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Synthesis of 16-Electron (η^3-Cyclooctenyl)metallacarboranes of Rhodium(III) and Iridium(III) with the New Sterically Demanding $[(4'\text{-MeC}_6\text{H}_4)_2\text{C}_2\text{B}_9\text{H}_9]^{2-}$ Carborane Ligand. Molecular Structures of $[3\text{-}\{(1-3\text{-}\eta^3)\text{-C}_8\text{H}_{13}\}\text{-}1,2\text{-}(4'\text{-MeC}_6\text{H}_4)_2\text{-}3,1,2\text{-}\textit{pseudocloso}\text{-MC}_2\text{B}_9\text{H}_9]$ (M = Rh, Ir) and $[(\eta^6\text{-MeC}_6\text{H}_4)\text{Rh}(\text{C}_2\text{B}_9\text{H}_9\text{C}_6\text{H}_4\text{Me})\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})]_2$, a Dimeric Byproduct Containing Distorted 13-Vertex $\{4,9,1,10\text{-Rh}_2\text{C}_2\text{B}_9\}$ Cluster Units

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Reactions of the $[\text{K}]^+$ salt of the $[7,8\text{-}(4'\text{-MeC}_6\text{H}_4)_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_{10}]^-$ monoanion with the COD−rhodium and COD−iridium μ-chloride complexes $[(\eta^4\text{-COD})_2\text{M}_2(\mu\text{-Cl})_2]$ proceed in benzene at ambient temperature with the formation of the 16-electron complexes $[3\text{-}\{(1-3\text{-}\eta^3)\text{-C}_8\text{H}_{13}\}\text{-}1,2\text{-}(4'\text{-MeC}_6\text{H}_4)_2\text{-}3,1,2\text{-}\textit{pseudocloso}\text{-MC}_2\text{B}_9\text{H}_9]$ (**5**, M = Rh(III); **6**, M = Ir(III)), respectively, whose pseudocloso strucrure has been confirmed by single-crystal X-ray diffraction studies. The major species **5** is formed along with a small amount of the dimeric rhodacarborane $[(\eta^6\text{-MeC}_6\text{H}_4)\text{Rh}(\text{C}_2\text{B}_9\text{H}_9\text{C}_6\text{H}_4\text{Me})\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})]_2$ (**7**), which, as found from X-ray structure determinations, is composed of two distorted $\{4,9,1,10\text{-Rh}_2\text{C}_2\text{B}_9\}$ cluster units joined together through η^6 coordination of the 4-tolyl cage substituent of one unit to one of the rhodium atoms of the second unit and vice versa.

Introduction

Metalation of the C,C′-disubstituted *nido*-carborane $[7,8\text{-R}_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_{10}]^-$ monoanions having bulky substituents at the cage carbon atoms generally yields *exo-nido*-metallacarborane complexes rather than their closo tautomers, due to a highly steric congestion caused between the M(η-L) capping group and the carborane cage substituents[1] (or their lone pairs of electrons[2]) in the *closo*-metallacarborane molecules. However, if starting salts of such *nido*-$\text{R}_2\text{C}_2\text{B}_9$ carborane monoanions are deprotonated prior to use, the situation is radically altered. Coordination of the disubstituted $[7,8\text{-R}_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_9]^{2-}$ dianions (dicarbollide ligands) to the metal atoms creates either structurally deformed metallacarboranes with broken C−C polyhedral connectivity (the so-called pseudocloso and semipseudocloso clusters[2a,3]) or, more rarely, *closo*-metallacarboranes which display a large slipping distortion.[4] Moreover, a number of these metalation reactions can occur according to the low-temperature "1,2 → 1,7" or "1,2 → 1,2" carbon atom isomerization schemes, affording *closo*-metallacarboranes with polyhedrally isomerized carborane ligands.[5]

Our recent study[5e] has extended the family of sterically demanding *nido*-C_2B_9-carborane ligands by introducing a new C,C′-disubstituted $[7,8\text{-}(4'\text{-MeC}_6\text{H}_4)_2\text{-}7,8\text{-}\textit{nido}\text{-C}_2\text{B}_9\text{H}_{10}]^-$ monoanion (**1**). This allowed, for example, the isolation of the partially open complex $[3,3\text{-}\{(2,3,8\text{-}\eta^3)\text{:}(5,6\text{-}\eta^2)\text{-C}_7\text{H}_7\text{CH}_2\}\text{-}1,2\text{-}(4'\text{-MeC}_6\text{H}_4)_2\text{-}3,1,2\text{-}\textit{pseudocloso}\text{-RhC}_2\text{B}_9\text{H}_9]$ (**2**), which is observed as an apparent intermediate in the metalation reaction of **1** with the rhodium reagent $[\{(2,3,5,6\text{-}\eta^4)\text{-C}_7\text{H}_7\text{-}2\text{-CH}_2\text{OH}\}\text{RhCl}]_2$, to finally give isomerized products based on the $\{\textit{closo}\text{-}2,1,8\text{-RhC}_2\text{B}_9\}$ cluster unit.[5e] In an effort to further exemplify the reactivity of this new anionic 11-vertex *nido*-carborane **1**, we

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(1) (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.

(2) (a) Teixidor, F.; Vinas, C.; Flores, M. A.; Rosair, G. M.; Welch, A. J.; Weller, A. S. *Inorg. Chem.* **1998**, *37*, 5394. (b) Barberà, G.; Viñas, C.; Teixidor, G. M.; Rosair, G. M.; Welch, A. *J. J. Organomet. Chem.* **2002**, *663*, 221.

