is confirmed by the essentially square-planar coordination around the Rh center in both cases. In fact, the Rh atoms are displaced from the least-squares planes including H(br)H(8)C(12M)C(56M) [C(12M) and C(56M) are the midpoints of the double bonds C(1)=C(2) and C(5)=C(6) in COD] and H(br)H(8)C(O)P(3) by 0.08 and 0.03 Å in **4** and **10**, respectively. Similar square-planar coordination around 16-electron metal centers was observed earlier for $[RuRh(\mu\text{-}Cl)(\mu\text{-}H)(\eta^4\text{-}COD)(dppm)]BF_4$,[23] $[Rh_2(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$,[5] or $RhPt(\mu\text{-}H)(\mu\text{-}CO)(PEt_3)(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$,[7] wherein the existence of a metal−metal bond has been assumed. In addition, according to the electron-counting formalism adopted for bimetallic complexes with bridging hydride ligands,[30] compounds **4** and **10** should be considered as unsaturated species having 32 valence electrons, and it seemed, therefore, that there also should be a single metal−

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[29] Darensbourg, M. Y.; Atwood, J. L.; Burch, R. R., Jr.; Hunter, W. E.; Walker, N. *J. Am. Chem. Soc.* **1979**, *101*, 2632.

[30] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

metal bond in these complexes. At the same time, the separations between two metals established for **4** [2.889(1) Å] and **10** [2.845(1) Å] fall in the range of M−M distances found for hydrido-bridged bimetallic compounds with a metal−metal bond[31] (see also ref 22 for Ru−Rh bond length) or without such a bond.[32] That is why the existence or absence of a metal−metal bond in the bimetallic complexes **4**, **5**, and **10** could not be truly confirmed on the basis of the structural as well as the spectroscopic data obtained for these compounds.

An Estimation of Metal−Metal Bond Order in the Model Complex (CO)(PH$_3$)Rh(μ-H)Ru(PH$_3$)$_2$(η^5-C$_2$B$_9$H$_{11}$) (13) by an Extended Hückel Molecular Orbital Calculation. In connection with this particular problem we have estimated the net Mulliken Ru−Rh bond order in the model complex (CO)(PH$_3$)Rh(μ-H)Ru(PH$_3$)$_2$(η^5-C$_2$B$_9$H$_{11}$) (**13**) by the extended Hückel molecular orbital method in valence bond approximation,[33,34] for which the structural parameters established for **10** have been used. The calculated value of the Ru−Rh bond order for **13** proved to be positive, but very small (0.025), and even considerably smaller than that obtained, for instance, for the Rh−H bonds involving bridging H atoms in the same molecule [Rh−H(B), 0.308; Rh−H(Ru), 0.422]. It should be noted, however, that the metal−metal bonds in transition metal carborane and non-carborane clusters seem to yield somewhat decreased bond orders in the extended Hückel calculations. Thus, in the known cluster (Cp)$_3$Rh$_3$(μ-CO)$_3$[36] with the Rh$_3$-triangle and in the dimeric *closo*-rhodacarborane [Rh(PPh$_3$)C$_2$B$_9$H$_{11}$]$_2$,[4] both having metal−metal bonds, the Mulliken Rh−Rh bond order was calculated as 0.145 and 0.103, respectively. Even taking this into account, the value of the Ru−Rh bond order, 0.025, calculated for the model complex **13** is, apparently, too small to be considered as a real bonding interaction between the two metal centers in the bimetallacarboranes synthesized in this work. We have thus suggested that the type of bonding mode between two metal-containing moieties in complexes **4**, **5**, and **10** should rather be discussed in terms of two three-center two-electron bond systems, which does not imply the significant degree of metal−metal bonding (i.e., close to an “open” M(μ-H)M bond system[25]). A quite similar type of bonding was earlier suggested for the electronically unsaturated square-planar dimeric complex {HRh[P(O-Pr^i)$_3$]$_2$}$_2$,[37] wherein the M−(μ-H$_2$)−M arrangement on the basis of an X-ray diffraction study and molecular orbital analysis has been considered as two four-center (Rh$_2$H$_2$) two-electron bond systems.

