Stable Agostic (C−H···M) *closo*-Irida- and *closo*-Rhodacarboranes with σ,η^2-Cyclooctenyl Ligands. Crystal and Molecular Structure of *closo*-3,3-(σ,η^2-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$

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Agostic (C−H···M) complexes [*closo*-3,3-(σ,η^2-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$] (**5**) and [*closo*-3,3-(σ,η^2-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (**9**), stable in the solid state, have been prepared via the reaction of [M(η^4-COD)Cl]$_2$ (M = Ir, Rh) with the K^+ salt of the [*nido*-7,8-μ-(*ortho*-xylylene)-7,8-$C_2B_9H_{10}]^-$ anion and characterized by a combination of analytical (in the case of **5**) and multinuclear NMR data, including a single-crystal X-ray diffraction study of **5**. The crystallographic study confirmed the agostic structure of **5** and revealed that the orientation of the σ,η^2-cyclooctenyl moiety relative to the carborane ligand is substantially influenced by the specific intramolecular C−H···π interaction between the agostic hydrogen and the π-system of the cage aromatic substituent. In solution, **5** exhibited both "side-to-side" agostic hydrogen migration and reversible interconversion with [*closo*-3-(η^3-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$] (**8**). The agostic rhodium complex (**9**), in contrast, converts irreversibly both in the solid state and in solution to its η^3-cyclooctenyl isomer [*closo*-3-(η^3-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (**11**), which thus could be obtained as a pure solid. In solution, complex **11** is fluxional and shows an agostic C−H···Rh interaction. The fluxional process involves the exchange between the *endo* hydrogen atoms, on one hand, and the *exo* and allyl hydrogens of the C_8-ring, on the other hand, confirmed by 2D [^{1}H−^{1}H]-EXSY spectroscopy. Solution structures of the agostic complexes obtained are discussed in detail on the basis of normal and low-temperature ^{1}H and ^{13}C/^{13}C{^{1}H} NMR spectroscopic data.

Introduction

One of the most frequently employed synthetic routes to anionic and neutral *closo*-(η^4-cyclodiene)rhodacarboranes, from which other derivatives could be prepared, relies on the reactions of appropriate (η^4-diene)rhodium complexes such as [Rh(η^4-diene)Cl]$_2$[1−3] or [Rh(η^4-diene)(acac)][2] with in situ generated dianions [*nido*-7,*n*-R,R′-$C_2B_9H_9]^{2-}$ (n = 8, 9)[1,2] or their "charge-compensated" analogues such as [9-Me_2S-*nido*-$C_2B_9H_{10}]^-$.[3] It seemed probable that this general ligand-exchange method could easily be modified for the syntheses of anionic *closo*-(η^4-cyclodiene)iridacarboranes. However, using the analogous procedure[1,2] starting from [Ir(η^4-COD)Cl]$_2$ (**1**) or [Ir(η^4-COD)(acac)] (**2**) and [*nido*-7,8-μ-(*ortho*-xylylene)-7,8-$C_2B_9H_9]^{2-}$, we have not been able to isolate the desired anionic *closo*-(η^4-COD)iridacarborane species as their $[PPN]^+$ salts. Both reactions led to the decomposition of the starting iridium complexes with liberation of the hydrocarbon ligand and precipitation of the $[PPN]^+$ salt of the [*nido*-7,8-μ-(*ortho*-xylylene)-7,8-$C_2B_9H_{10}]^-$ anion (**3**) as the only carborane-containing product (see Experimental Section).

In the search for a more powerful method for the synthesis of *closo*- and/or *exo*-*nido*-(η-cyclodiene/cyclodienyl)iridacarboranes, we followed the procedure reported long ago by Hawthorne and co-workers[4] for the syntheses of *exo*-*nido*-bis(phosphine)rhodacarboranes starting from $RhCl(PPh_3)_3$ and Cs^+ or Tl^+ salts of [*nido*-7,8-R,R′-7,8-$C_2B_9H_{10}]^-$ (R, R′ = H, Alk, ArAlk) in a C_6H_6/EtOH mixture, as the most suitable solvent. Recently, using a slightly modified procedure,[4] several new *exo*-*nido* rhodium-monothiocarborane complexes of the general formula [*exo*-*nido*-Rh(PPh_3)$_2$(7-SPh-8-R-7,8-$C_2B_9H_{10}$)] (R = Alk, Ar) have been prepared.[5] In addition, a series of some other related complexes, [*exo*-*nido*-Rh(η^4-COD)-(7-SR-8-R′-7,8-$C_2B_9H_{10}$)], which incorporated an ancilliary COD ligand, have also been obtained by the reaction of Cs^+ or Me_4N^+ salts of the respective *nido*-monothiocarboranes with [Rh(η^4-COD)(acac)], which was treated, prior to use, by 1 equiv of $HClO_4$ or HBF_4 in THF.[6]

In our recent attempt to simplify the synthesis of catalytically active [*closo*-3,3-($\eta^{3,2}$-$C_7H_7CH_2$)-3,1,2-$RhC_2B_9H_{11}$] and [*closo*-2,2-($\eta^{3,2}$-$C_7H_7CH_2$)-2,1,7-$RhC_2B_9H_{11}$] (where C_7H_7 is 2,5-norbornadien-2-yl),[7] excellent yields

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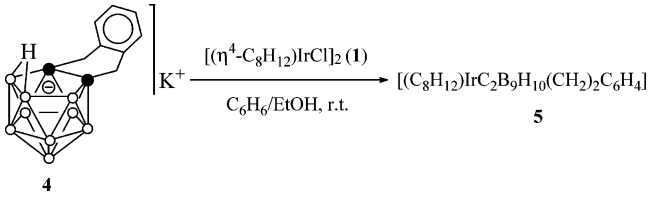
Scheme 1



of the desired products have been achieved when K^+ salts of [*nido*-7,*n*-$C_2B_9H_{12}]^-$ (n = 8 and 9) reacted with μ-halide rhodium dimer [(η^4-C_7H_7-2-CH_2OH)RhCl]$_2$ in a C_6H_6/EtOH mixture at ambient temperature.[8] In addition, a number of related *closo*-rhodacarboranes with metal-coordinated η-carbocyclic ligands derived from cycloocta-1,5-diene and dicyclopentadiene were also successfully prepared.[8] The exceptionally high efficiency of this particular method in the case of carbocycle-containing rhodium-carborane complexes and the first positive results in the synthesis of a few iridium congeners, including species with an agostic C−H···Ir interaction,[8−10] prompted us to extend further the range of the related *closo*-(η-carbocycle)metallacarboranes of the same metals.

We now wish to report the synthesis and characterization of the agostic (C−H···M) *closo*-irida- and *closo*-rhoda-1,2-μ-(*ortho*-xylylene)carboranes bearing a σ,η^2-cyclooctenyl ligand derived from 1,5-cyclooctadiene at the metal vertex. We have confirmed the agostic structure of the isolated species and investigated in considerable detail their fluxionality in solution using variable-temperature multinuclear NMR spectroscopic data as well as an X-ray diffraction study performed on a crystal of [*closo*-3,3-(σ,η^2-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$] (**5**).