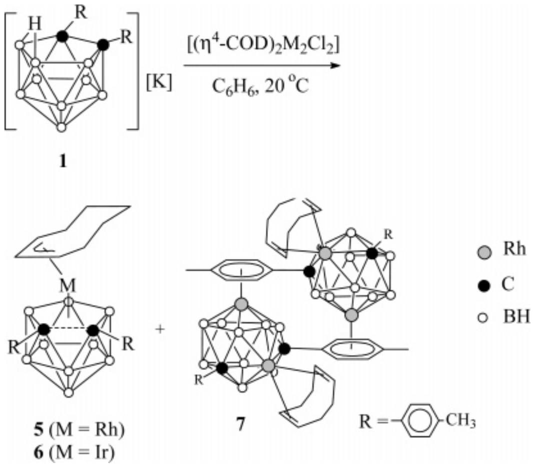
(3) Selected for Rh and Ir derivatives: (a) Lewis, Z. G.; Welch, A. J. *J. Organomet. Chem.* **1992**, *430*, C45. (b) Brain, P. T.; Bühl, M.; Cowie, J.; Lewis, Z. G.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1996**, 231. (c) Grädler, U.; Weller, A. S.; Welch, A. J.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1996**, 335. (d) McWhannel, M. A.; Rosair, G. M.; Welch, A. J.; Teixidor, F.; Viñas, C. *J. Organomet. Chem.* **1999**, *573*, 165. (e) Reed, D.; Welch, A. J.; Cowie, J.; Donohoe, D. J.; Parkinson, J. A. *Inorg. Chim. Acta* **1999**, *289*, 125. (f) Garrioch, R. M.; Rosair, G. M.; Welch, A. J. *J. Organomet. Chem.* **2000**, *614*−*615*, 153. (g) Welch, A. J. Steric Effects in Metallacarboranes. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; p 26 (a review).

(4) (a) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 605. (b) Kyd, G. O.; Yellowlees, L. G.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1994**, 3129. (c) McGrath, T. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1995**, 1755. (d) Robertson, S.; Ellis, D., Rosair, G. M.; Welch, A. J. *J. Organomet. Chem.* **2003**, *680*, 286.

(5) For the latest works see: (a) Barbera, G.; Dunn, S.; Fox, M.; Garrioch, R. M.; Hodson, B. E.; Low, K. S.; Rosair, G. M.; Teixidor, F.; Viñas, C.; Welch, A. J.; Weller, A. S. In *Contemporary Boron Chemistry*; Davidson, M. G., Hughes, A. K., Marder, T. B., Wade K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000; p 329. (b) Hodson, B. E.; Ellis, D.; McGrath, T. D.; Monaghan, J. J.; Rosair, G. M.; Welch, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 715. (c) Tatsusaus, O.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Teixidor, F. *Chem. Commun.* **2003**, 2458. (d) Robertson, S.; Ellis, D.; Rosair, G. M.; Welch, A. J. *Appl. Organomet. Chem.* **2003**, *17*, 518. (e) Safronov, A. V.; Dolgushin, F. M.; Petrovskii, P. V.; Chizhevsky, I. T. *Organometallics* **2005**, *24*, 2964. (f) Robertson, S.; Garrioch, R. M.; Ellis, D.; McGrath, T. D.; Hodson, B. E.; Rosair, G. M.; Welch, A. J. *Inorg. Chim. Acta* **2005**, *338*, 1485. (g) McIntosh, R. D.; Ellis, D.; Giles, B. T.; Macgregor, S. A.; Rosair, G. M.; Welch, A. J. *Inorg. Chim. Acta* **2006**, *359*, 3745.

10.1021/om0609721 CCC: $37.00

Scheme 1



now report the results of its reaction with COD-containing metalation reagents such as [(η^4-COD)$_2$M$_2$(μ-Cl)$_2$] (**3**, M = Rh; **4**, M = Ir) (Scheme 1).

Results and Discussion

In contrast to the general trends observed for the above metalation reactions, the K$^+$ salt of **1** without prior deprotonation has been found to react readily with reagents **3** and **4** in benzene at room temperature, primarily, for 2.0−2.5 h to afford after column chromatography the new 16-electron Rh(III) and Ir(III) pseudocloso-type complexes [3-{(1−3-η^3)-C$_8$H$_{13}$}-1,2-(4′-MeC$_6$H$_4$)$_2$-3,1,2-*pseudocloso*-MC$_2$B$_9$H$_9$] (**5**, M = Rh; **6**, M = Ir) in 55−65% yields. Note that the reaction between **1** and **3** produced, along with the predominantly formed complex **5**, a minor amount of the dark purple crystalline product [(η^6-MeC$_6$H$_4$)Rh(C$_2$B$_9$H$_9$C$_6$H$_4$Me)Rh(η^4-C$_8$H$_{12}$)]$_2$ (**7**), the detailed structure of which will be discussed further below. Another more efficient route to **5** involves the reaction of the Cs$^+$ salt of **1** with the reagent **3** under gentle reflux in benzene. Although [Cs]**1** is effectively insoluble in benzene at room temperature, this reaction when carried out under mild heating for 2.5 h gave **5** in 71% isolated yield[6] and, interestingly, no traces of a byproduct **7** were formed in this case. The yield of complex **6** can also be improved up to 95% by longer treatment (ca. 24 h) of [K]**1** with **4** in benzene at room temperature.

The crystallographic studies of **5** and **6** (Figures 1 and 2) established these species to be new electron-deficient *pseudocloso*-metallacarboranes with the η^3-cyclooctenyl ligand at the metal vertex. Although a number of 12-vertex[8] and 13-vertex[9] metallacarborane complexes containing the same or alkyl-substituted η^3-C$_8$H$_{13}$ ligands are known, among these, only one species, [3-{(1−3-η^3)-C$_8$H$_{13}$}-1-SPh-2-Ph-3,1,2-*pseudocloso*-RhC$_2$B$_9$H$_9$], has been determined as having a 16-electron pseudocloso structure.[10,11]

