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New Acyclic (π-Allyl)-*closo*-rhodacarboranes with an Agostic $CH_3\cdots Rh$ Bonding Interaction That Operate as Unmodified Rhodium-Based Catalysts for Alkene Hydroformylation

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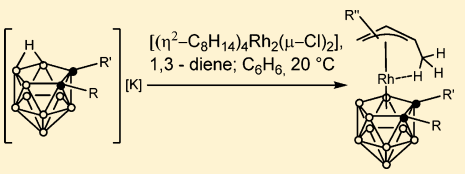
Supporting Information

ABSTRACT: A series of new agostic ($CH_3\cdots Rh$) (π-allyl)-*closo*-rhodacarboranes (π-allyl = 1,1-dimethylallyl, 1,2-dimethylallyl, 1,1,2-trimethylallyl, 1,2,3-trimethylallyl), stable in the solid state, have been synthesized via one-pot reactions between the K^+ salts of the [7-R-8-R′-7,8-*nido*-$C_2B_9H_{10}]^-$ monoanions (**1a**, R = R′ = Me; **1b**, R,R′ = μ-(*o*-xylylene); **1c**, R,R′ = μ-$(CH_2)_3$) and the di-μ-chloro cyclooctene rhodium dimer $[(\eta^2\text{-}C_8H_{14})_4Rh_2(\mu\text{-}Cl)_2]$ (**2**) in the presence of a 3-fold excess of the conjugated 1,3-dienes 2-methylbuta-1,3-diene (isoprene, **3**), 2,3-dimethylbuta-1,3-diene (**4**), and 3-methylpenta-1,3-diene (**5**). The agostic structures of [3-{(1−3-η^3)-1,1-dimethylallyl}-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**7a**) and [3-{(1−3-η^3)-1,1,2-trimethylallyl}-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**8a**) have been unambiguously confirmed by single-crystal X-ray diffraction studies. Two of these π-allyl complexes prepared were evaluated for their efficacy in hydroformylation of the model alkenes under syngas (CO/H_2) using supercritical carbon dioxide ($scCO_2$) as the solvent, and both display excellent conversion and high regioselectivity in the formation of aldehyde products.



Acyclic (π-allyl)-*closo*-metallacarborane clusters are, at present, well documented among 12-vertex icosahedral metallacarboranes;[1−3] some other (π-allyl)-metallacarborane complexes with different vertices were also reported.[4] Many of them are very versatile starting materials with great potential in the carborane-containing cluster chemistry of the d-block metals and play a significant role in the development of novel chemistry in this area.[1a,2d,4c,d] On the other hand, none of these (π-allyl)metallacarboranes found in the literature can be regarded as the agostic (C−H···M or $CH_3\cdots M$) species that could be potentially valuable in homogeneous catalysis by metallacarboranes.[5] In this connection, the development of a simple and efficient synthesis of π-allyl-containing metallacarborane systems stabilized via an agostic bonding interaction and assessment of their role in catalysis are of considerable interest.

Herein, we report our preliminary results on facile one-pot reactions leading to isolation of acyclic (π-allyl)-*closo*-rhodacarboranes of the general formula [3-{π-(R″-allyl)}-1-R-2-R′-3,1,2-*closo*-$RhC_2B_9H_9$] (where R″ is an aliphatic substituent) that exhibit an agostic $CH_3\cdots Rh$ bonding interaction. Two of these phosphorus-free π-allyl complexes have been tested as catalyst precursors for the regioselective hydroformylation of model alkenes under syngas (CO/H_2) using supercritical carbon dioxide ($scCO_2$) as the solvent. Both species, even in the absence of the typical cocatalysts such as phosphines and phosphites, exhibit excellent conversion and high regioselectivity in the formation of the desired saturated formyl derivatives.