Results and Discussion

Synthesis and NMR Spectroscopic Characterization of [*closo*-3,3-(σ,η^2-cyclooctenyl)-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$] (5). Initially, the reaction of [Ir(η^4-COD)Cl]$_2$ (**1**) with the K^+ salt of the [*nido*-7,8-μ-(*ortho*-xylylene)-7,8-$C_2B_9H_{10}]^-$ anion (**4**), in a solution of a 1:4 benzene/ethanol mixture, has been carried out (Scheme 1). As a result, a high yield of a neutral pale yellow complex was obtained whose analytical data as well as its FAB mass spectrum were consistent with the formulation [(C_8H_{12})Ir$C_2B_9H_{10}$(CH_2)$_2$$C_6H_4$] (**5**).

Taking into account the similarity of the procedure used for the synthesis of **5** and that reported for the preparation of a series of *exo*-*nido*-bis(phosphine)rhodacarboranes,[4] species **5** might be expected to have either the 16-electron *exo*-*nido* structure **A** or the alternative 18-electron diene-hydride *closo* structure **B** depicted in Chart 1. Several stable iridium diene-hydride isoelectronic analogues of the general formula [Cp′Ir(H)(η^4-C_8H_{12})]$^+$ (**6**, Cp′ = C_5H_5 or its alkyl-substituted derivatives) with the C_8-ring bound to the metal atom as 1,3-conjugated[11] or, more likely, as the 1,5-nonconjugated[12] diolefin have been reported. On the other hand, a few examples of *closo*-(η-carbocycle)-metallacarboranes have also been reported in which the metal atom attains its 18-electron configuration via an agostic C−H···M interaction.[1a,8−10,13] Among these, one species, [*closo*-3,3-(σ,η^2-C_8H_{13})-1,2-Me_2-3,1,2-$RhC_2B_9H_9$] (**7**), which exhibited fluxional behavior in solution, has been determined by Hawthorne and co-workers[1b] to be the thermally unstable intermediate of the protonation reaction of the anionic complex [*closo*-3,3-(η^4-C_8H_{12})-1,2-Me_2-3,1,2-$RhC_2B_9H_9$][PPN] with CF_3COOH. By analogy, **5** could also be assumed to have an agostic (C−H···Ir) ground state *closo* structure with a σ,η^2-cyclooctenyl ligand at the iridium vertex.

Complex **5** was further characterized by NMR spectroscopy. In the room-temperature ^{1}H NMR spectrum of **5** the C_8-hydrocarbon ring is represented by a set of six well-defined multiplets, which were integrated as having exactly two protons each, along with a unique single resonance of 1H intensity area in a high-field region of the spectrum at δ −5.32 ppm. No other upfield peaks attributable to bridging protons of B−H−B and/or B−H···Ir bonds were observed in the ^{1}H NMR spectrum. These observations, taken together, do not fit with both *exo*-*nido* and diene-hydride *closo* structure of **5** (Chart 1, structures **A** and **B**, respectively). The only structure that could account for such a unique set of resonances would be the one having the agostic (C−H···Ir) interaction and undergoing rapid, on the NMR time scale, "side-to-side" migration of the agostic hydrogen (Chart 1, structure **C** and **C′**). In this case, due to simultaneous interaction of the agostic hydrogen with the iridium and two olefinic carbon atoms C(1) and C(6) or, alternatively, C(2) and C(5), an effective mirror plane containing the iridium atom, midpoints of both C(7)−C(8) and C(3)−C(4) bonds of the C_8-ring, and midpoints of both antipodal cage bonds C(1)−C(2) and B(9)−B(12) would have been expected to appear in the solution of **5**. The detailed examination of a series of variable-temperature ^{1}H, ^{13}C{^{1}H}/^{13}C NMR (vide infra) and ^{11}B{^{1}H}/^{11}B NMR spectra as well as combined 2D [^{1}H−^{1}H]-COSY and [^{13}C−^{1}H]-HETCOR correlation spectra of **5** has proved the above postulation to be the case.

Thus, in the [^{1}H−^{1}H]-COSY spectrum there are two cross-peaks (both are strong) that connect a high-field resonance at δ −5.32 ppm to the C_8-ring multiplets at

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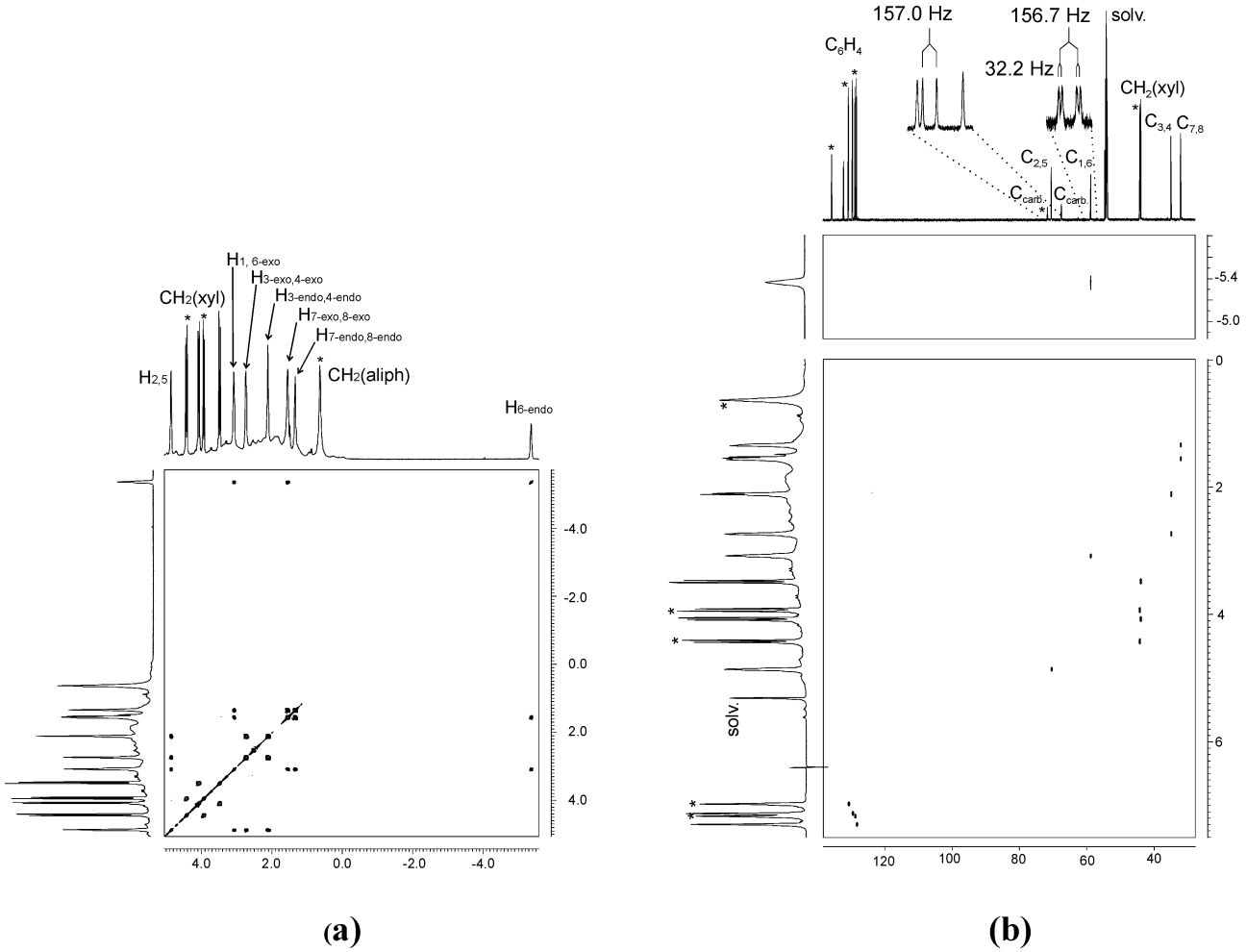
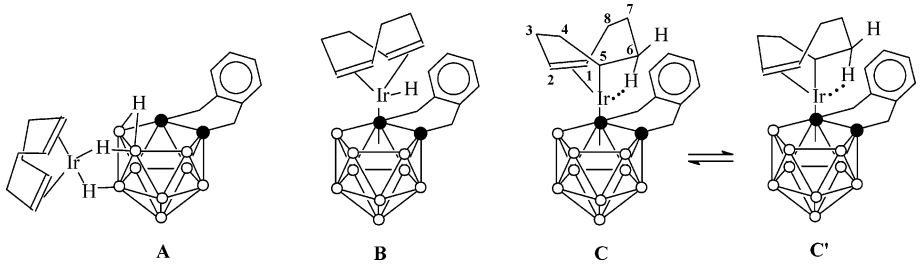