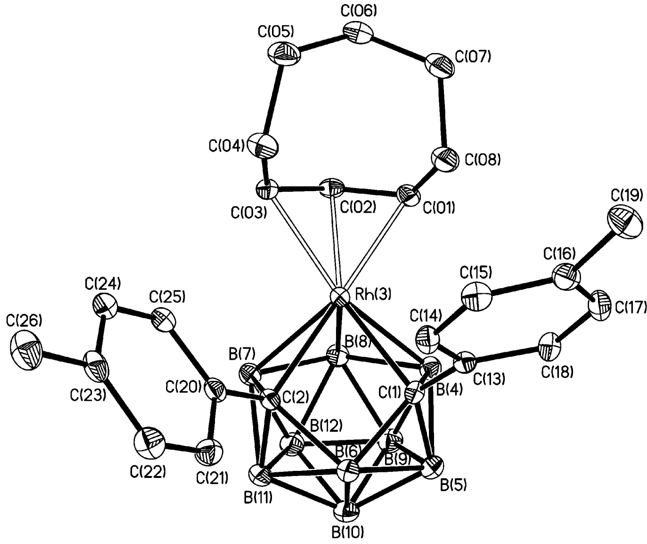


Figure 1. ORTEP drawing of the molecular structure of complex **5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(3)−C(1), 2.115(1); Rh(3)−C(2), 2.197(1); Rh(3)−C(01), 2.182(1); Rh(3)−C(02), 2.142(1); Rh(3)−C(03), 2.226(1); Rh(3)···B(6), 3.007(2); Rh(3)···C(04), 3.071(1); Rh(3)···C(08), 2.989(1); Rh(3)···H(04B), 2.81; Rh(3)···H(08A), 2.74; C(1)···C(2), 2.420(2); C(01)−C(02), 1.414(2); C(02)−C(03), 1.408(2); C(01)−C(08), 1.512(2); C(03)−C(04), 1.518(2); C(02)−C(03)−C(04), 124.0(1); C(02)−C(01)−C(08), 125.8(1); C(03)−C(02)−C(01), 122.1(1); C(01)−C(08)−C(07), 113.2(1).

The η^3-allylic mode of coordination of the C$_8$H$_{13}$ ring in both structures **5** and **6** is clearly seen from Figures 1 and 2, respectively. In spite of the formal 16-electron structure of these η^3-cyclooctenyl complexes **5** and **6**, no direct evidence for the presence of a C−H···M agostic bonding interaction was obtained from their single-crystal structures. Indeed, the separations between the M(III) atoms and the endo hydrogen atoms at the C(04) or C(08) carbons lying adjacent to the allyl unit of the C$_8$ ring in **5** (2.74 and 2.81 Å) and **6** (2.98 and 2.55 Å), respectively, are notably longer than those observed for the M···H(ag) distances in the known agostic-type metallacarborane complexes, where they typically range from ca. 1.8 to ca. 2.2 Å.[8f,g,9,12] In addition, no significant differences are observed both in the deviations of the C(04) and C(08) atoms with respect to the plane of the allylic moiety (0.831 and 0.756 Å for **5** and

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[6] In order to determine what is the fate of the bridging endo hydrogen atom of salts **1** during their transformations to complexes **5** and **6**, we have synthesized a sample of [Cs][10-*endo*-D-7,8-(4′-MeC$_6$H$_4$)$_2$-7,8-*nido*-C$_2$B$_9$H$_9$] (**9**) with a high degree of monodeuteration (ca. 83%) by the method of Hawthorne et al.[7] and studied the metalation reaction of **9** with **3** under the experimental conditions described for the non-deuterated analogue. An examination of the deuterated pseudocloso complex thus obtained by the comparison of its ^{2}H NMR spectrum with the ^{1}H{^{11}B} NMR spectrum of **5** (see the Supporting Information) provided evidence for the presence of the endo deuterium atom in this species mostly on C(4)−C(8) carbon atoms of the carbocyclic C$_8$ ring.

[7] Howe, D. E.; Jones, C. J.; Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 2516.

[8] (a) Speckman, D. M.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1985**, *4*, 426. (b) 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. (c) Chizhevsky, I. T.; Zinevich, T. V.; Petrovskii, P. V.; Antonovich, V. A.; Zakharkin, L. I. *Metalloorg. Khim.* **1991**, *4*, 1411; *Organomet. Chem. USSR (Engl. Transl.)* **1991**, *4*, 703. (d) Jeffery, J. C.; Stone, F. G. A.; Topaloğlu, I. *Polyhedron* **1993**, *12*, 319. (e) Zinevich, T. V.; Safronov, A. V.; Vorontsov, E. V.; Petrovskii, P. V.; Chizhevsky, I. T. *Russ. Chem. Bull.* **2001**, *50*, 1702. (f) Safronov, A. V.; Zinevich, T. V.; Dolgushin, F. M.; Vorontsov, E. V.; Tok, O. L.; Chizhevsky, I. T. *J. Organomet. Chem.* **2003**, *680*, 111. (g) Safronov, A. V.; Zinevich, T. V.; Dolgushin, F. M.; Tok, O. L.; Vorontsov, E. V.; Chizhevsky, I. T. *Organometallics* **2004**, *23*, 4970.

[9] Hodson, B. E.; McGrath, T. D.; Stone, F. G. A. *Organometallics* **2005**, *24*, 1638.

[10] Teixidor, F.; Flores, M. A.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *J. Am. Chem. Soc.* **2000**, *122*, 1963.

[11] A C,C′-diphenylated analogue of **5**, [3-{(1−3-η^3)-C$_8$H$_{13}$}-1,2-Ph$_2$-3,1,2-*pseudocloso*-RhC$_2$B$_9$H$_9$], is also known; although selected structural data (C(1)···C(2) and Rh(3)···B(6) distances of 2.41 and 3.01 Å) for this species have been given in a review,[3g] no further details, as far as we are aware, have been reported.

[12] See for example: (a) Esteruelas, M. A.; Olivan, M.; Oro, L. A.; Schutz, M.; Sola, E.; Werner, H. *Organometallics* **1992**, *11*, 3659. (b) Kaduk, J. A.; Poulos, A. T.; Ibers, J. A. *J. Organomet. Chem.* **1977**, *127*, 245.