With some exceptions,[1] the most frequently employed synthetic routes to the reported anionic or neutral/zwitterionic 18-electron (π-allyl)-*closo*-metallacarboranes involve the direct reactions of the dicarbollide [*nido*-7,*n*-R,R′-$C_2B_9H_9]^{2-}$ (*n* = 8, 9) dianions with appropriately constructed π-allyl transition metal halide complexes.[2,3] We found that the room-temperature reactions of the K^+ salts of the [7-R-8-R′-7,8-*nido*-$C_2B_9H_{10}]^-$ monoanions (**1a**, R = R′ = Me; **1b**, R,R′ = μ-(*o*-xylylene); **1c**, R,R′ = μ-$(CH_2)_3$) with the di-μ-chloro cyclooctene rhodium complex $[(\eta^2\text{-}C_8H_{14})_4Rh_2(\mu\text{-}Cl)_2]$ (**2**) in the presence of a 3-fold molar excess of the conjugated 1,3-dienes 2-methylbuta-1,3-diene (isoprene, **3**), 2,3-dimethylbuta-1,3-diene (**4**), and 3-methylpenta-1,3-diene (**5**) proceed smoothly in benzene, yielding together a short series of seven new (π-allyl)-*closo*-rhodacarboranes: [3-{(1−3-η^3)-C_5H_9}-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**6a** and **7a**, two isomers) and [3-{(1−3-η^3)-C_5H_9}-1,2-μ-(*o*-xylylene)-3,1,2-*closo*-$RhC_2B_9H_9$] (**6b** and **7b**, two isomers), [3-{(1−3-η^3)-1,1,2-trimethylallyl}-1-R-2-R′-3,1,2-*closo*-$RhC_2B_9H_9$] (**8a**−**c**), and [3-{(1−3-η^3)-1,2,3-trimethylallyl}-R-2-R′-3,1,2-*closo*-$RhC_2B_9H_9$] (**9a**,**b**), respectively (Scheme 1).

In contrast to the last two series of compounds **8a**−**c** and **9a**,**b**, complexes **6** and **7** exist in solution as a mixture of isomers with 1,2-dimethylallyl (**6a**,**b**) and 1,1-dimethylallyl (**7a**,**b**) ligands at the rhodium vertex, which are, moreover, in equilibrium. Thus, lowering of the temperature of the ^1H NMR spectra of **6** or **7** from +22 to −80 °C leads to a change in the relative ratio of isomers from ca. 1:1.5 to 1:2.25 for **6a** and **7a** and from ca. 1:1 to 1:1.5 for **6b** and **7b**, respectively. Note that

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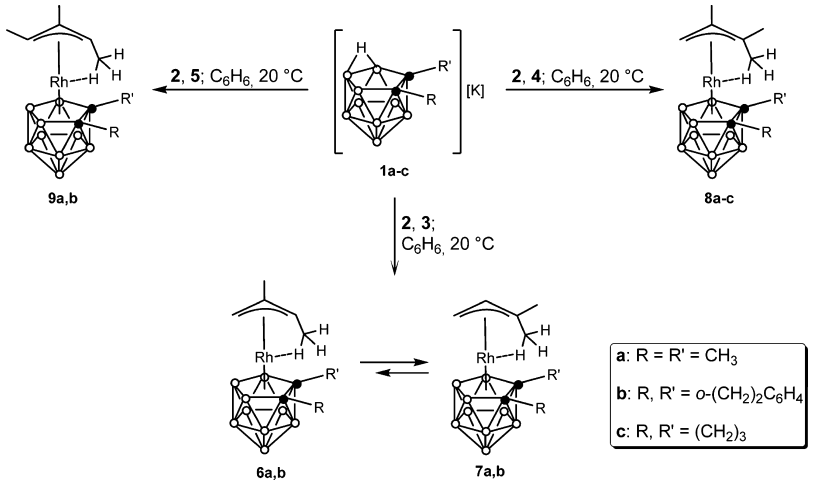
Scheme 1