Figure 1. (a) [^{1}H−^{1}H] (500.13 MHz) COSY spectrum for **5** in CD_2Cl_2 solution at 25 °C showing the assignment of the proton resonances. The resonances of **8** are labeled with stars; (b) [^{13}C−^{1}H] (125.76/500.13 MHz) HETCOR experiment with fragments of the ^{13}C NMR spectrum (above) for **5** in CD_2Cl_2 solution at 25 °C showing the assignment of the carbon resonances and ^1J(C,H) values. The resonances of **8** are labeled with stars.

Chart 1. Schematic Representation of Possible Structures for 5



δ 3.03 and 1.54 ppm (Figure 1a), thus strongly supporting the agostic nature of the unique high-field proton. On the basis of chemical shifts, multiplicities, and the observed 2H relative intensities of resonances at δ 3.03 and 1.54 ppm and the fact that they share a cross-peak, these resonances were assigned to protons H(1,6-*exo*) and H(7-*exo*,8-*exo*), respectively. It is well known from the spectra of numerous metal complexes with COD-based ligands[14] that low-field multiplets within a set of *endo* and *exo* methylene protons normally correspond to *exo* protons. Cross-peaks observed between the resonances H(7-*exo*,8-*exo*) and H(7-*endo*,8-*endo*) at δ 1.38, on one hand, and between H(1,6-exo), H(7-*exo*,8-*exo*), and the 2H multiplet at δ 4.87 ppm, on the other, permit the latter signal to be assigned to H(2,5), the other pair of the protons that derived from the former olefinic C_8-ring bonds. The equivalency of protons in each pair H(1,6-exo) and H(2,5) can reasonably be explained by a 1,4-agostic hydrogen shift in the fast-exchange limit. In agreement with this, in the [^{13}C−^{1}H]-HETCOR spectrum two olefinic carbon resonances that appear in the lowest field of a set of four originating from the C_8-ring, at δ 57.5 and 69.3 ppm, are connected by cross-peaks to the proton resonances at δ 3.03 and 4.87 ppm,

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respectively, and only one of these signals, at δ 57.5 ppm, is coupled with the agostic resonance at δ −5.32 ppm (Figure 1b). On the basis of the observed cross-peaks between other signals in the [^{1}H−^{1}H]-COSY and [^{13}C−^{1}H]-HETCOR spectra of **5**, we made the remaining assignments, as shown in Figure 1a.

Interestingly, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **5** proved to be quite different in comparison with those described earlier for the fluxional agostic (C−H···Rh) species **7**,[1b] where, in particular, the C_8-ring olefinic protons as well as some aliphatic protons have been shown to appear as equivalent in the ^{1}H NMR spectra. This fact, coupled with a lack of olefinic carbon resonances in the ^{13}C{^{1}H} NMR spectrum of **7** at −53 °C, has been attributed to rapid 1,2- and 1,4-hydrogen shifts involving the agostic hydrogen.[1b] In our case, examination of the ^{13}C NMR spectrum of **5** showed that the resonance at δ 57.5 ppm assigned above to C(1,6) is split into a doublet of doublets with ^1J(C,H) = 156.7 and 32.2 Hz, while that signal derived from C(2,5) at δ 69.3 ppm was observed as a pure doublet with ^1J(C,H) = 157.0 Hz (Figure 1b). Assuming that ^2J(C(1),H(ag)) = 0 Hz, the observed value of 32.2 Hz of one of the doublet components of the C(1,6) signal should arise from the average of a static ^1J(C(6),H(ag)) value of 64.4 Hz, and the other of ^1J(C,H) = 156.7 Hz is obtained for the noninteracting C(6)−H(6-*exo*) bond. Since C(2) and C(5) are not involved in the interaction with the agostic hydrogen, no additional splitting of a doublet resonance at δ 69.3 ppm is observed in the ^{13}C NMR spectrum of **5**. These observations are in accord with the idea that fluxional species **5** undergoes rapid metal-assisted 1,4-hydride shifts in solution.[15] One may reasonably anticipate that an intramolecular fluxional process such as that observed for **5** in solution could likely proceed via an 18-electron diene-hydride intermediate, earlier depicted as **B** in Chart 1.

A particularly noteworthy feature of the ^{1}H NMR spectrum of **5** is an unusual double set of resonances attributed to the C,C′-*ortho*-xylylene cage substituent. Indeed, there are two different AB quartets of equal intensity with the doublet components at δ 4.43 and 3.91 ppm (J_{AB} = 16.5 Hz) and 4.08 and 3.46 ppm (J_{AB} = 17.1 Hz) arising from the bridging methylene protons along with a set of four multiplets of aromatic protons in the lowest field of the spectrum. Furthermore, an additional unresolved broad aliphatic signal at δ 0.64 ppm, integrated as four protons, is also observed in the ^{1}H NMR spectrum of **5**. Accordingly, the room-temperature ^{13}C-{^{1}H} NMR spectrum of **5** also displays a double set of signals originating both from the exopolyhedral cage substituent and the carborane cage itself. In particular, there are two cage carbon resonances of lower intensities at δ 70.9 and 66.8 ppm, two bridging methylene resonances at δ 43.6 and 43.3 ppm, and a set of six low-field resonances in the range δ 127.4−134.9 ppm due to the C_6-ring carbon atoms. Those resonances, observed at δ 134.9 and 131.4 ppm, were considerably reduced in intensity and can thus be attributed to the *ipso*-carbons of the aromatic ring. The corresponding carborane ligand signals revealed in the ^{11}B{^{1}H}/^{11}B NMR spectra of **5** were mostly overlapping peaks too complicated for assignment. However, in the low-field part of the spectra two peaks of equal intensity appeared separately at δ 3.7 and −0.3 ppm, of which each can apparently be taken as arising from a single boron atom. The integration of these peaks relative to other resonances observed indicates that the whole set of signals accounts for the area approximately 2 times as big as one would have expected for **5**. Considering all these data, it is reasonable to assume that fast equilibrating σ,η^2-cyclooctenyl complexes are not the only species that can be observed in the solution of **5**. Thus, an additional set of resonances attributed to the exopolyhedral *ortho*-xylylene group in the ^{1}H and ^{13}C NMR spectra might be retained as slow exchange patterns of another highly fluxional complex closely related to **5**. For the assignment of this new species low-temperature ^{1}H and ^{13}C-{^{1}H} NMR studies were performed (vide infra). Before this, however, an X-ray diffraction study of complex **5**, undertaken in order to rule out the possible diene-hydride structure of **4** in the solid state, needs to be discussed.