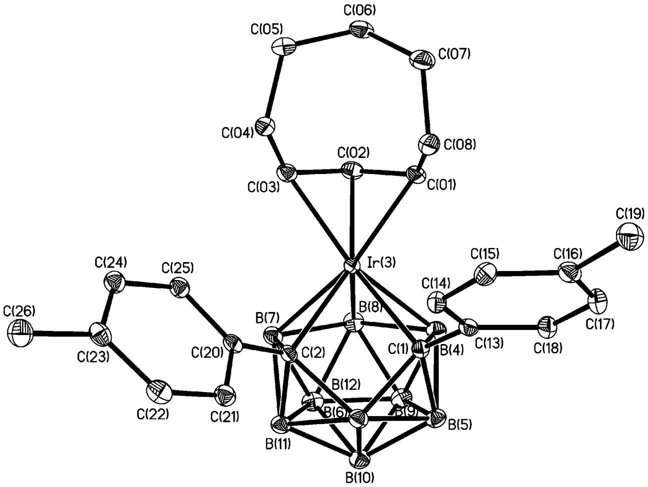

Figure 2. ORTEP drawing of the molecular structure of complex **6** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(3)−C(1), 2.140(2); Ir(3)−C(2), 2.168(2); Ir(3)−C(01), 2.163(2); Ir(3)−C(02), 2.145(2); Ir(3)−C(03), 2.213(2); Ir(3)···B(6), 2.998(2); Ir(3)···C(04), 3.170(2); Ir(3)···C(08), 2.852(2); Ir(3)···H(04A), 2.98; Ir(3)···H(08B), 2.55; C(1)···C(2), 2.438(3); C(01)−C(02), 1.416(3); C(02)−C(03), 1.431(3); C(01)−C(08), 1.511(3); C(03)−C(04), 1.536(3); C(02)−C(03)−C(04), 124.5(2); C(02)−C(01)−C(08), 123.2(2); C(03)−C(02)−C(01), 120.9(2); C(01)−C(08)−C(07), 113.6(2).

0.963 and 0.686 Å for **6**) and in the M(3)···C(04) (3.071(1) and 3.170(2) Å) and M(3)···C(08) (2.989(1) and 2.852(2) Å) bond lengths in **5** and **6**, respectively.

The cluster geometries in molecules **5** and **6** are substantially distorted. The anomalous lengthening of a cage C(1)···C(2) connectivity of up to 2.420(2) Å in **5** and 2.438(3) Å in **6** creates a nearly square C(1)M(3)C(2)B(6) open face with the contracted M(3)···B(6) distances of 3.007(2) and 2.998(2) Å, respectively. All of these structural features observed in these species are in good agreement with those found in other known *pseudocloso*-metallacarboranes referred to above.

Analytical and spectroscopic data are entirely consistent with the formulation of both species **5** and **6**. Complexes were characterized by combined ^{1}H, ^{11}B/^{11}B{^{1}H}, and ^{13}C/^{13}C{^{1}H} NMR data. The room-temperature ^{1}H NMR spectra of compounds **5** and **6** in CD_2Cl_2 each display two separate medium-field allylic resonances characteristic of the η^3-cyclooctenyl ligand having effective mirror symmetry: 2H quartets at δ 5.38 and 5.14 and 1H triplets at δ 4.75 and 5.30 ppm, respectively. In addition, resonances originating from the carborane cage substituents are observed as equivalent in the spectra: 6H singlets both at δ 2.32 ppm arising from the two methyl groups along with a set of two lowest field 2H doublets of aromatic ortho and meta protons. The methylene groups of the aliphatic part of the C_8 ring of **5** and **6** give rise to sets of multiplets of 2:1:2:2:1:2 and 3:4:1:2 relative intensities, respectively, in the range from δ +1.8 to +0.8 ppm. These latter resonances, in the spectrum of **5**, were separated enough to enable the exact assignment of each pair of exo and endo protons of the carbocyclic methylene groups using the standard homo- and heteronuclear 2D chemical shift correlation technique (the corresponding 2D [^{1}H−^{1}H]-COSY of **5** and [^{1}H−^{13}C]-HETCOR spectra of **5** and **6** are given as Supporting Information). Since none of these aliphatic resonances appear in the negative zone of the spectra of **5** and **6**, no agostic C−H···M interaction involving the η^3-cyclooctenyl ligands could be truly postulated. A very similar ^{1}H NMR picture for the aliphatic part of the η^3-C_8H_{13} ligand in the 16-electron Rh(III) closo species [3-{(1−3-η^3)-C_8H_{13}}-1,2-Me$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_9$] was reported by Hawthorne and co-workers.[8a]

The ^{13}C{^{1}H} NMR spectra of **5** and **6** both display very similar patterns, with the only difference that some resonances in the spectrum of rhodium complex **5** have a doublet multiplicity due to the ^{13}C−^{103}Rh coupling. In particular, the resonances derived from the allylic part of the carbocyclic ligand appear as doublets with J(C,Rh) = 4.4 Hz for C(2) and 7.7 Hz for C(1) and C(3). The absolutely normal values of coupling constants ^1J(C,H) found from the proton-coupled ^{13}C NMR spectrum of **5** for both sp^2 (165 Hz) and sp^3 carbon atoms (120−127 Hz) of the C_8 ring provided additional evidence for the nonagostic structure of this complex in solution. The ^{11}B{^{1}H} NMR spectrum of **5** consists of six signals with 1:1:2:2:2:1 relative intensity, as expected for the symmetrical structure of this complex. However, some of the corresponding signals in the spectrum of **6** are occasionally coalesced, being in an intensity ratio of 2:2:4:1. The calculated weighted average ^{11}B chemical shifts, $\langle\delta(^{11}\mathrm{B})\rangle$, are +4.32 and +1.57 ppm for **5** and **6**, respectively. Interestingly, these values lie to somewhat lower frequency when compared with the weighted averages of pseudocloso complexes with an 18-electron metal configuration: for example, [3-(η^5-C$_5$Me$_5$)-1,2-Ph$_2$-3,1,2-*pseudocloso*-MC$_2$B$_9$H$_9$] (**8**, M = Rh[3a] (δ +6.0 ppm); **9**, M = Ir[3e] (δ +3.28 ppm)) and complex **2**[5e] (δ +6.15 ppm[13]). Moreover, unlike the second-row Rh and Ru *pseudocloso* 18-electron complexes, which have $\langle\delta(^{11}\mathrm{B})\rangle$ values in a narrow range (from ca. +5.4 to 6.4 ppm), their third-row Ir pseudocloso analogues with both 18- and 16-electron structures appear to be characterized by $\langle\delta(^{11}\mathrm{B})\rangle$ values substantially shifted to lower frequency.