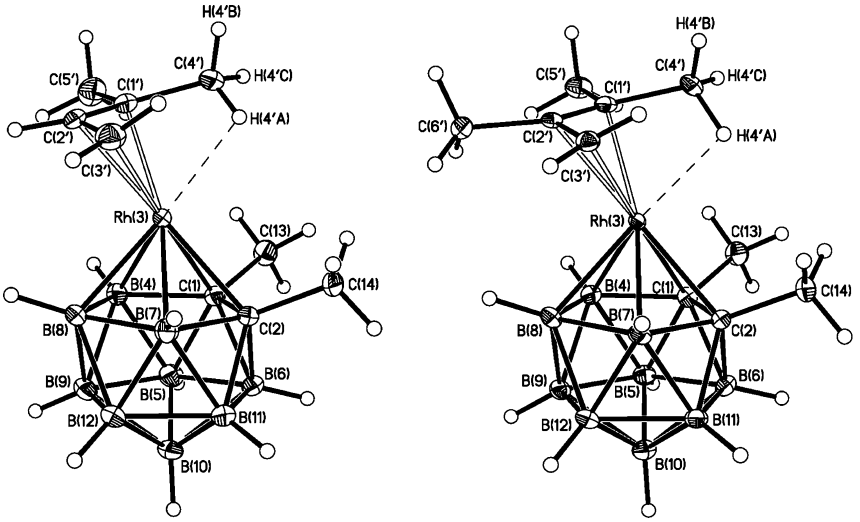


Figure 1. ORTEP representation of the molecular structures of **7a** (left) and **8a** (right) with the numbering scheme for these complexes. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) for complexes **7a** and **8a**, respectively, are as follows: Rh(3)−C(1) = 2.180(2), 2.180(2), Rh(3)−C(2) = 2.146(2), 2.140(2), Rh(3)−B(4) = 2.188(3), 2.190(2), Rh(3)−B(7) = 2.199(3), 2.202(2), Rh(3)−B(8) = 2.135(3), 2.138(2), Rh(3)−C(1′) = 2.168(3), 2.168(2), Rh(3)−C(2′) = 2.164(2), 2.187(2), Rh(3)−C(3′) = 2.172(3), 2.153(2), Rh(3)···C(4′) = 2.515(3), 2.484(2), Rh(3)···H(4′A) = 2.09(4), 2.03(3), C(1)−C(2) = 1.790(4), 1.839(3), C(1′)−C(2′) = 1.403(4), 1.415(3), C(2′)−C(3′) = 1.429(4), 1.423(3); C(1′)−C(2′)−C(3′) = 119.8(3), 116.71(17), C(4′)−H(4′A)−Rh(3) = 53(3), 52.9(14).

the most likely intermediates through which these isomeric complexes **6a**,**b** and **7a**,**b** undergo interconversion appeared to be the classical diene hydride species[6] with the terminal hydride at the rhodium vertex, [3-(η^4-diene)-3-H-1-R-2-R′-3,1,2-*closo*-$RhC_2B_9H_9$]. These intermediate species, however, could not be observed at the lowest temperature limit that was achieved experimentally (−80 °C for both **6** and **7** series).

Since all of the above π-allyl complexes proved to be quite stable both in the solid state and in solution, these compounds would be expected to contain a two-electron, three-center bonding arrangement, either C−H···Rh or CH_3···Rh. Indeed, an analysis of the ^{1}H and ^{13}C{^{1}H} NMR spectra of each pair of isomeric complexes **6a**/**7a** and **6b**/**7b** as well as of other π-allyl complexes **8a**−**c** and **9a**−**c** show the presence of the one unique π-allyl methyl resonance with very high shielding values compared to the others (**6a**, δ, ppm (−80 °C) −0.21 (CH_3-agost) and 12.7 (CH_3-agost); **7a**, δ, ppm (−80 °C) −0.17 (s, CH_3-agost) and 18.1 (CH_3-agost); **8b**, δ, ppm (22 °C) −0.9 (s, CH_3-agost) and 16.7 (CH_3-agost); **9a**, δ, ppm, (22 °C) +0.29 (s, CH_3-agost) and +12.8 (CH_3-agost)); the room- and low-temperature ^{1}H NMR spectra for **6b**/**7b** are given in the Supporting Information. Such methyl resonances observed in the highest field of the NMR spectra of the above species which, in addition, displayed no visible $J(^{103}Rh,H_{ag.})$ coupling in the ^{1}H NMR spectra are typical of π-allyl organometallic complexes in which the CH_3 group is involved in the agostic CH_3···M interaction.[7]

A low-temperature X-ray diffraction study of **7a** and **8a**[8] provided firm confirmation of their agostic structure (Figure 1). The high quality of monocrystals grown from both samples allowed us to locate objectively and reliably refine all hydrogen atoms, including those forming the agostic bond. As expected, one of the methyl groups in complexes **7a** and **8a**, positioned anti to the π-allyl ligands, is involved (through one of its H atoms) in the agostic bonding interaction to the rhodium center, thus forming the very short H(4′A)···Rh distances 2.09(4) and 2.03(3) Å in **7a** and **8a**, respectively. The latter distances, although they are at the upper limit for known

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Table 1. Results of Hydroformylation Reactions of Selected Alkenes Catalyzed by (π-Allyl)-*closo*-rhodacarboranes 8c and 9a[a]