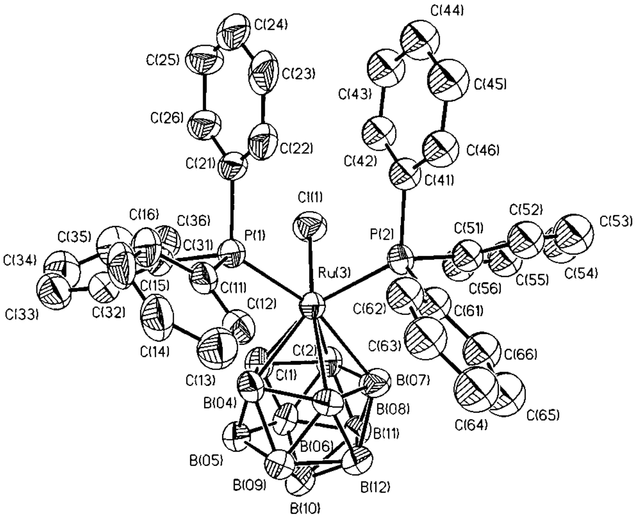

Figure 3. Molecular structure of the anion of complex **7**. Carboranyl and phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(3)−P(1), 2.346(2); Ru(3)−P(2), 2.344(2); Ru(3)−C(1), 2.194(7); Ru(3)−C(2), 2.195(7); Ru(3)−B(4), 2.223(8); Ru(3)−B(7), 2.249(8); Ru(3)−B(8), 2.291(8); Ru(3)−Cl(1), 2.515(2); P(1)−Ru(3)−P(2), 100.3(1); Cl(1)−Ru(3)-P(2), 90.5(1).

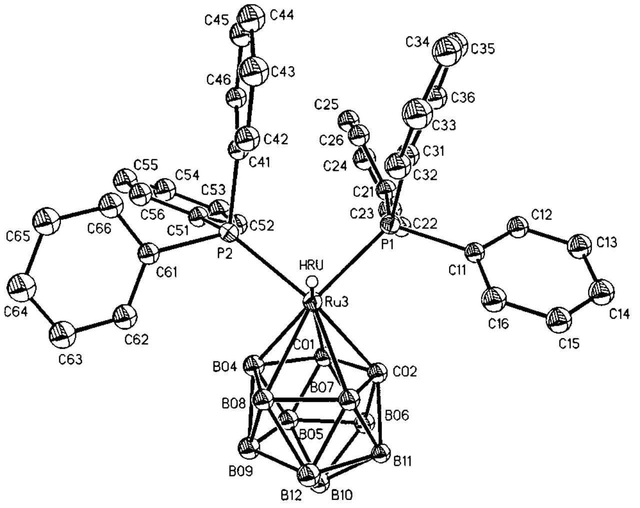

Figure 4. Molecular structure of the anion of complex **8**. Phenyl groups and carboranyl terminal hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(3)−P(1), 2.322(3); Ru(3)−P(2), 2.294(3); Ru(3)−C(1), 2.301(12); Ru(3)−C(2), 2.250(11); Ru(3)−B(4), 2.258(15); Ru(3)−B(7), 2.258(15); Ru(3)−B(8), 2.315(15); Ru(3)−H(Ru), 1.67(9); P(1)−Ru(3)-P(2), 95.7(1); H(Ru)−Ru(3)−P(1), 84(3); H(Ru)-Ru(3)−P(2), 82(3).

X-ray Diffraction Studies of Mononuclear Anionic Complexes 7 and 8. The molecular structures of clusters **7** and **8** are shown in Figures 3 and 4, respectively. The ruthenium atoms in both structures **7** and **8** are bound to three monodentate ligands and are η^5-coordinated by *nido*-carborane cages which occupy, formally, three additional facial coordination sites around the metal centers, thus confirming a coordination number of six for the Ru(II) atoms in these anionic complexes. The Ru−P distances of 2.346(2) and 2.344(2) Å in **7** and 2.322(3) and 2.294(3) Å in **8** are close to those found in the known *closo*-ruthenacarboranes **6** [2.377(1) and 2.380(1) Å][13] and *closo*-2,2-(PPh$_3$)$_2$-2,2-H$_2$-2,1,7-RuC$_2$B$_9$H$_{11}$ (**14**) [2.342(4) and 2.301(4) Å],[38]which, however, belong to a group of neutral seven-coordinate Ru(IV) complexes. At the same time, there are some differences in Ru−Cl and Ru−H bond lengths in the

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[31] Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

[32] Immirzi, A.; Porzio, W.; Bachechi, F.; Zambonelli, L.; Venanzi, L. M. *Gazz. Chim. Ital.* **1983**, *113*, 537, and references therein.