We have also succeeded in growing of single crystals of the minor byproduct **7** suitable for an X-ray diffraction experiment, and the resulting molecular structure is shown in Figure 3. This study revealed that the molecule **7** has a number of interesting features. First, it exists as two 13-vertex birhodacarborane {-(η^4-C$_8$H$_{12}$)Rh$_2$C$_2$B$_9$H$_9$(C$_6$H$_4$Me)$_2$} fragments attached to each other through a η^6 coordination of the 4-tolyl cage substituent of one unit to the rhodium atom of the second unit, and vice versa, while other two rhodium atoms are each bound to the 1,5-cyclooctadiene ligand in a η^4 coordination mode. Second, each of these two cluster units in **7** has two four-connected vertices (C(1) and B(2) atoms) and one six-connected vertex (Rh(4) atom), with the remaining cluster vertices being five-connected, thus demonstrating that not all of the polyhedral faces of **7** are triangulated. Indeed, one of the faces, within each of the polyhedral frameworks in **7**, is a trapezium; the observed separations between C(1/1′)···Rh(9/9′) and B(2/2′)···B(5/5′) are all too long to be regarded as bonding interactions. Thus, the respective cage geometry of the 13-vertex bimetallacarborane units in **7** may be described as henicosahedral in shape, a variation[14] of the basic docosahedral cage geometry usually adopted by 13-vertex metallacarborane clusters. The novelty of species **7** is related not only to its unusual dimeric henicosahedron-shaped structure but also to the fact that carbon atoms in each of the 13-vertex moieties of **7** are substantially separated: namely, by two boron-containing units. This, as far as we are aware, has never been observed in the known “carbons-apart” 13-vertex metallacarborane clusters with either

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(13) Note that the value of the weighted average ^{11}B chemical shifts reported in the text of ref 5e for the compound **2** is in error and should be read as +6.15 ppm.

(14) McIntosh, R.; Ellis, D.; Gil-Lostes, J.; Dalby, K. J.; Rosair, G. M.; Welch A. J. *Dalton Trans.* **2005**, 1842.

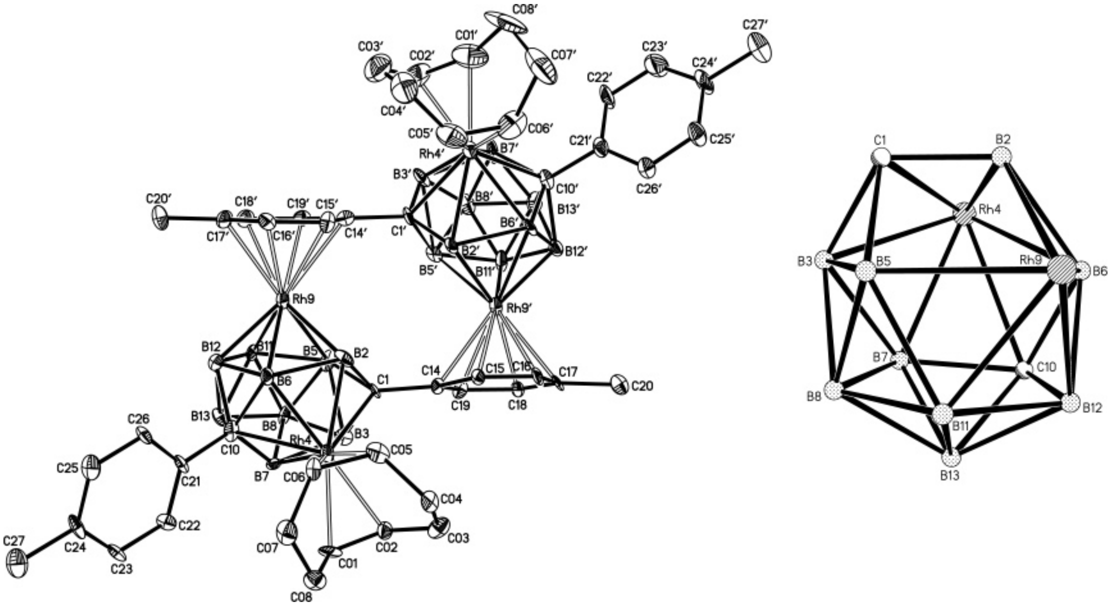

Figure 3. ORTEP drawing of the molecular structure of complex **7** with thermal ellipsoids at the 50% probability level: (left) full dimeric structure of **7**; (right) separate $\{C_2B_9Rh_2\}$ henicosahedron unit. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Rh(9)···C(1), 3.034(8), Rh(9′)···C(1′), 3.013(9); Rh(9)−B(2), 2.150(9), Rh(9′)−B(2′), 2.142(10); Rh(9)−B(5), 2.260(8), Rh(9′)−B(5′), 2.238(10); Rh(9)−B(6), 2.214(9), Rh(9′)−B(6′), 2.227(9); Rh(9)−B(11), 2.130(9), Rh(9′)−B(11′), 2.145(10); Rh(9)−B(12), 2.125(9), Rh(9′)−B(12′), 2.146(9); Rh(9)−C(14′−19′), 2.300−2.351(8), Rh(9′)−C(14−19), 2.303−2.407(8); Rh(4)−C(1), 2.241(7), Rh(4′)−C(1′), 2.229(8); Rh(4)−B(2), 2.216(9), Rh(4′)−B(2′), 2.272(9); Rh(4)−B(3), 2.291(9), Rh(4′)−B(3′), 2.311(10); Rh(4)−B(6), 2.213(9), Rh(4′)−B(6′), 2.270(9); Rh(4)−B(7), 2.221(9), Rh(4′)−B(7′), 2.240(10); Rh(4)−C(10), 2.341(8), Rh(4′)−C(10′), 2.328(8); Rh(4)−C(01), 2.205(7), Rh(4′)−C(01′), 2.186(10); Rh(4)−C(02), 2.196(7), Rh(4′)−C(02′), 2.130(9); Rh(4)−C(05), 2.221(8), Rh(4′)−C(05′), 2.175(10); Rh(4)−C(06), 2.219(7), Rh(4′)−C(06′), 2.199(10); C(1)−B(2), 1.481(11), C(1′)−B(2′), 1.500(12); C(1)−B(5), 1.800(11), C(1′)−B(5′), 1.780(12); B(2)···B(5), 2.300(13), B(2′)···B(5′), 2.312(13).