	8c		9a	
substrate R in RCH=CH$_2$	conversn,[b] %	regioselectivity,[b] branched/linear	conversn,[b] %	regioselectivity,[b] branched/linear
Ph	100	88/12	100	88/12
Ph[c]	92	66/34	30	66/34
4-Me-Ph	93	89/11	91	86/14
4-Br-Ph	100	89/11	100	97/3
4-^{i}Pr-Ph	45	92/8	95	88/12
^{t}Bu	98	0/100	100	0/100
(*S*)-limonene	83	0/100	76	0/100

[a]All reactions were performed in a stainless steel high-pressure autoclave (10 mL capacity): the catalysts (0.01 mmol) and substrate (2 mmol) were placed into a reactor which was pressurized with syngas (30 atm, CO/H$_2$ = 1/1) and then filled with scCO$_2$ via a syringe press. The mixture was allowed to equilibrate to the reaction temperature (60 °C, ~10 min) and stirred for 3–5 h. The reactor was cooled to 5 °C and slowly depressurized. [b]Conversion and regioselectivity were determined from the analysis of the ^{1}H NMR spectra of the liquid reaction mixture (see the Supporting Information). [c]Reactions were carried out in toluene under reflux.

agostic C–H···M distances (1.77–2.2 Å),[6c,9] may usefully be compared with that found in [{(1–3-η^3)-C$_6$H$_{11}$}Rh(η^5-C$_5$Me$_5$)] (CH$_2$–H···Rh = 1.88 Å),[10] the known Cp* analogue of **8a**. Interestingly, both complexes **7a** and **8a** are characterized by rather long C(1)···C(2) cluster distances of 1.790(4) and 1.839(3) Å, respectively. These values seem to be typical of so-called *semipseudocloso* type metallacarboranes, which are now well recognized.[11]

The one-pot method we currently explored for the synthesis of the agostic complexes **6**, **7**, **8a–c**, and **9a,b** is conceptually based on the ligand-exchange reactions. The first step of these reactions would involve the displacement of cyclooctene ligands from **2** for the acyclic diene **3**, **4**, or **5** to form one of the two possible intermediate species, either [(η^4-diene)$_2$RhCl] or [(η^4-diene)RhCl]$_2$, as might be expected by analogy with reactions of the same dienes **3** and **4** with [(C$_2$H$_4$)$_2$RhCl]$_2$,[12] a closely related acyclic analogue of **2**. Since the *endo*-hydrogen atom in the *nido*-carboranes **1a,b** displays acidic character, one may consider that the second step of these three-component reactions is, probably, protonation at the metal center of the aforementioned intermediate complexes; then a metal hydride could add to one of the double bonds of the η^4-diene ligands, giving rise to an unsymmetrical η^3-allyllic unit. The ultimate formation of (π-allyl)-*closo*-rhodacarboranes can be readily explained through an open-face metalation of the *nido*-carborane cage ligand formed as the dianionic {7-R-8-R′-*nido*-C$_2$B$_9$}$^{2-}$ species after elimination of an *endo*-hydrogen atom from starting monoanions **1a,b**.

The preliminary screening of two arbitrarily selected π-allyl complexes, **8c** and **9a**, as catalyst precursors for the hydroformylation of the model alkenes under syngas using either scCO$_2$ or toluene as solvent has been performed. Examination revealed (Table 1) that both rhodacarborane compounds are unique in their catalytic activity and display success in the conversion of styrene, its 4-substituted derivatives, and some other alkenes and terpenoids into their saturated aldehyde products, where very good to excellent yields (in some cases quantitative) as well as high regioselectivities have been achieved. Remarkably, these procatalysts work very well even without phosphine or phosphite as cocatalyst. Although the catalytic hydroformylation of alkenes with a rare unmodified rhodium-based system is known,[13] the efficient use of such phosphorus-free carborane-containing procatalysts, as far as we are aware, is unprecedented for hydroformylation under the conditions described above.