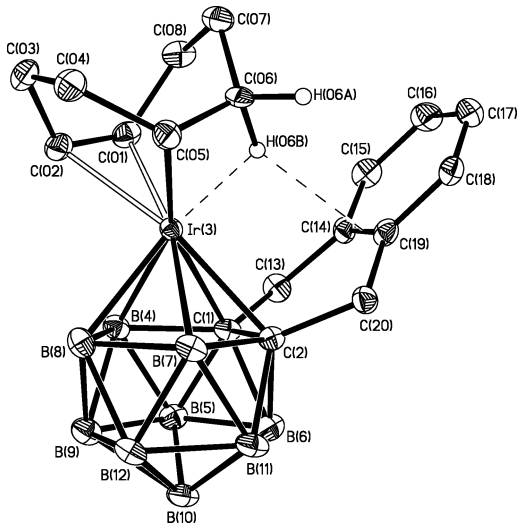

Figure 2. ORTEP representation of the molecular structure of **5** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms (except for H(06a) and H(06b)) are omitted for clarity.

Single-Crystal X-ray Diffraction Study of Complex 5. Crystals of **5** suitable for an X-ray diffraction study were grown at −10 °C from the same CD_2Cl_2 solution that was used for the NMR measurements. ORTEP representation of the molecular structure of **5** is shown in Figures 2 and 3, and selected bond distances and angles are listed in Table 1.

The overall geometry of **5**, as determined by the X-ray diffraction study, confirmed this species to be *closo*-iridacarborane, where the metal atom is π-coordinated by the C(01)−C(02) double bond to the carbocyclic C_8H_{13} ligand; it also forms a σ-bond with the C(05) atom and participates in the agostic C(06)−H···Ir interaction. The separations between the Ir atom and those carbocyclic carbon atoms involved in the coordination proved to be quite informative. Indeed, the Ir−C(01) (2.202(4) Å) and Ir−C(02) (2.190(4) Å) distances agree well with those reported for iridium−olefin distances in a number of COD-based iridium complexes.[16] In agreement with the

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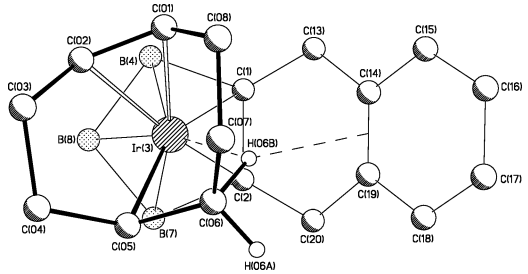

Figure 3. Top view of **5**, showing the orientation of the agostic hydrogen with respect to the carborane cage substituent. The lower belt of the carborane cage as well as hydrogen atoms (except for H(06a) and H(06b)) are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 5

Ir(3)−C(1)	2.263(4)	C(14)−C(15)	1.388(6)
Ir(3)−C(2)	2.236(4)	C(14)−C(19)	1.397(6)
Ir(3)−B(4)	2.168(5)	C(15)−C(16)	1.386(6)
Ir(3)−B(7)	2.238(5)	C(16)−C(17)	1.384(7)
Ir(3)−B(8)	2.207(5)	C(17)−C(18)	1.376(6)
Ir(3)−C(01)	2.202(4)	C(18)−C(19)	1.402(6)
Ir(3)−C(02)	2.190(4)	C(19)−C(20)	1.522(5)
Ir(3)−C(05)	2.098(4)	C(01)−C(02)	1.402(6)
Ir(3)−C(06)	2.313(4)	C(01)−C(08)	1.529(6)
Ir(3)−H(06B)	1.77(5)	C(02)−C(03)	1.515(6)
C(06)−H(06A)	0.99(5)	C(03)−C(04)	1.531(6)
C(06)−H(06B)	1.14(5)	C(04)−C(05)	1.514(6)
C(1)−C(2)	1.630(5)	C(05)−C(06)	1.480(6)
C(1)−C(13)	1.522(6)	C(06)−C(07)	1.534(6)
C(2)−C(20)	1.519(5)	C(07)−C(08)	1.542(6)
C(13)−C(14)	1.517(6)		

Ir(3)−H(06B)−C(06)	103(3)	C(14)−C(19)−C(20)	123.3(4)
C(13)−C(1)−C(2)	117.7(3)	C(18)−C(19)−C(20)	117.5(4)
C(20)−C(2)−C(1)	118.0(3)	C(2)−C(20)−C(19)	114.9(3)
C(14)−C(13)−C(1)	115.4(3)	C(02)−C(01)−C(08)	122.4(4)
C(15)−C(14)−C(19)	119.0(4)	C(01)−C(02)−C(03)	123.7(4)
C(15)−C(14)−C(13)	118.4(4)	C(02)−C(03)−C(04)	110.6(3)
C(19)−C(14)−C(13)	122.6(4)	C(05)−C(04)−C(03)	111.6(3)
C(16)−C(15)−C(14)	121.4(4)	C(06)−C(05)−C(04)	122.8(4)
C(17)−C(16)−C(15)	119.6(4)	C(05)−C(06)−C(07)	120.5(4)
C(18)−C(17)−C(16)	119.8(4)	C(06)−C(07)−C(08)	111.4(3)
C(17)−C(18)−C(19)	121.1(4)	C(01)−C(08)−C(07)	115.0(4)
C(14)−C(19)−C(18)	119.1(4)		

existence of the Ir−C σ-bond and the C−H···Ir interaction in **5**, the separations between the Ir atom and the C(05) and C(06) are quite different, 2.098(4) and 2.313(4) Å, respectively. Although, no structural information for iridacarborane complexes with σ,η^2-cyclooctenyl ligands is available, the Ir−C(05) and Ir···C(06) separations found in **5** can usefully be compared with the Rh−C (σ-bond, 2.08 and 2.054 (av) Å) and Rh···C (agostic bond, 2.36 and 2.373 (av) Å) distances found in the agostic (C−H···Rh) complexes [*closo*-3,3-(σ,η^2-norbornenyl)-1,2-$(CH_3)_2$-3,1,2-$RhC_2B_9H_9$][1a] and [*closo*-3,3-(σ,η^2-dicyclopentenyl)-1-R-3,1,2-$RhC_2B_9H_{10}$] (R = CH═CH_2; CH_2OH),[13] respectively. The comparison of both the Ir···C(06) and Ir···H(ag.), 1.77(5) Å, distances in **5** with those found in the known agostic [*closo*-3-{η^3-(*endo*-1,5-Me_2COD)}-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$] (Ir−C, 2.66(1) and Ir···H(ag.), 2.22(8) Å[10]) leads to the conclusion that the agostic interaction in **5** is much stronger. Accordingly, the related C−H(ag.) bond length of 1.14(5) Å found in **5** is noticeably elongated as compared to a nonbridging C−H bond from the aliphatic part of the ligand, in the range from 0.86 to 0.99 Å. Such a C−H(ag.) elongation appears to be typical for complexes with a C−H···M interaction.[17] We note in this context that the Ir···H(ag.) distance of 1.77(5) Å observed in **5** is, actually, shorter than the typical metal−hydrogen distances observed in the majority of agostic transition metal complexes, which are usually in the range 1.8−2.2 Å.[17]