Table 1. Crystal Data and Data Collection and Structure Refinement Parameters for 5−7

	5	6	7
formula	$C_{24}H_{36}B_9Rh$	$C_{24}H_{36}B_9Ir$	$C_{48}H_{70}B_{18}Rh_4\cdot CH_2Cl_2$
mol wt	524.73	614.02	1338.19
cryst color, habit	red prism	red prism	violet plate
temp, K	100(2)	100(2)	120(2)
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$Pbca$	$P2_1/c$
a, Å	9.0203(3)	15.7173(7)	23.385(3)
b, Å	17.9386(6)	17.0705(8)	11.940(2)
c, Å	15.9726(5)	18.6670(9)	19.861(2)
β, deg.	100.601(1)		95.955(4)
V, Å^3	2540.4(1)	5008.4(4)	5516(1)
Z	4	8	4
d(calcd), g cm^{-3}	1.372	1.629	1.612
diffractometer	SMART APEX II		SMART 1000 CCD
θ_{max}, deg	30.0	30.0	27.0
μ(Mo Kα), cm^{-1} ($\lambda = 0.710\,73$ Å)	6.85	53.44	13.09
abs cor	face-indexing procedure		SADABS
transmissn factors, T_{min}/T_{max}	0.860/0.913	0.143/0.263	0.704/0.928
no. of unique rflns (R_{int})	7395 (0.0440)	7258 (0.0393)	12 033 (0.1319)
no. of obsd rflns ($I > 2\sigma(I)$)	6313	6046	5154
R1 (on F for obsd rflns)[a]	0.0228	0.0190	0.0564
wR2 (on F^2 for all rflns)[b]	0.0561	0.0444	0.1133

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

one or two distorted triangular faces,[14,15] and as such, species **7** represents the only such example reported to date.[16]

The ^1H and $^{13}C\{^1H\}$ NMR and analytical data obtained gave full assurance that **7** retains the same cluster structure both in the solid state and in solution. Thus, the coordinated COD ligand gave rise to four doublet resonances in the region from 86 to 100 ppm with the characteristic $J(^{103}Rh,C)$ coupling equal to 7.7−9.9 Hz, indicative of vinyl carbons, together with four singlet resonances for the COD aliphatic CH_2 groups, shifted upfield to δ ca. 30−40 ppm. Also, a double set of signals originating from both the coordinated and free exopolyhedral cage aromatic substituents are observed in the $^{13}C\{^1H\}$ NMR spectrum of **7**, and these resonances could be adequately assigned with the aid of its 2D [$^1H-^{13}C$]-HETCOR spectrum. In the ^1H NMR spectrum of **7** the majority of signals arising from the COD ligand appear as separate multiplets, and only two vinyl resonances at 4.70 ppm are coincidently overlapped. Other sets of resonances correspond to aromatic protons, giving rise to a significant difference in chemical shifts. This observation is in accord with the presence in this molecule of *p*-tolyl cage substituents both coordinated by the rhodium atom and noncoordinated.

In contrast to the results obtained from the reaction discussed above, metalation of the di-Na$^+$ salt of the C,C′-diphenylated *nido*-carborane $[7,8\text{-}Ph_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$ dianion with the same COD−rhodium reagent **3** in THF, which has been studied earlier by Welch and co-workers,[5b] produced the 18-electron "1,2 → 1,7" isomerized closo complex [3,3-{(1−3-η^3):(5,6-η^2)-C_8H_{11}}-1,8-Ph_2-2,1,8-*closo*-$RhC_2B_9H_9$] (**10**), along with a minor amount of the unusual cubane-like compound [{Rh(η^5-$Ph_2C_2B_9H_9$)(μ_3-OH)}$_4$], as a byproduct. Evidently, a sequence of reactions occurring on the way to complexes **10** and **5** (or **6**) is quite different and could not be conclusively recognized without a detailed mechanistic study. Nevertheless, the chemical results of both metalation reactions seem to be important for at least two reasons. First, they demonstrated that there are striking differences in the reactivities of monoanionic and dianionic sterically encumbered *nido*-$R_2C_2B_9$-carborane systems toward the same metalation reagents. Second, and most important, they established, together with a few other examples,[10,17] that the generation of coordinatively and electronically unsaturated metal centers in metallacarborane clusters of the pseudocloso type does not cause the destabilizing effect.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon. All solvents were distilled from appropriate drying agents under an argon atmosphere. Silica gel (Merck; 230−400 mesh) was used for column chromatography. the starting reagents [K]**1**,[5e] **3**,[18] and **4**[19] were prepared according to published methods. The ^1H, ^2H, $^{11}B/^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR as well as 2D [$^1H-^1H$]-COSY and [$^1H-^{13}C$]-HETCOR spectra were obtained with Bruker AMX-400 (^1H at 400.13 MHz, ^{13}C at 100.61 MHz, ^{11}B at 128.33 MHz) and Avance-600 (^1H at 600.22 MHz, ^{13}C at 150.92 MHz) spectrometers. IR spectra were recorded on a Carl-Zeiss M-82 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