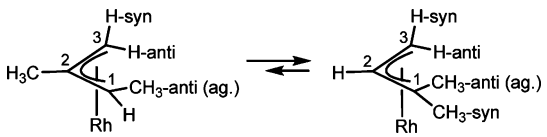
The reactivity associated with these and related acyclic π-allyl metal carborane complexes of rhodium and iridium as well as a detailed study of the catalytic activity of (π-allyl)-*closo*-rhodacarboranes of these series (other then **8c** and **9a**), including comparisons with the related Cp* rhodium derivatives with the aim of elucidating the role of carborane ligands in the catalytic process, are currently in progress in our group.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents, including those used for column chromatography, were distilled from appropriate drying agents under argon prior to use. Chromatography columns (ca. 12–15 cm in length and 1.8 cm in diameter) were packed with silica gel (Acros, 230–400 mesh). The starting rhodium and *nido*-carborane reagents **2**,[14] **1a**,[15] and **1c**[16] were prepared as described in the literature; [1,2-μ-(*o*-xylylene)-1,2-*closo*-C$_2$B$_{10}$H$_{10}$][17] was degraded to form **1b** according to the literature methods.[15] The ^{1}H, ^{11}B, and ^{13}C NMR spectra were obtained on Bruker AMX-400 and Avance-600 instruments (*J* values are given in Hz). IR spectra in KBr were recorded on a Nicolet Magna-750 spectrometer. Proton and boron chemical shifts were referenced to residual protons in CD$_2$Cl$_2$ (5.32 ppm vs Me$_4$Si), with downfield shifts taken as positive. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

General Method for the Synthesis of *closo*-(π-Allylic)-rhodacarborane Complexes 6, 7, 8a–c, and 9a,b. To a solution of **2** (0.1 mmol) in 5 mL of degassed benzene was added dropwise the 1,3-diene **3**, **4**, or **5** (0.3 mmol). The resulting mixture was stirred for 0.5 h at ambient temperature, and then the corresponding potassium salt of *nido*-carborane **1a**, **1b**, or **1c** (0.24 mmol) was added in one portion as a solid. After 1–3 h of vigorous stirring the reactions were complete (TLC control, eluent CH$_2$Cl$_2$/*n*-hexane, 1/1), and the deep red solution that formed was purified by column chromathography. Eluting with CH$_2$Cl$_2$/*n*-hexane (1/2) gave a colored fraction, removal of solvent from which followed by washing with *n*-hexane afforded **6**, **7**, **8a–c**, or **9a,b** as crystalline solids that could be successfully recrystallized from a CH$_2$Cl$_2$/*n*-hexane mixture.

Preparation of Isomeric Complexes [3-{(1–3-η^3)-C$_5$H$_9$}-1,2-(CH$_3$)$_2$-3,1,2-*closo*-RhC$_2$B$_9$H$_9$] (6a and 7a). The general method described above was employed: **2** (50 mg, 0.07 mmol), **3** (21 μL, 0.21 mmol), **1a** (35 mg, 0.175 mmol), degassed benzene (2 mL), reaction time, 2 h. Yield of **6** (light red microcrystals): 37 mg (82%).



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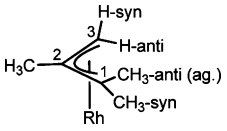
Selected NMR characterization data are as follows. ^{1}H NMR (600 MHz, CD_2Cl_2, −80 °C; *J*(H,H), Hz; ratio of isomers **6a**:**7a** = 1:2.25): 6.00 [br s, 1H, H(1′), **6a**], 4.75 [t-like, 1H, H(2′), **7a**], 4.25 [m, 2H, H(3′-*syn*)-**6a**, **7a**], 2.66 [br s, 1H, H(3′-*anti*), **6a**], 2.55 [br d, 1H, J_{vic} = 9.8, H(3′-*anti*), **7a**], 2.33 [s, 3H, CH_3(*syn*), **7a**], 2.21 and 2.13 (s, 3H + 3H, CH_3-carb, **6a**), 2.17 and 2.08 (s, 3H + 3H, CH_3-carb, **7a**), 1.65 [s, 3H, CH_3(2′), **6a**], −0.17 [s, 3H, CH_3(*anti*, agost), **7a**], −0.21 [s, 3H, CH_3(agost), **6a**]. $^{13}C\{^1H\}$ NMR (100.61 MHz; CD_2Cl_2, 25 °C; *J*(C,Rh), Hz): 119.7 [C(2′), **6a**], 102.6 [C(1′), **7a**], 102.1 [C(2′), **7a**], 93.5, 91.4, 85.9−84.9 (C-carb, **6a**, **7a**), 84.2 [C(1′), **6a**], 58.9 [C(3′), **6a**], 55.7 [d, *J* = 7.9, C(3′), **7a**], 31.1, 31.2, 29.0, 28.4 (CH_3-carb, **6a**, **7a**), 24.7 [CH_3(*syn*), **7a**], 22.3 [C(2′)-CH_3, **6a**], 18.1 [CH_3(*anti*, agost), **7a**], 12.7 [CH_3(*anti*, agost), **6a**].