[33] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[34] The values of ionization potentials (I, eV) and the Slater exponent arguments (ζ) used in the extended Hückel calculations were as follows:[35] Ru, I(5s), 8.6; I(5p), 3.28; I(4d), 11.12; ζ(5s), 2.078; ζ(5p), 2.043; ζ_1(4d), 5.378(0.534); ζ_2(4d), 2.303(0.6365); Rh, I(5s), 8.09; I(5p), 4.57; I(4d), 12.5; ζ(5s), 2.135; ζ(5p), 2.100; ζ_1(4d), 4.29(0.5007); ζ_2(4d), 1.97(0.6585); P, I(3s), 18.6; I(3p), 14.0; ζ(3s) = ζ(3p), 1.6; B, I(2s), 15.2; I(2p), 8.5; ζ(3s) = ζ(3p), 1.3; C, I(2s), 21.4; I(2p), 11.4; ζ(2s) = ζ(2p), 1.625; H, I(1s), 13.6; ζ(1s), 1.3. The two-exponent bases were used for the d-orbitals of Ru and Rh; the coefficients in the series representing the d-orbitals as the sums of two Slater functions with the ζ_1 and ζ_2 exponent arguments are given in parentheses.

latter compounds as compared with those found in **7** and **8**, respectively. Thus the Ru−Cl bond length in **7** [2.515(2) Å] is somewhat longer than was found in **6** [2.429(1) Å] or in the anionic complex [3,3-$(CO)_2$-3-Cl-3,1,2-$RuC_2B_9H_{11}$][$Au(PPh_3)_2$] (**15**)[14] [2.452(1) Å], recently published by Stone et al. The Ru−H distance of 1.67(9) Å in **8** is comparable with that found in 3,3-$(PPh_3)_2$-3,3-H_2-3,1,2-$RuC_2B_9H_{11}$ [1.58(6) and 1.65(6) Å][39] but noticeably longer that that found in **6** [1.49(5) Å]. However, all these values of Ru−H bond lengths for the listed compounds are in the range frequently observed for metal−hydrogen distances[40] including those compounds that have terminal hydrogen at the ruthenium center.[41]

Experimental Section

General Considerations. All reactions were carried out in Schlenk equipment under an atmosphere of dry argon using standard Schlenk techniques.[42] Synthesis of complexes **7** and **8** and all procedures for their purification were carried out in the glovebox under an Ar atmosphere. All solvents including those used for column chromatography as eluents were distilled from appropriate drying agents under an argon atmosphere. Starting reagents **2** and **3**,[43] $(Ph_3P)_3RuHCl\cdot PhCH_3$,[44] $Me_3NH[7,8\text{-}C_2B_9H_{12}]$,[45] and $Tl_2[7,8\text{-}C_2B_9H_{11}]$[27] were prepared according to published methods. The ^1H, ^{13}C, ^{31}P, and ^{11}B NMR spectra were obtained with a Bruker WP-200 (200.133 and 50.320 MHz) and Bruker AM-500 FT-NMR (202.46 and 160.463 MHz, see below). Proton, phosphorus, and boron chemical shifts were referenced to residual protons in the deuterated solvents (CD_2Cl_2, 5.32 ppm; C_6D_6, 7.15 ppm; both vs Me_4Si), to external 85% H_3PO_4 or to external $BF_3\cdot Et_2O$, respectively, with downfield shifts taken as positive. Infrared spectra were obtained as Nujol mulls (or NaCl) on a Beckman FT-1100 instrument. Mass spectral data were obtained with a Kratos Model MS 902 instrument. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