Preparation of [3-(η^3-C_8H_{13})-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*pseudocloso*-$RhC_2B_9H_9$] (5) and the Dirhodacarborane Dimer [(η^6-MeC_6H_4)-Rh($C_2B_9H_9C_6H_4$Me)Rh(η^4-C_8H_{12})]$_2$ (7). (a) To a stirred suspension of the K^+ salt of **1** (85 mg, 0.24 mmol) in 15 mL of C_6H_6 was added the dimeric complex **3** (50 mg, 0.1 mmol) in the solid state at room temperature, and the mixture was stirred additionally for 2 h. After the solvent was evaporated, the residue was dissolved in a minimum amount of CH_2Cl_2 and treated by column chromatography on silica gel. The first red band eluted from the column using a CH_2Cl_2/*n*-hexane (3:2) mixture was collected; the solvent was evaporated under reduced pressure to give, followed by recrystallization of the crystalline solid from a CH_2Cl_2/*n*-hexane mixture, 72 mg (66%) of analytically pure deep red crystals of **5**. Anal. Calcd for $C_{24}H_{36}B_9Rh$: C, 54.93; H, 6.92; B, 18.54. Found: C, 54.92; H, 7.09; B, 18.45. IR (KBr, cm^{-1}): 2563 (ν_{B-H}). ^1H NMR (CD_2Cl_2, 600.22 MHz, 22 °C; $J = J(H,H)$, Hz): 7.65 (d, 4H, $J = 8.1$, C_6H_4 ortho), 7.15 (d, 4H, $J = 8.1$, C_6H_4 meta), 5.38 (q-like, 2H, $J = 8.5$, H_1, H_3), 4.75 (t-like, 1H, $J = 7.6$, H_2), 2.32 (s, 6H, CH_3), 1.76 (m, 2H, H_4 exo, H_8 exo), 1.68 (m, 1H, H_6 exo), 1.50 (m, 2H, H_5 exo, H_7 exo), 1.36 (m, 2H, H_5 endo, H_7 endo), 1.23 (m, 1H, H_6 endo), 0.79 (m, 2H, H_4 endo, H_8 endo). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150.93 MHz, 22 °C, $J = J(Rh,C)$, Hz [^{13}C NMR, multiplicity, $J(C,H)$, Hz]): 142.5 (s, C_6H_4 ipso [s, −]), 138.8 (s, C_6H_4 ipso [s, −]), 129.2 (s, C_6H_4 meta [d, 154]), 128.2 (s, C_6H_4 ortho [d, 154]), 116.78 (s br, C_{carb} [s br, −]), 109.1 (d, $J = 4.4$, C_2 [d, 165]), 84.8 (d, $J = 7.7$, C_1, C_3 [d, 165]), 32.5 (s, C_4, C_8 [t, 127]), 29.1 (s, C_5, C_7 [t, 127]), 22.2 (s, C_6 [t, 120]), 20.9 (s, CH_3 [q, 127]). $^{11}B\{^1H\}/^{11}B$ NMR (CD_2Cl_2, 128.38 MHz, 22 °C, $J = J(B,H)$, Hz): 22.0 (d, 1B, $J = 160$), 16.3 (d, 1B, $J = 147$), 9.0 (d, 2B, $J = 151$), 2.4 (d, 2B, $J = 149$), −1.1 (d, 2B, $J = 143$), −20.2 (d, 1B, $J = 153$). The second narrow violet band was then eluted with a CH_2Cl_2/*n*-hexane (1:1) mixture to afford, after evaporation, 1.0 mg (4%) of the pure dimeric complex **7** as deep violet microcrystals. Anal. Calcd for $C_{48}H_{70}B_{18}Rh_4 \cdot CH_2Cl_2$: C, 43.96; H, 5.42; B, 14.54. Found: C, 44.47; H, 5.49; B, 14.71. ^1H NMR (CD_2Cl_2, 600.22 MHz, 22 °C; $J = J(H,H)$, Hz): 7.37, 6.94 (d, 2H each, $J = 8$, $C_6\mathit{H}_4CH_3$), 7.08, 6.91, 6.86, 6.24 (d, 1H each, $J = 7$, η^6-$C_6\mathit{H}_4CH_3$), 5.33 (s, CH_2Cl_2) 4.70 (m, 2H, $C\mathit{H}{=}C\mathit{H}$), 4.52 (q-like br, 1H, $J \approx 8$, $C\mathit{H}{=}CH$), 4.32 (t-like br, 1H, $J \approx 8$, $CH{=}C\mathit{H}$), 2.51, 2.25 (s, 6H each, $C_6H_4C\mathit{H}_3$), 2.19, 2.13, 2.04, 1.58 (m, 1H each, $CH\mathit{H}$ exo), 1.98, 1.78, 1.40, 0.96 (m, 1H each, $CH\mathit{H}$ endo). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150.93 MHz, 22 °C, $J = J(Rh,C)$, Hz): 145.8, 139.0, 135.2, 125.4 (s, $\mathit{C}_6H_4CH_3$ ipso), 128.2, 125.7 (s, $\mathit{C}_6H_4CH_3$), 115.4, 111.9, 110.0, 109.7 (s, η^6-$\mathit{C}_6H_4CH_3$), 99.5, 89.6, (d, $J = 7.7$, $\mathit{C}H{=}\mathit{C}H$), 95.0, 87.0 (d, $J = 8.8$ and 9.9, $\mathit{C}H{=}\mathit{C}H$), 95.4, 82.7 (s br, C_{carb}), 39.3, 34.7, 29.7, 28.8 (s, CH_2), 20.4, 19.9 (s, $C_6H_4\mathit{C}H_3$).

(b) To a suspension of the Cs^+ salt of **1** (40 mg, 0.089 mmol) in 10 mL of C_6H_6 was added complex **3** (20 mg, 0.041 mmol) in the solid state. The resulting mixture was stirred under reflux for 2.5 h. This mixture, after it was cooled and exactly the same workup and purification procedure as described above were used, afforded 30 mg (71%) of red crystalline product, which from analysis of its ^1H NMR spectrum was deduced to be pure complex **5**.