Preparation of Isomeric Complexes [3-{(1−3-η^3)-C_5H_9}-1,2-μ-(*o*-xylylene)-3,1,2-*closo*-$RhC_2B_9H_9$] (6b and 7b). The general method described above was employed: **2** (72 mg, 0.1 mmol), **3** (30 μL, 0.3 mmol), **1b** (69 mg, 0.25 mmol), degassed benzene (5 mL), reaction time 1 h. Yield of **6b** and **7b** (deep red microcrystals): 53 mg (62%). Selected NMR characterization data are as follows. ^{1}H NMR (600 MHz, CD_2Cl_2, −80 °C; *J*(H,H), Hz; ratio of isomers **6b**:**7b** = 1:1.5): 7.21−6.91 (8H, H-aryl, **6b**, **7b**), 5.81 [q, 1H, J_q = 6.2, H(1′), **6b**], 4.54 [dd, 1H, $J_{vic(1)}$ = 7.4, $J_{vic(2)}$ = 10.4, H(2′), **7b**], 4.41 [br s, 1H, H(3′-*syn*), **6b**], 4.39 [br d, 1H, J_{vic} = 7.4, H(3′-*syn*), **7b**], 4.01 [d, 1H, J_{AB} = 17.0, C*H*H-aryl, **6b**], 3.85 (d, 1H, J_{AB} = 17.0, CH*H*-aryl, **6b**), 3.88 − 3.56 (3 m, 6H, CH_2-aryl, **6b**, **7b**), 2.29 [br d, 1H, J_{vic} = 10.4, H(3′-*anti*), **7b**], 2.23 [s, 3H, CH_3(*syn*), **7b**], 2.05 [br s, 1H, H(3′-*anti*), **6b**], 1.45 [s, 3H, CH_3(2′), **6b**], −0.38 [d, 3H, J_d = 6.2, CH_3(agost), **6b**], −1.03 [s, 3H, CH_3(*anti*, agost), **7b**]. $^{13}C\{^1H\}$ NMR (101 MHz; CD_2Cl_2, 22 °C; *J*(C,Rh), Hz): 134.0, 132.5, 130.6, 130.5, 130.3, 129.9, 129.6, 129.0, 128.8 (C-aryl), 119.8 [C(2′), **6b**], 102.2 [C(1′), **7b**], 102.1 [C(2′), **7b**], 80.2 [d, *J* = 7.4, (C(1′), **6b**], 78.6, 74.9, 74.3, 72.1 (C-carb), 68.4 [d, *J* = 4.0, C(3′), **6a**], 60.6 [d, *J* = 10.4, C(3′), **7a**], 43.9, 43.4, 43.4, 43.0 (CH_2-aryl), 25.4 [CH_3(*syn*), **7b**], 22.7 [C(2′)-CH_3, **6b**], 16.6 [CH_3(*anti*, agost), **7b**], 12.3 [CH_3(*anti*, agost), **6b**].

Preparation of [3-{(1−3-η^3)-C_6H_{11}}-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (8a). The general method described above was employed: **2** (72 mg, 0.1 mmol), **4** (34 μL, 0.3 mmol), **1a** (50 mg, 0.25 mmol), degassed benzene (4 mL), reaction time 0.5 h. Yield of **8a** (light red microcrystals): 65 mg, 94%.

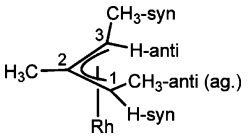


^{1}H NMR (600 MHz, CD_2Cl_2, −40 °C): 4.13 [br s, 1H, H(3′-*syn*)], 2.46 [br s, 1H, H(3′-*anti*)], 2.24 [s, 3H, CH_3(*syn*)], 2.17(s, 3H, CH_3-carb), 2.11 (s, 3H, CH_3-carb), 1.64 [s, 3H, CH_3(2′)], −0.24 [s, 3H, CH_3(*anti*, agost)]. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, −40 °C; *J*(C,Rh), Hz): 111.5 [d, *J* = 6.1, C(2′)], 97.4 [d, *J* = 5.6, C(1′)], 88.8 (C-carb), 78.9 (C-carb), 55.8 [d, *J* = 10.2, C(3′)], 30.9 (CH_3-carb), 27.3 (CH_3-carb), 20.0 [CH_3(*syn*)], 19.2 [C(2′)-CH_3], 18.4 [CH_3(*anti*, agost)].