The carbocyclic ligand in **5** is positioned in a peculiar way with respect to the rest of the molecule (Figure 3). It has an orientation such that both the C(01) and C(06) carbon atoms of the C_8-ring and the agostic hydrogen atom are directed toward the C,C′-*ortho*-xylylene cage substituent. This orientation preference seems to be rather unusual since it may cause relatively close contacts between the cage substituent and the part of the carbocyclic ligand involving the C(01)−$(CH_2)_2$−C(06) fragment. In this respect, the orientation of the carbocyclic ligand, in which the agostic C−H···Ir bond is as far away from the cage *ortho*-xylylene group as possible, would have been far more reasonable than the one actually observed in the crystal structure. The *ortho*-xylylene substituent itself is displaced significantly from the C_2B_3 plane of the cage toward the metal atom; the angle between the normals to the cage pentagonal plane and the least-squares plane defined by the aromatic nucleus and bridging methylene carbons is 50.5°. This angle is greater than that found in [*closo*-3,3-$(PPh_3)_2$-3-H-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (38.7°),[18] where some steric repulsion between the *ortho*-xylylene group and the metal-containing moiety could, in principle, be expected. It is known that a similar angle is increased up to 82° in the reported C,C′-*ortho*-xylylene cage-substituted *exo-nido*-metallacarboranes, [*exo-nido*-6,10-{$(PPh_3)(PCy_3)$Rh}-6,10-μ-$(H)_2$-10-H-7,8-μ-(*ortho*-xylylene)-7,8-$C_2B_9H_7$][18] and [*exo-nido*-5,6,10-{$Cl(PPh_3)_2$Os}-5,6,10-μ-$(H)_3$-10-H-7,8-μ-(*ortho*-xylylene)-7,8-$C_2B_9H_6$],[19] where no such steric interaction is observed. Since in C−H···M third-row systems the agostic hydrogen is known to become acidic due to effective interaction with an essentially electrophilic metal center,[17] a specific double C−H···Ir/C−H···π interaction would be expected to occur in **5**. Thus, such a sterically unfavored conformation of the carbocyclic ligand observed in the crystal of **5** is likely a reflection of the existence of a weak intramolecular hydrogen bond of the C−H···π type where either the whole aromatic ring or only one of the aromatic bonds can be the basic center acting as a proton acceptor. Indeed, the agostic hydrogen atom H(06B) is oriented over an aromatic ring of the cage xylylene group with a C−H···centroid distance of 2.93 Å. A relatively short distance is also observed between the H(06B) atom and the midpoint (MP) of the C(14)−C(19) aromatic bond, 2.50 Å, and the corresponding C−H···MP angle is 150°. These values seem to be typical

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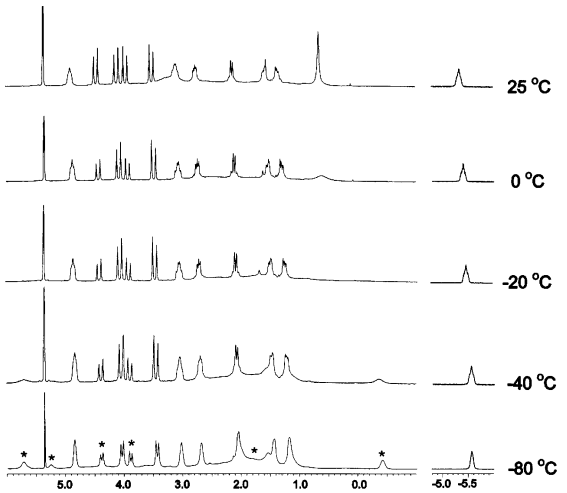


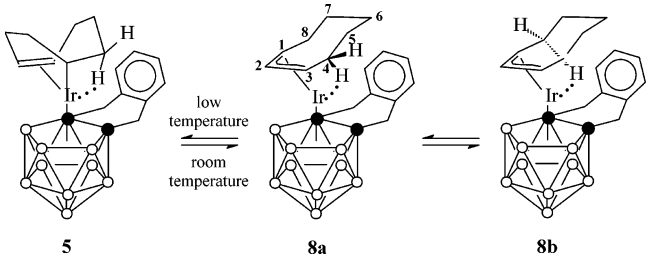
Figure 4. 500.13 MHz variable-temperature ^{1}H NMR spectra for **5** from −80 to 25 °C in CD_2Cl_2 solution (aromatic region of the spectra is not displayed). The resonances of complex **8** in the spectrum at −80 °C are labeled with stars.

for C−H···π interactions,[20] and their role in the organization of different complex molecules is now well recognized.[20a]

The coordination geometry at the iridium atom in **5** can be considered pseudooctahedral, where the carborane cage and the σ,η^2-carbocyclic ligand involving the agostic hydrogen H(06B) each occupies three coordination sites around the metal center. Since the agostic hydrogen is asymmetrically located on one side of the C_8-ring, namely, at the carbon atom C(06), this complex does not have mirror symmetry in the solid state. Nevertheless, such an effective mirror plane containing the iridium atom, midpoints of both C(07)−C(08) and C(03)−C(04) bonds of the carbocyclic ligand, and midpoints of both antipodal cage bonds C(1)−C(2) and B(9)−B(12) may appear in a solution of **5** due to the rapid "side-to side" migration of the agostic hydrogen.

Low-Temperature NMR Study of Complex 5. To determine the origin of an additional set of resonances observed in the room-temperature NMR spectrum of **5**, a variable-temperature study of the dynamic behavior of **5** in solution was undertaken (Figure 4). The low-temperature ^{1}H NMR spectrum of **5** in CD_2Cl_2 taken at −80 °C was found to exhibit several new resonances in addition to those that appeared in the room-temperature spectrum. Specifically, the coordinated C_8-ring gave rise to two nonresolved multiplets at δ 5.73 and 5.22 ppm of a relative intensity ratio of 2:1, respectively, and a high-field broadened singlet at δ −0.47 ppm, which has an intensity equal to that of either of the two doublets of the AB system derived from *ortho*-xylylene methylene groups. Furthermore, at least two partly overlapped multiplets of inherent complexity have appeared in the range from 1.5 to 2.3 ppm, while a single four-proton resonance primarily observed in the room-temperature spectrum at 0.64 ppm has collapsed into the baseline on cooling. The low-temperature ^{1}H NMR spectrum thus unambiguously confirmed the presence of one more species in the solution of **5** which can reasonably be formulated as an agostic [*closo*-3-(η^3-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$] (**8**). The low-temperature (−93 °C) 2D [^{1}H−^{1}H]-COSY spectrum showed that the resonance at δ −0.47 ppm shares two cross-peaks (one of strong and one of middle intensity) with the new aliphatic resonances centered at δ 2.00 and 1.50 ppm. In addition, there is a weak cross-peak connecting the high-field resonance with the signal at δ 5.73 ppm (allylic 2H), while the latter is coupled only to the other allylic signal at δ 5.22 ppm (allylic 1H). The unique resonance at δ −0.47 ppm is therefore best attributed to an agostic hydrogen involved in a rapid exchange between the two *endo* hydrogen atoms H(4) and H(8), which are adjacent to the η^3-allyl unit of the carbocyclic ligand (Scheme 2); aliphatic resonances at δ 2.00 and 1.51 ppm can thus be assigned to *exo* methylene protons H(4,8) and H(5,7), respectively. We note, at the lowest temperature limit that was achieved experimentally (−93 °C), complex **8** is still fluxional in solution. The low activation energy for this complex prevented us from obtaining a "static" low-temperature spectrum in which one would expect to distinguish two asymmetric isomeric structures **8a** and **8b** of complex **8**.