Preparation of [(η^4-COD)Rh(μ-H)Ru$(PPh_3)_2$(η^5-$C_2B_9H_{11}$) (4) from *exo-nido*-Ruthenacarborane 1. To a suspension of **1** (150 mg, 0.19 mmol) in 25 mL of absolute ethanol was added an excess of crushed KOH (40 mg, 0.7 mmol), and the mixture was stirred at ambient temperature (~0.5 h) until all starting material was dissolved. Dimeric complex **2** (60 mg, 0.12 mmol) in the solid state was then added to the resulting dark orange solution, and the mixture was stirred for another 1.5 h followed by filtration of precipitate. The orange crystalline solid product was washed with 10 mL of ethanol and dried in a vacuum for 2 h. The recrystallization of the crude material obtained from C_6H_6/*n*-hexane afforded 122 mg (66% yield) of analytically pure compound **4**: IR (KBr, cm^{-1}) 2560 (ν_{B-H}); ^1H NMR [C_6D_6, 500.135 MHz, J (Hz)] 7.42 and 6.85 (m+m, 30H, Ph), 5.18 (m, 4H, CH=CH), 2.67 (s br, 2H, CHcarb), 2.17 (m, 4H, CH_2), 1.68 (q-like, 4H, CH_2), −6.22 (q br, 1H, $J_{H-B} = 83$, BH···Rh), −14.42 (t of d, 1H, $J_{H-Rh} = 20.4$, $J_{H-P} = 19.5$, Ru−H−Rh); $^{31}P\{^1H\}$ NMR (C_6D_6, 202.459 MHz) 49.03 (s br); ^{11}B NMR (C_6D_6, 160.463 MHz) 7.6 [d, 1B, $J_{B-H} = 87$, B(8)], −3.0 (s br, 1B), −10.7 (s br, 4B), −19.5 (s br, 2B), −24.4 (s br, 1B); $^{13}C\{^1H\}$ NMR [CD_2Cl_2, 50.32 MHz, J (Hz)] 138.1 (d, $J_{C-P} = 18.9$, Ph−C_1), 134.3 (s br, Ph−$C_{2,6}$), 129.5 (s, Ph−C_4), 128.2 (s br, Ph−$C_{3,5}$), 81.5 (d, $J_{C-Rh} = 11.6$, CH=CH), 40.9 (s br, Ccarb), 31.7 (s, CH_2); FAB MS (in the range 500−1000, *m*/*z*) 969 $[M]^+$, 861$[M - (COD)]^+$, 783 $[M - (COD + Ph)]^+$, 707 $[M - (PPh_3)]^+$, 599 $[M - (COD + PPh_3)]^+$, 522 $[M - (COD + PPh_3 + Ph)]^+$. Anal. Calcd for $C_{46}H_{54}B_9P_2RhRu$: C, 56.95; H, 5.57; B, 10.03; P, 6.40; Rh, 10.63; Ru, 10.42. Found: C, 56.84; H, 5.71; B, 9.72; P, 6.31; Rh, 10.76; Ru, 10.14.

Preparation of (η^4-COD)Rh(μ-H)Ru$(PPh_3)_2$(η^5-$C_2B_9H_{11}$) (4) from Neutral or Anionic *closo*-Ruthenacarborane 6 or 8. To a clear solution of **6** (150 mg, 0.19 mmol) and powdered KOH (40 mg, 0.71 mmol) generated under gentle reflux in 20 mL of absolute ethanol was added dimeric complex **2** (60 mg, 0.12 mmol) in the solid state at room temperature, and the mixture was stirred additionally for 1.5 h. The resulting orange precipitate was collected by filtration, washed twice with absolute ethanol, and dried under vacuum. Recrystallization of the crude solid from the same solvent mixture afforded 72 mg (39% yield) of product, which from analysis of its ^1H and ^{11}B NMR spectra is deduced to be cluster **4**.