Preparation of [3-{(1−3-η^3)-C_6H_{11}}-1,2-μ-(*o*-xylylene)-3,1,2-*closo*-$RhC_2B_9H_9$] (8b). The general method described above was employed: **2** (50 mg, 0.07 mmol), **4** (21 μL, 0.21 mmol), **1b** (48 mg, 0.175 mmol), degassed benzene (2 mL), reaction time 1 h. Yield of **8b** (deep red crystals): 35 mg (58%). ^{1}H NMR (600 MHz, CD_2Cl_2, 24 °C; *J*(H,H), Hz): 7.18 (m, 2H, H-aryl), 7.03 (dd, 2H, J_1 = 21.9, J_2 = 6.8, H-aryl), 4.20 [br s, 1H, H(3′-*syn*)], 3.69−3.89 (m, 4H, CH_2-aryl), 2.22 [m, 4H, CH_3-*syn*, H(3′-*anti*)], 1.64 [s, 3H, CH_3(2′)], −0.9 [s, 3H, CH_3(*anti*, agost)]. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 24 °C; *J*(C,Rh), Hz): 133.4, 132.2, 130.0, 129.9, 128.3, 128.2 (C-aryl), 112.9 [d, *J* = 6.0, C(2′)], 97.0 [d, *J* = 6.7, C(1′)], 75.3 (C-carb), 72.2 (C-carb), 61.0 [d, *J* = 10.8, C(3′)], 43.8, 43.0 (CH_2-aryl), 21.1 [CH_3(*syn*)], 19.0 [C(2′)-CH_3], 16.7 [CH_3(*anti*, agost)].

Preparation of [3-{(1−3-η^3)-C_6H_{11}}-1,2-μ-$(CH_2)_3$-3,1,2-*closo*-$RhC_2B_9H_9$] (8c). The general method described above was employed: **2** (100 mg, 0.142 mmol), **4** (50 μL, 0.43 mmol), **1c** (74 mg, 0.35 mmol), degassed benzene (4 mL), reaction time 3 h. Yield of **8c** (deep red crystals): 76 mg (76%). ^{1}H NMR (400 MHz, CD_2Cl_2, 22 °C; *J*(H,H), Hz): 4.39 [d, 1H, J_{gem} = 1.7, H(3′-*syn*)], 2.75 [m, 2H, H(3′-*anti*), −CH_2-carb], 2.66 (t, 2H, *J* = 7.7, −CH_2-carb), 2.51 (m, 1H, −CH_2-carb), 2.40 (m, 1H, −CH_2-carb), 2.34 [s, 3H, CH_3(*syn*)], 2.11 (s, 1H, −CH_2-carb), 1.68 [d, 3H, *J* = 2.3 Hz, CH_3(2′)], +0.09 [s, 3H, CH_3(*anti*, agost)]. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 22 °C; *J*(Rh,C), Hz): 112.9 [d, *J* = 6.2, C(2′)], 97.9 [d, *J* = 6.5, C(1′)], 89.5 (C-carb), 84.9 (C-carb), 58.5 [d, *J* = 11.1, C(3′)]; 39.9, 38.5, 33.1 (−CH_2-carb), 21.3 [CH_3(*syn*)], 19.5 [C(2′)-CH_3], 19.1 [CH_3(*anti*,agost)].

Preparation of [3-{(1−3-η^3)-C_6H_{11}}-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (9a). The general method described above was employed: **2** (53 mg, 0.074 mmol), **5** (27 μL, 0.222 mmol), **1a** (37 mg, 0.187 mmol), degassed benzene (4 mL), reaction time 0.3 h. Yield of **8a** (orange microcrystals): 33 mg, 65%.



^{1}H NMR (400 MHz, CD_2Cl_2, 22 °C): 5.81 [br m, 1H, H(1′-*syn*)], 3.71 [br m, 1H, H(3′-*anti*)], 2.36 (s, 3H, CH_3-carb), 2.11 (s, 3H, CH_3-carb), 1.96 [br s, 3H, CH_3(*syn*)], 1.69 [br s, 3H, CH_3(2′)], 0.29 [br s, 3H, CH_3(*anti*, agost)]. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 22 °C): 118.8 [C(2′)], 90.1, 84.0 (C-carb), 80.4 [C(1′)], 78.3 [C(3′)], 30.3 (CH_3-carb), 28.7 (CH_3-carb), 18.4 [C(2′)-CH_3], 15.5 [CH_3(*syn*)], 12.8 [s, CH_3(*anti*, agost)].