Scheme 2



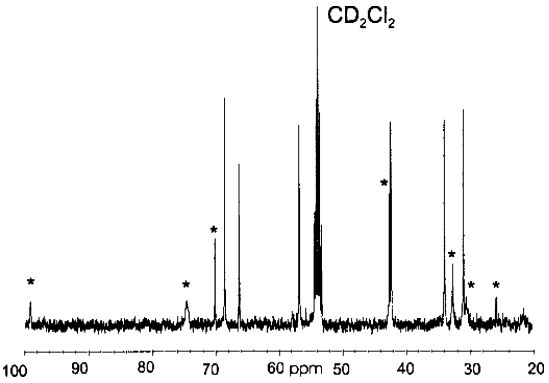


Figure 5. 100.61 MHz low-temperature (−73 °C, CD_2Cl_2) $^{13}C\{^1H\}$ NMR spectrum for **5** in the 20−100 ppm region (aromatic region of the spectra is not displayed). The resonances of complex **8** are labeled with stars.

The low-temperature (−73 °C) $^{13}C\{^1H\}$ NMR spectrum, along with the expected resonances derived from **5**, displayed a set of resonances assignable to the C,C′-*ortho*-xylylene-substituted carborane ligand of **8** including those from aromatic and cage *ipso*-carbons and most of the carbon atoms of the η^3-cyclooctenyl ligand (Figure 5). Although all carbon carbocyclic signals of **8** were broad and those from the aliphatic region even partly overlapped, characteristic allylic resonances at 99.22 (allylic 1C) and 74.54 ppm (allylic 2C) could easily be identified due to their splitting into doublets in the low-

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temperature proton-coupled ^{13}C NMR spectrum. It should be noted, in this context, that in the low-temperature (−93 °C) 2D [$^{13}C-^{1}H$]-HETCOR spectrum of this sample, the connectivities between the carbon and proton resonances were revealed mostly for complex **5**, except for those cross-peaks of **8** originating from the C,C′-*ortho*-xylylene cage substituent. This may be due to much larger line widths of the C_8-ring carbon signals of **8** compared with those of **5**.

We note that lowering of the temperature of a ^{1}H NMR sample of **5** to −20 °C leads to a change in the relative ratio of **5** and **8** from 1:1 to ca. 2:1; on warming from low to room temperature, this ratio returns to 1:1. This reversible process could be precisely monitored via integration of the bridging methylene AB signals derived from the C,C′-*ortho*-xylylene cage substituents of complexes **5** and **8** at different temperatures (Figure 4). The same is true for the ^{1}H NMR sample of **5** in CD_2Cl_2 which was stepwise diluted by the same solvent to a half and then to one-third of the initial concentration. We therefore discount as a possible explanation of this phenomenon the precipitation of complex **8** at low temperature and tend to conclude that the observed spectra correspond to the reversible equilibrium between the agostic σ,η^2-cyclooctenyl and η^3-cyclooctenyl isomeric complexes **5** and **8**. The examination of the room-temperature 2D [$^{1}H-^{1}H$]-EXSY spectrum of **5**, where intensive exchange cross-peaks between AB methylene resonances of **5** and **8** that derived from their *ortho*-xylylene groups are observed, provided direct spectroscopic evidence for the existence of such an equilibrium, and this is given in the Supporting Information.

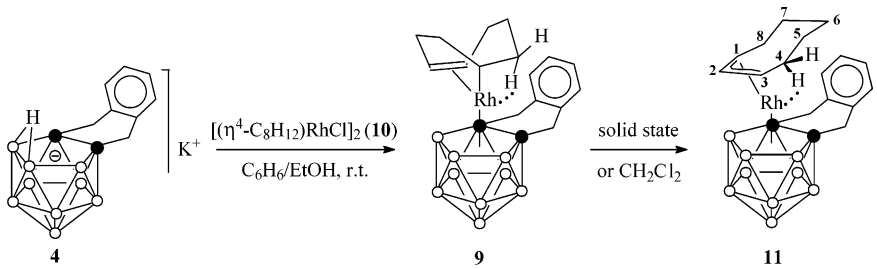
Synthesis, Characterization, and Solution Behavior of [*closo*-3,3-(σ,η^2-Cyclooctenyl)-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (9). In view of the results described above, it was of interest to synthesize and examine the solution behavior of [*closo*-3,3-(σ,η^2-cyclooctenyl)-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (**9**), the rhodium analogue of **5**. It was found that **9** could be prepared in high yield by a procedure similar to that used for **5**, starting from *nido*-carborane salt **4** and dimer [Rh(η^4-COD)Cl]$_2$ (**10**) (Scheme 3). Complex **9** proved, however, to be surprisingly labile in solution due to a relatively fast irreversible conversion into its isomer [*closo*-3-(η^3-cyclooctenyl)-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (**11**). This, in fact, prevented us from obtaining complex **9** in analytically pure form free from inorganic impurities (such as starting salt **4** or KCl) using either column chromatography on silica gel or recrystallization from a CH_2Cl_2/*n*-hexane mixture. Hence, only fast NMR spectroscopic measurements were used for its characterization in solution. Furthermore, it was found that **9** could eventually be converted to **11** even in the solid state by storing at ambient temperature for ca. 1 week (Scheme 3).

The room-temperature ^{1}H NMR spectrum of **9** in CD_2Cl_2, even taken immediately after mixing, already shows resonances that reveal the existence of a mixture of isomers **9** and **11**. In contrast to the equilibrium between **5** and **8** studied earlier, the observed equilibrium for complexes **9** and **11** shifts very quickly toward complex **11**, and after ca. 2.5 h the final product **11** could be observed as the only visible species in the spectrum. These results indicate that complex **9** is thermodynamically much less stable in solution than complex **11**. A comparison of the room-temperature ^{1}H NMR spectrum of **9** in a half-time of transition into **11** with that of **5** measured at low-temperature (−80 °C) showed that both display very similar patterns. Thus, multiplet resonances arising from olefinic and aliphatic parts of the σ,η^2-cylcooctenyl ligand of **9** were found at δ 5.32 (H(2,5)) and 3.48 (H(1,6)) ppm and between 2.90 and 1.22 ppm, respectively. Besides, there is a unique high-field resonance at δ −4.41 ppm, which is apparently due to the hydrogen involved in the agostic bonding interaction with the metal atom in **9**. Owing to the fast shift of the equilibrium for **9** and **11** toward complex **11** occurring in solution, the assignment of boron resonances corresponding to complexes **9** and **11** in the $^{11}B\{^{1}H\}$/^{11}B NMR spectra could be made. The comparison of quickly recorded $^{11}B\{^{1}H\}$/^{11}B NMR spectra of **9** with those formed after several hours, which consisted of four principal peaks with a 1:3:3:2 intensity ratio due to **11**, permitted us to identify signals belonging to complex **9** (see Experimental Section).

Since complex **11** proved to be stable both in the solid state and in solution and could be prepared as a very pure product, its detailed NMR spectroscopic study was undertaken. Standard homo- and heteronuclear 2D chemical shift correlation techniques were used to assign proton and carbon signals in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **11**. The corresponding 2D [$^{1}H-^{1}H$]-COSY and [$^{13}C-^{1}H$]-HETCOR spectra of **11** are given as Supporting Information.