An alternative route to **4** consisted of the reaction of **8** (0.24 g, 0.27 mmol) and **2** (0.07 g, 0.14 mmol) in 25 mL of absolute ethanol in the presence of crushed KOH (28 mg, 0.5 mmol) at 20° C. The mixture of reagents was stirred for 3−5 h, while the color of the solution became dark orange. After the solvent was removed, the crude solid obtained was purified using a short silica gel column (silica gel was treated by Ar under reflux in hexane for 0.5 h before use in column chromatography). The orange band eluting with 1:1 benzene/ether mixture was collected and concentrated under vacuum. The solid material obtained was then recrystallized from a C_6H_6/*n*-hexane mixture, resulting in the isolation of 160 mg of pure **4** (61%) as reddish-orange crystals.

Preparation of (η^4-NBD)Rh(μ-H)Ru$(PPh_3)_2$(η^5-$C_2B_9H_{11}$) (5). To a stirred orange solution generated from **1** (150 mg, 0.19 mmol) and KOH (40 mg, 0.7 mmol) in 20 mL of absolute ethanol as described for **4** (from **1**) was added a suspension of **3** (50 mg, 0.108 mmol) in 5 mL of ethanol in one portion. The resulting mixture was stirred at room temperature for 1 h, followed by collection of a brown precipitate by filtration. After washing on the filter by ethanol, the product was dried under vacuum and collected as a reddish-brown powder, 102 mg (56% yield). Our attempts to obtain an analytically pure form of **5** by column chromatography on silica gel or by recrystallization from CH_2Cl_2/*n*-hexane failed due to the partial decomposition of **5** in solution. Recrystallization of **5** from C_6H_6 by adding an excess of *n*-hexane afforded a yellow-brown powder along with some amount of slightly reddish-orange crystals, which were then collected and characterized as **5** by spectroscopic methods: IR (KBr, cm^{-1}) 2550 (ν_{B-H}); ^1H NMR [CD_2Cl_2, 200.12 MHz, J (Hz)] 7.56 and 7.18 (m+m, 30H, Ph), 4.44 (q-like, 4H, $J_q = 2.4$, CH=CH), 3.82 (m, 2H, CH), 2.22 (s br, 2H, CHcarb), 1.39 [(t-like, 2H, $J_t = 1.5$, H(7α,β)], −6.46 (q br, 1H, $J_{H-B} = 90$, BH···Rh), −14.11 (1:3:3:1 q-like, 1H, $J_{H-Rh}=22.8$, Ru−H−Rh); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.02 MHz) 49.83 (s br); FAB MS (in the range 500−1000, *m*/*z*) 953 $[M]^+$, 861 $[M - (NBN)]^+$.

Preparation of (CO)(PPh_3)Rh(μ-H)Ru$(PPh_3)_2$(η^5-$C_2B_9H_{11}$) (10), Mononuclear Complexes *closo*-$(CO)_2(PPh_3)$-Ru(η^5-$C_2B_9H_{11}$) (11), and *closo*-(CO)$(PPh_3)_2$Ru(η^5-$C_2B_9H_{11}$) (12). To a stirred solution generated from **1** (600 mg, 0.76 mmol) and KOH (160 mg, 2.80 mmol) in 20 mL of MeOH was added solid complex $[(CO)_2RhCl]_2$ (160 mg, 0.42 mmol). The

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(35) (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (b) Jorgensen, K. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 1867.

(36) Mills, O.S.; Paulus, E. F. *J. Organomet. Chem.* **1967**, *10*, 331.

(37) Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1806.

(38) Wong, E. H. S.; Hawthorne, M. F. *J. Chem Soc., Chem. Commun.* **1976**, 257.

(39) Wong, E. H. S.; Hawthorne, M. F. Unpublished data.

(40) Frenz, B. A.; Ibers, J. A. In *Transition Metal Hydrides*; Muetterties, E. E., Ed.; Marcel Dekker: New York, 1971; p 42.

(41) (a) Skapski, A. C.; Troughton, P. G. H. *J. Chem. Soc., Chem. Commun.* **1968**, 1230. (b) Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Chem. Commun.* **1969**, 1008. (c) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 1317. (d) Cotton, F. A.; Hunter, D. L. *Inorg. Chim. Acta* **1975**, *15*, 155. (e) Lemke, F. R.; Brammer, L. *Organometallics.* **1995**, *14*, 3980, and references therein.

(42) Shriver, D. F. *The manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(43) Chatt, J.; Vananzi, L. M. *J. Chem. Soc.* **1957**, 4735.