Preparation of [3-(η^3-C_8H_{13})-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*pseudocloso*-**$IrC_2B_9H_9$]** (**6**). Complex **6** was prepared from the K^+ salt of **1** (60 mg, 0.16 mmol) and **4** (50 mg, 0.07 mmol) in 40 mL of C_6H_6 for 2.5 h, using the same procedure as employed for **5**. Purification of **6** was accomplished using a short silica gel column, the red band being eluted with a 1:1 C_6H_6/*n*-hexane mixture. Recrystalization of the crude solid obtained from a CH_2Cl_2/*n*-hexane mixture afforded 53 mg (55%) of analytically pure **6** as deep red microcrystals. Anal. Calcd for $C_{24}H_{36}B_9Ir$: C, 46.95; H, 5.91; B, 15.85. Found: C, 46.75; H, 5.79; B, 15.83. IR (KBr, cm^{-1}): 2556 (ν_{BH}). ^1H NMR (CD_2Cl_2, 400.13 MHz, 22 C; $J(H,H)$, Hz): 7.60 (d, 4H, $J = 8.1$, C_6H_4 ortho), 7.11 (d, 4H, $J = 8.1$, C_6H_4 meta), 5.30 (t-like br (overlapped), 1H, H_2), 5.14 (q-like br, 2H, $J \approx 8$, H_1, H_3), 2.32 (s, 6H, CH_3), 1.73 (m, 3H, H_4 exo, H_8 exo, H_6 exo), 1.47 (m, 4H, H_5, H_7), 1.09 (m, 1H, H_6 endo), 0.87 (m, 2H, H_4 endo, H_8 endo). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.61 MHz, 22 °C): 142.9 (s, C_6H_4 ipso), 138.4 (s, C_6H_4 ipso), 129.2 (s, C_6H_4 meta), 128.1 (s, C_6H_4 ortho), 102.7 (s, C_2), 94.1 (br s, C_{carb}), 75.8 (s, C_1, C_3), 34.4 (s, C_4, C_8), 30.3 (s, C_5, C_7), 23.3 (s, C_6), 20.9 (s, CH_3). $^{11}B\{^1H\}/^{11}B$ NMR (CD_2Cl_2, 128.38 MHz, 22 °C): 13.9 (d, 2B, $J = 137$), 9.6 (d, 2B, $J = 150$), −3.2 (d, 4B, $J = 143$), −20.3 (d, 1B, $J = 141$).

A similar reaction of [K]**1** (40 mg, 0.113 mmol) and **4** (34 mg, 0.051 mmol) was carried out by stirring the reaction mixture in 30 mL of C_6H_6 for 24 h. The product formed was then treated by column chromatography and purified, using the same purification procedure as described above, to afford 60 mg (95%) of pure

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(15) (a) Churchill, M. R.; DeBoer. B. G. *Inorg. Chem.* **1974**, *13*, 1411. (b) Hewes. J. D.; Knobler; C. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 206. (c) Lo, F. Y.; Strouse, C. E.; Callahan, K. P.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 428. (d) Alcock, N. W.; Taylor, J. G.; Wallbridge, G. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1805. (e) Donaghy, K. J.; Carrol, P. J.; Sneddon, L. G. *J. Organomet. Chem.* **1998**, *550*, 77. (f) Crennell, S. J.; Devore, D. D.; Henderson, S. J. B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1363. (g) Carr, N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1993**, *12*, 1131. For the latest reviews see: (h) Boyd, A. S. F.; Burke, A.; Ellis, D.; Ferrer, D.; Giles, B. T.; Laguna, M. A.; McIntosh, R.; Macgregor, S. A.; Ormsby, D. L.; Rosair, G. M.; Schmidt, F.; Wilson, N. M. M.; Welch, A. J. *Pure Appl. Chem.* **2003**, *75*, 1325. (i) Deng, L.; Xie, Z. *Coord. Chem. Rev.*, in press.

(16) Further experiments to attempt to find more powerful methods for the preparation of **7** and/or its derivatives and studies designed to establish the mechanism of formation of **7** are currently underway in our laboratory.

(17) (a) Kim, J.-H.; Lambrani, M.; Hwang, J.-W.; Do, Y. *J. Chem. Soc., Chem. Commun.* **1997**, 1761. (b) Carr, N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1992**, *11*, 3697.

(18) Giordane, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *28*, 88.

(19) Crabtree, R. H.; Quirk, J. M. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.

complex **6**. The ^{1}H and ^{11}B{^{1}H}/^{11}B NMR spectra of a sample of **6** were absolutely identical with those represented above.

X-ray Crystallographic Structure Determinations. Details of crystal data, data collection, and the structure refinement of complexes **5**−**7** are given in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 with anisotropic temperature factors for non-hydrogen atoms. All hydrogen atoms of the carborane ligands as well as of the allylic unit of the C_8 ring in each complex were located from the Fourier synthesis; the remaining H atoms were placed geometrically. All hydrogen atoms were included in the structure factor calculation in the riding motion approximation. The SHELXTL-97 program package[20] was used throughout the calculations, which were carried out on an IBM PC.

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Note Added After ASAP Publication. In the version of this paper published on the web on June 14, 2007, the formula for compound **7**, which appears in the title and throughout the paper, was incorrect. The formula that now appears is correct. We thank Prof. Russell N. Grimes for bringing this problem to our attention.

Supporting Information Available: CIF files giving crystal data for for **5**−**7** and figures giving the room-temperature 2D [^{1}H−^{1}H]-COSY spectrum of **5** as well as the 2D [^{13}C−^{1}H]-HETCOR spectra of **5** and **6** and the ^{2}H NMR spectrum of the deuterated analogue of complex **5** together with the ^{1}H{^{11}B} NMR spectrum of a non-deuterated sample of **5** in the aliphatic region (for comparison). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0609721

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[20] Sheldrick, G. M. SHELXTL-97, Version 5.10; Bruker AXS Inc., Madison, WI, 1997.