The ^{1}H NMR spectrum of **11** provides unambiguous support for the structure of this species. This spectrum contains two separate resonances at δ 5.90 (q, 2H) and 4.45 (t, 1H), typical for olefinic protons of the allyl moiety of the C_8-ring, whereas each pair of *exo* and *endo* protons of the aliphatic methylene groups appears as a single 2H multiplet in the region from δ 2.16 to −0.25 ppm, as can be expected for an η^3-cyclooctenyl species with effective mirror symmetry. On the basis of the ^{1}H NMR spectrum of the iridium congener **8**, the resonances at δ −0.25 ppm of 2H intensity area can be attributed to the exchange average of the two *endo* CH hydrogen atoms adjacent to the allyl unit of the car-

Scheme 3



4 **9** **11**

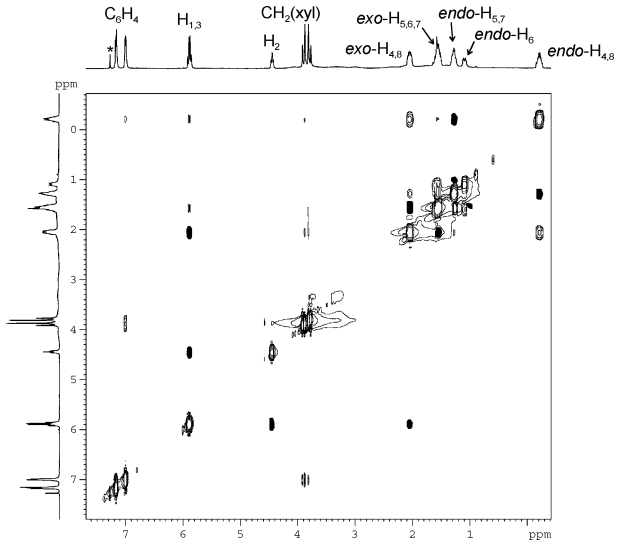


Figure 6. 400.13 MHz ^{1}H NMR EXSY spectrum for **11** in $CDCl_3$ solution at 60 °C. Exchange cross-peaks are marked as black spots.

bocyclic ligand which are alternately involved in the agostic C−H···Rh interaction; the value of the chemical shift of this signal in the ^{1}H NMR spectrum of **11**, if compared with that observed for **8** (δ −0.47 ppm), indicates that the agostic C−H···M bond is somewhat weaker in the rhodacarborane complex.

The 2D [^{1}H−^{1}H]-EXSY spectrum of **11** in $CDCl_3$ at 60 °C was studied next. It is well known that two principal exchange processes may be observed for simple unsubstituted η^3-cyclooctenyl organometallic systems.[17] The first involves the exchange of *endo* hydrogens that are alternately involved in coordination to the metal center, which is believed to proceed via the formation of the symmetrical 16-electron η^3-cycloallylic intermediate. Due to the usually low activation energy of such processes resulting in fast hydrogen exchange, all pairs of side hydrogens of the η^3-cyclooctenyl ligand are usually averaged to a single resonance in the ^{1}H NMR spectra. The second process involves the exchange between the allyl and *exo* hydrogens of the η^3-cyclooctenyl system and occurs via the diene-hydride intermediate species that governs the [1,2] metal or [1,2] allyl migration around the ring. The combined effect of the two processes will result in the scrambling of (a) all *endo* hydrogens including the agostic one and (b) all *exo* and allyl hydrogens of the carbocyclic system. This is precisely what we observed in the EXSY spectrum of **11** at the observation (60 °C) temperature (Figure 6). As can be seen from the spectrum, there are clear exchange cross-peaks (marked as black spots in the spectrum) between the *endo* hydrogen signals H(4,8) and H(5,7) as well as between the latter one and the *endo* H(6) resonance. The spectrum also displays a set of exchange cross-peaks connecting the allyl signals themselves and the allyl H(1,3) and the average resonance of the *exo* hydrogen H(4,8) as well as between these latter signals and the corresponding resonance of the other *exo* hydrogen atoms H(5,6,7). These overall EXSY experimental data confirm the hydrogen exchange mechanism discussed above for η^3-cyclooctenyl organometallic complexes and thus may be taken as good evidence for the existence of the agostic C−H···Rh bonding interaction in **11**.

Concluding Remarks

The complexes described above are novel examples of stable agostic hydrocarbon-containing *closo*-metallacarboranes. A very simple and potentially useful method applied in their preparation is based on the reaction of dimeric μ-halide diene-metal complexes [M(η^4-diene)Cl]$_2$ (M = Ir, Rh) with the K^+ salt of C,C′-*ortho*-xylylene-substituted *nido*-C_2B_9-carborane monoanion.[8] It is known from numerous examples found in the literature[1a,14c,15c,21] that η^3-cyclooctenyl complexes once formed could not usually be converted back to the hydrido-diene or the agostic σ,η^2-type precursors due to their thermodynamically more stable structure. These observations correlate well with the rapid irreversible conversion of **9**, both in solution and in the solid state, into isomeric complex **11**. The existence of the reversible equilibrium between the hydrido-diene and the η^3-cyclooctenyl organometallic complexes has earlier been established only for a series of related hydridoruthenium complexes [HRu(η^4-1,5-COD)(η^6-arene)]$^+$ (where arene = C_6H_6, 1,3,5-$Me_3C_6H_3$, C_6Me_6,[22] and phenanthrene[23]), for which the hydrido-diene species were shown to be predominant in solution. In this context we note the equilibrium between **5** and **8** described above, as far as we are aware, represents the only known example of reversible behavior for agostic σ,η^2- and η^3-cyclooctenyl complexes.

Experimental Section

General Considerations. All reactions and manipulations except for column chromatography were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents used for the reactions were dried under appropriate drying agents and distilled under argon prior to use. Short chromatographic columns (ca. 12 cm in length and 1.5 cm in diameter) packed with silica gel (Merck, 230−400 mesh) were used for purification of the complexes. Starting rhodium and iridium compounds [(η^4-COD)RhCl]$_2$,[24] [(η^4-COD)IrCl]$_2$,[25] and [Ir(η^4-COD)(acac)][26] were prepared as described in the literature. The compound [*closo*-1,2-μ-(*ortho*-xylylene)-1,2-$C_2B_{10}H_{10}$] was prepared[27] and further degraded[28] according to the literature methods. The ^{1}H, ^{11}B/^{11}B{^{1}H}, and ^{13}C/^{13}C{^{1}H} as well as the room- and low-temperature 2D correlation NMR spectra were recorded on Bruker AMX-400 (^{1}H at 400.13 MHz, ^{13}C at 100.61 MHz, and ^{11}B at 128.33 MHz) and Bruker DRX-500 (^{1}H at 500.13 MHz, ^{13}C at 125.76 MHz) spectrometers. Mass spectra were recorded on a Kratos MS-902 instrument. IR spectra were obtained on a Carl-Zeiss M-82 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

An Attempt to Synthesize the [PPN]$^+$ Salt of the [*closo*-3,3-(η^4-1,5-COD)-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$]$^-$ Anion by the Reactions of Iridium Complexes 1 or 2 with in Situ Generated [*nido*-7,8-μ-(*ortho*-xylylene)-7,8-$C_2B_9H_9$]$^{2-}$. To a solution of sodium isopropoxide prepared

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from NaH (30 mg, 1.25 mmol) and 3 mL of absolute 2-propanol was added **4** (41 mg, 0.15 mmol) in the solid state, and the suspension was stirred for ca. 1 h. Complex **1** (50 mg, 0.075 mmol) was added to the resulting mixture, which was vigorously stirred an additional 45 min followed by filtration from the precipitate formed. The filtered solution obtained was then mixed with a solution of [PPN]Cl (86 mg, 0.15 mmol) in 1 mL of the same solvent, and the white precipitate was collected by filtration, washed with 1 mL of 2-propanol, and dried in vacuo, affording 31 mg of **3** (27% yield), which was characterized as such by spectroscopy. ^{1}H NMR (acetone-d_6, 25 °C; 400.13 MHz; J(H,H), Hz): 7.75−7.54 (m, 30H, C_6H_5-PPN), 7.03−6.97 (m, 4H, $C_6H_4(CH_2)_2$), 3.09 (d, 2H, J = 15.0, C_6H_4-(CH_2)), 2.84 (d, 2H, J = 15.0, $C_6H_4(CH_2)$), −2.61 (br m, 1H, B−H−B). ^{11}B NMR (acetone-d_6, 25 °C; 128.33 MHz; J(B,H), Hz): −8.0 (d, 2B, J = 139), −9.3 (d, 1B, J = 168), −17.7 (d, 2B, J = 128), −18.7 (d, 2B, J = 137), −32.6 (dd, 1B, J_{bridge} = 49, $J_{term.}$ = 131), −35.0 (d, 1B, J = 139).