(44) Schunn, R. A.; Wonchoba, E. R. *Inorg. Synth.* **1972**, *13*, 131.

(45) Weisboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

Table 1. Crystal Data and Details of the X-ray Experiments for 4, 7, 8, and 10

	4	**7**	**8**	**10**
mol formula	$C_{49}H_{54}B_9P_2RhRu{\cdot}C_6H_{14}$	$C_{46}H_{61}B_9ClNP_2Ru{\cdot}C_4H_8O$	$C_{46}H_{62}B_9NP_2Ru$	$C_{57}H_{57}B_9OP_3RhRu{\cdot}C_6H_6{\cdot}0.75CH_3OH$
mol wt	1056.3	995.8	889.3	1251.3
cryst size	0.12 × 0.12 × 0.18	0.4 × 0.45 × 0.6	0.26 × 0.2 × 0.4	0.2 × 0.2 × 0.3
cryst color, habit	red parallelepipeds	deep red parallelepipeds	yellow parallelepipeds	orange parallelepipeds
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/n$
radiation	MoKα	MoKα	MoKα	MoKα
monochromator	graphite	graphite	graphite	graphite
diffractometer	Huber	Picker FACS-1	Huber	Siemens P3/PC
temp, K	298	298	298	148
a, Å	14.2917(5)	11.640(1)	11.954(3)	14.360(4)
b, Å	15.1341(6)	16.942(1)	12.391(3)	21.100(5)
c, Å	24.0509(9)	26.155(3)	31.307(8)	20.496(6)
β, deg		97.425(4)	98.787(7)	94.61(2)
V, Å^3	5202(4)	5114	4583	6190(3)
Z	4	4	4	4
D(calcd), g cm^{-3}	1.35	1.29	1.29	1.343
F(000)	2176	2080	1856	2554
μ, cm^{-1}	6.9	4.5	3.9	6.3
below $K_{\alpha}1$	1.3	1.3	1.3	1.05
above $K_{\alpha}2$	1.6	1.5	1.5	1.05
scan rate, deg min^{-1}	6	6	3.0	2.02−29.30
$2\theta_{max}$, deg	60	54	45	48
structure solution	heavy atom	heavy atom	heavy atom	direct method
H-atoms refinement	positional parameters of bridging atoms refined, other H atoms calculated	positional parameters of carboranyl H atoms were refined	positional parameters of carboranyl H atoms and hydride atom were refined	all H atoms refined isotropically
reflns measured	h, k, l	$h, k, \pm l$	$h, k, \pm l$	$h, k, \pm l$
no. of unique reflns	8289	11 166	5993	8739
no. of observed reflns	4685	6467	3298	5917
no. of params refined	463+21	473	228	905
R	0.050	0.070	0.075	0.054
R_w	0.059	0.083	0.086	0.060
GOF	1.42	2.19	1.90	1.88