Preparation of [3-{(1−3-η^3)-C_6H_{11}}-1,2-μ-(*o*-xylylene)-3,1,2-*closo*-$RhC_2B_9H_9$] (9b). The general method described above was employed: **2** (150 mg, 0.21 mmol), **5** (71 μL, 0.63 mmol), **1b** (144 mg, 0.525 mmol), degassed benzene (6 mL), reaction time 3 h. Yield of **9b** (deep red microcrystals): 118 mg, 67%). ^{1}H NMR (600 MHz, CD_2Cl_2, −50 °C; *J*(H,H), Hz): 7.31 (m, 1H, H-aryl), 7.26 (d, 1H, J_d = 7.3, H-aryl), 7.15 (t-like, 1H, J_t = 7.1, H-aryl), 5.66 [q-like, 1H, J_q = 6.8, H(1′-*syn*)], 4.10 [d, 1H, J_{AB} = 16.3, C*H*H-aryl], 4.05 (d, 1H, J_{AB}= 16.3, CH*H*-aryl), 3.58 (d, 1H, J_{AB}= 16.4, C*H*H-aryl), 3.37 (d, 1H, J_{AB}= 16.4, CH*H*-aryl), 2.21 [br s, 1H, H(3′-*anti*)], 1.78 [d, 3H, J_d = 5.5, CH_3(*syn*)], 1.28 [s, 3H, CH_3(2′)], 0.56 [d, 3H, J_d = 6.8, CH_3(*anti*)]. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C, *J*(C,Rh), Hz): 134.6, 131.0, 129.5, 129.1, 128.7, 126.8 (C-aryl), 118.6 [d, *J* = 5.2, C(2′)], 89.9 [br s, C(3′)], 77.0 (C-carb), 75.8 [d, *J* = 8.5, C(1′)], 66.3 (C-carb), 43.0 (CH_2-aryl), 42.8 (CH_2-aryl), 19.6 [C(2′)-CH_3], 15.3 [CH_3(*anti*, agost)], 14.7 [CH_3(*syn*)].

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data for complexes **7a** and **8a**, selected figures giving ^{1}H NMR spectra of hydroformylation products, room- and low-temperature ^{1}H NMR spectra of the isomeric mixture **6b**/**7b**, low-temperature ^{1}H NMR and [^{1}H−^{1}H]-COSY spectra of **6a**/**7a** as well as [^{13}C−^{1}H]-HSQC NMR spectra of complexes **8a** and **9b**, and text giving some additional characterization data (analytical, IR, $^{11}B/^{11}B\{^1H\}$ NMR) of complexes **6**, **7**, **8a**−**c**, and **9a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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(8) Crystal data for **7a**: $C_9H_{24}B_9Rh$, M = 332.48, monoclinic, $P2_1/n$, a = 12.5652(7) Å, b = 8.0607(4) Å, c = 16.2176(9) Å, β = 112.459(1)°, V = 1518.0(1) Å^3, Z = 4, d_{calc} = 1.455 g/cm^3, μ = 10.98 cm^{-1}, $F(000)$ = 672, θ_{max} = 29°, T = 100(2) K, R1(F) = 0.0325 for 3500 observed reflections with $I > 2\sigma(I)$, wR2(F^2) = 0.0785 and S = 1.009 for all 3995 unique reflections (R_{int} = 0.0279). Crystal data for **8a**: $C_{10}H_{26}B_9Rh$, M = 346.51, monoclinic, $P2_1/c$, a = 7.4499(3) Å, b = 15.1491(7) Å, c = 13.8738(7) Å, β = 90.677(1)°, V = 1565.7(1) Å^3, Z = 4, d_{calc} = 1.470 g/cm^3, μ = 10.68 cm^{-1}, $F(000)$ = 704, θ_{max} = 29°, T = 100(2) K, R1(F) = 0.0249 for 3597 observed reflections with $I > 2\sigma(I)$, wR2(F^2) = 0.0579 and S = 1.035 for all 4110 unique reflections (R_{int} = 0.0268).
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