resulting mixture was allowed to stir at ambient temperature for 1 h. Solvent was evaporated under reduced pressure, and the residue was treated by column chromatography on Florisil. The first band eluted from the column using a benzene/*n*-hexane (1:1) mixture was found to contain crude **11** and **12**. The second band was then eluted with benzene to afford 400 mg (46%) of pure **10**: IR (KBr, cm^{-1}) 2554 (ν_{B-H}), 1988 (ν_{CO}); ^{1}H NMR [C_6D_6, 200.12 MHz, J (Hz)] 7.53−6.95 (m, 45H, Ph), 2.67 (br s, 2H, CHcarb), −4.96 (q-like, 1H, BH···Rh), −9.81(t of d of d, 1H, $J_{H-Rh} = 21.1$, $J_{H-P(Ru)} = 20.9$, $J_{H-P(Rh)} = 35.5$, Ru−H−Rh); ^{31}P{^{1}H} NMR (C_6H_6, 81.01 MHz) 49.06 (s), 40.3 (d, $J_{P-Rh} = 156.5$ Hz); ^{11}B NMR (C_6H_6, 64.2 MHz) 11.6 [d, 1B, $J_{B-H} = 67$ Hz, B(8)], −4.7, −6.1, −10.8, −19.9 (br bands, 8B); ^{13}C{^{1}H} NMR [CH_2Cl_2, 50.32 MHz, J (Hz)] 192.2 (d of d, CO, $J_{C-Rh} = 73.7$, $J_{C-P} = 16$), 127.6−138.0 (Ph), 41.0 (br s, Ccarb); FAB MS (in the range 500−1000, m/z) 1151 [M]$^+$, 1123 [M − CO]$^+$, 1074 [M − Ph]$^+$, 1046 [M − (CO + Ph)]$^+$, 861 [M − (CO + PPh$_3$)]$^+$, 784 [M − (CO + PPh$_3$ + Ph]$^+$. Anal. Calcd for $C_{58}H_{59}B_9OP_3Cl_2RhRu$ (**10**·CH_2Cl_2): C, 56.29; H, 4.77; B, 7.86; P, 7.52; Cl, 5.74. Found: C, 56.30; H, 4.79; B, 7.86; P, 7.60; Cl, 6.37. The mixture of **11** and **12** was separated then by repeated column chromatography on Florisil (eluent benzene/*n*-hexane, 1:1) to give 15 mg (3%) and 30 mg (5%) of pure **11** and **12**, respectively, which were characterized by spectral data: **11**, IR (KBr, cm^{-1}) 2550 (ν_{B-H}), 2048, 1996 (ν_{CO}); ^{1}H NMR ($CDCl_3$, 200.12 MHz) 7.50−7.15 (m, 15H, Ph), 2.13 (s br, 2H, CHcarb); ^{31}P NMR (CD_2Cl_2, 81.01 MHz) 40.60 (s); ^{13}C{^{1}H} NMR [$CDCl_3$, 50.32 MHz, J (Hz)] 196.0 (d, $J_{C-P} = 14.8$, CO), 128.1−134.3 (Ph), 47.6 (s, Ccarb). Anal. Calcd for $C_{22}H_{28}B_9O_2PRu$: C, 47.88; H, 4.72. Found: C, 0.47.54; H, 4.73; **12**, IR (KBr, cm^{-1}) 2576 (ν_{B-H}), 1966(ν_{CO}); ^{1}H NMR (CD_2Cl_2, 200.12 MHz) 7.60−7.2 (m, 30H, Ph), 2.18 (s br, 2H, CHcarb); ^{31}P NMR (CD_2Cl_2, 81.01 MHz) 41.8 (s).

Preparation of [*closo*-3,3-(PPh$_3$)$_2$-3-Cl-3,1,2-RuC$_2$B$_9$H$_{11}$]-[Et$_4$N] (7). To a mixture of $(PPh_3)_3RuHCl{\cdot}PhCH_3$ (1.0 g, 0.984 mmol), $[Me_3NH][7,8\text{-}C_2B_9H_{12}]$ (193 mg, 1.0 mmol), and Et_4NCl (166 mg, 1.0 mmol) flushed with argon was added 125 mL of THF, and the resulting solution was gently refluxed for 4 h until the solution became orange. After cooling, the volume was reduced by approximately half and 50 mL of diethyl ether was then added, followed by recrystallization of precipitate from a THF/ether mixture, affording 570 mg (63% yield) of analytically pure deep red crystals of **7**. Anal. Calcd for $C_{46}H_{61}ClB_9NP_2Ru$: C, 59.82; H, 6.61; B, 10.53; P, 6.72; Ru, 10.95. Found: C, 60.21; H, 6.90; B, 9.61; P, 6.17; Ru, 12.21. IR (NaCl, cm^{-1}): 2510 (ν_{B-H}). ^{1}H NMR [acetone-d_6, 200.12 MHz, J (Hz)]: 7.62 and 6.87 (m+m, 30H, Ph), 3.48 (q, 8H, J_{H-H}=7.0, CH$_2$), 2.90 (br s, 2H, CHcarb), 1.18 (t, 12H, $J_{H-H} = 7.0$, CH$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, 81.01 MHz): 39.7 (s). ^{11}B{^{1}H} NMR (acetone, 160.46 MHz): −1.3 (1B), −6.1 (1B), −9.6 (2B), −12.3 (2B), −23.2 (1B), −25.8 (2B).

Preparation of [*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RuC$_2$B$_9$H$_{11}$]-[Et$_4$N] (8) by LiAlH$_4$ Reduction of 7. A mixture of **7** (4.0 g, 4.33 mmol) and $LiAlH_4$ (80 mg, 2 mmol) in 125 mL of THF was allowed to stir overnight. During this time the color of the solution turned from a reddish-orange to yellow. After filtration over a Celite pad the solvent was removed, and the resultant powder was washed with 10 mL of MeOH and ether and dried under vacuum. Recrystallization of the residual three times from a THF/ether mixture afforded 550 mg (13% yield) of pure **8** as yellow crystals. Negative-ion FAB MS (m/z): 758.5 [M − Et$_4$N]$^-$. IR (Nujol mull, cm^{-1}): 1943 (ν_{Ru-H}), 2488 (ν_{B-H}). ^{1}H NMR (acetone-d_6, 200.12, J (Hz)]): 7.36 and 7.04 (m+m, 30H, Ph), 3.15 (q, 8H, $J_{H-H} = 6.8$, CH$_2$), 1.63 (br s, 2H, CHcarb), 1.20 (t, 12H, $J_{H-H} = 6.8$, CH$_3$), −9.87 (t, 1H, $J_{H-P} = 34$, H$_{Ru}$). ^{31}P{^{1}H} NMR (CD_3CN, 81.01 MHz): 61.6 (s). ^{11}B{^{1}H} NMR (CD_3CN, 160.46 MHz): −8.0 (1B), −9.4 (1B), −11.8 (2B), −14.2 (2B), −25.6 (1B), −26.8 (2B).

Preparation of Complex 8 Using Tl$_2$[7,8-C$_2$B$_9$H$_{11}$]. To a solution of $(PPh_3)_3RuHCl{\cdot}PhCH_3$ (4.06 g, 4.0 mmol) in 200 mL of THF was added $Tl_2[7,8\text{-}C_2B_9H_{11}]$ (2.16 g, 4.0 mmol), and the mixture was stirred at ambient temperature overnight and filtered into a second flask containing Et_4NCl (662 mg, 4.0 mmol). After additional stirring for 24 h under the same conditions the resulting mixture was thoroughly filtered, partly concentrated, and then diluted by 150 mL of ether. Recrystallization of the microcrystals obtained from a THF/ether mixture afforded 2.99 g (84%) of yellow crystalline product, which from analysis of ^{1}H and ^{11}B NMR spectra is deduced to be anionic complex **8**.

X-ray Diffraction Studies of Complexes 4, 7, 8 and 10. Crystal and refinement data for complexes **4**, **7**, **8**, and **10** are given in Table 1. All calculations for structures **4**, **7**, and **8** were carried out with a VAX 3100 computer and with the help of programs written by Professor C. E. Strouse of UCLA. The calculations for structure **10** were performed on an IBM PC computer using the SHELXTL Plus (Version 4) programs. Scattering factors for hydrogen atoms were obtained from Stewart et al.,[46] and for other atoms were taken from The International Tables for X-ray Crystallography.[47]

Conclusions

The complexes described above are novel examples of mixed-metal metallacarboranes wherein the η^5-$C_2B_9H_{11}$ ligand is involved in coordination with the ruthenium atom which is simultaneously linked with different rhodium sources. New convenient methods have been offered for their preparation using available *exo*-*nido*-ruthenacarboranes as well as neutral and anionic *closo*-hydridoruthenacarboranes as precursors. It is envisaged that further application of the described synthetic approaches may be used for the syntheses of a variety of novel bi- and polymetallic carborane-containing clusters.

Acknowledgment. This research was supported in part by the United States National Science Foundation (Grant CHE-91-11437). I.T.C. also thanks the United States National Science Foundation for support and the Institute of Organoelement Compounds of the Russian Academy of Sciences for sabbatical leave. I.T.C., P.V.P., F.M.D., and A.I.Y. also gratefully acknowledge the financial support of the Russian Foundation for Basic Research (Grant Nos. 97-03-33783 and 97-03-32987).

Supporting Information Available: Tables of crystal data, position parameters, bond distances and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org

OM9806592

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(46) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(47) *The International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.