An alternate route to the desired anionic iridium-carborane complex consisted of the reaction of **4** (34 mg, 0.125 mmol) with sodium isopropoxide prepared from NaH (25 mg, 1.04 mmol) and **2** (50 mg, 0.125 mmol) under the conditions described above. The solid obtained in 52% yield was deduced to be compound **3** from analyses of the ^{1}H and ^{11}B NMR spectra.

Preparation of [*closo*-3-(σ,η^2-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$IrC_2B_9H_9$] (5). To a stirred solution of **4** (98 mg, 0.357 mmol) in 4 mL of absolute ethanol was added **1** (100 mg, 0.149 mmol) as a solid, and 1 mL of degassed benzene was then added via syringe. After 20 min of vigorous stirring the brownish precipitate formed was filtered to give a beige powder. This was dissolved in 3 mL of methylene chloride followed by filtration through a silica gel column. Solvent was removed in vacuo, affording analytically pure **5** (141 mg, 89% yield) as a pale yellow solid. IR spectrum (KBr, cm^{-1}): 2538 (ν_{BH}). ^{1}H NMR (CD_2Cl_2, 25 °C; 400.13 MHz; J(H,H), Hz; signals of **8** are marked by an asterisk; ratio **5**:**8** = 1:1): 7.31 (m, 2H, C_6H_4), 7.19* (m, 2H, C_6H_4), 7.14 (m, 2H, C_6H_4), 6.99* (m, 2H, C_6H_4), 4.87 (m, 2H, H_2, H_5), 4.43* (d, 2H, J_{AB} = 16.5, (CH_2)$_2$$C_6H_4$), 4.08 (d, 2H, J_{AB} = 17.1, (CH_2)$_2$$C_6H_4$), 3.91* (d, 2H, J_{AB} = 16.5, (CH_2)$_2$$C_6H_4$), 3.46 (d, 2H, J_{AB} = 17.1, (CH_2)$_2$$C_6H_4$), 3.03 (m, 2H, H_1, H_{6-exo}), 2.74 (m, 2H, H_{3-exo}, H_{4-exo}), 2.13 (q-like, 2H, ^3J = 8.4, H_{3-endo}, H_{4-endo}), 1.54 (m, 2H, H_{7-exo}, H_{8-exo}), 1.38 (m, 2H, H_{7-endo}, H_{8-endo}), 0.64* (m, 4H), −5.32 (m, 1H, H_{6-endo}). ^{1}H NMR (CD_2Cl_2, −80 °C; 400.13 MHz; J(H,H), Hz; signals of **8** are marked by an asterisk; ratio **5**:**8** = 1:0.65): 7.28 (m, 2H, C_6H_4), 7.14* (m, 2H, C_6H_4), 7.11 (m, 2H, C_6H_4), 6.95* (m, 2H, C_6H_4), 5.73* (2H, m, H_1, H_3), 5.22* (m, 1H, H_2), 4.81 (m, 2H, H_2, H_5), 4.36* (d, 2H, J_{AB} = 16.5, (CH_2)$_2$$C_6H_4$), 4.02 (d, 2H, J_{AB} = 17.1, (CH_2)$_2$$C_6H_4$), 3.87* (d, 2H, J_{AB} = 16.5, (CH_2)$_2$$C_6H_4$), 3.42 (d, 2H, J_{AB} = 17.1, (CH_2)$_2$$C_6H_4$), 3.01 (m, 2H, H_1, H_{6-exo}), 2.67 (m, 2H, H_{3-exo}, H_{4-exo}), 2.03 (m, 2H, H_{3-endo}, H_{4-endo}), 2.03−1.53* (br m, H_{4-exo}, H_5, H_6, H_7, H_{8-exo}), 1.43 (m, 2H, H_{7-exo}, H_{8-exo}), 1.17 (m, 2H, H_{7-endo}, H_{8-endo}), −0.41* (m, 2H, H_{4-endo}, H_{8-endo}), −5.57 (m, 1H, $H_{6-endo.}$). ^{13}C{^{1}H} (CD_2Cl_2, −73 °C; 100.61 MHz; signals of **8** are marked by an asterisk): 134.8* (C_6H_4-*ipso*), 131.2 (C_6H_4-*ipso*), 129.9*, 128.6, 128.1*, 127.6 (C_6H_4), 99.6* (C_2), 74.9* (C_1, C_3), 70.5* ($C_{carb.}$), 69.0 (C_2, C_5), 66.7 ($C_{carb.}$), 57.2 C_1, C_6), 43.0* (CH_2)$_2$$C_6H_4$), 42.7 (($CH_2$)$_2$$C_6H_4$), 34.3($C_3$, C_4), 33.0* (C_4, C_8), 31.3 (C_7, C_8), 30.8* (C_5, C_7), 26.2* (C_6). ^{11}B NMR ($CDCl_3$, 25 °C; 128.33 MHz; J(B,H), Hz): 3.7 (d, 1B, J = 137), −0.3 (d, 1B, J = 141), −4.9 (d, 3B, J = 139), −7.0 (d, 2B, J = 154), −8.4 (d, 2B, J = 151), −10.5 (d, 2B, J = 147), −14.2 (d, 3B, J = 136), −15.2 (d, 2B, J = 138), −20.9 (d, 2B, J = 152). FAB-MS (m/z): 536 (M^+, calcd 535.91). Anal. Calcd for $C_{18}H_{30}B_9Ir$: C, 40.34; H, 5.60; B, 18.15. Found: C, 40.30; H, 5.63; B, 17.83.

Preparation of [*closo*-3-(σ,η^2-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (9). To a stirred solution of **4** (60 mg, 0.217 mmol) in 1.5 mL of absolute ethanol was added dropwise a solution of **10** (100 mg, 0.203 mmol) in 2.5 mL of degassed benzene. The resulting mixture was stirred at room temperature for 15 min, followed by collection of the orange precipitate by filtration. The microcrystalline solid was dried in vacuo to give **9** (90 mg, 49% yield). ^{1}H NMR (CD_2Cl_2, 25 °C; 400.13 MHz; J(H,H), Hz): 7.35 (br s, 2H, C_6H_4), 7.18 (br s, 2H, C_6H_4), 5.32 (br s, 2H, H_2, H_5), 3.78 (d, 2H, J_{AB} = 17.7, (CH_2)$_2$$C_6H_4$), 3.47 (d, 4H, J_{AB} = 17.7, (CH_2)$_2$$C_6H_4$, H_1, H_{6-exo}), 2.90 (m, 2H, H_{3-exo}, H_{4-exo}), 2.19 (m, 2H, H_{3-endo}, H_{4-endo}), 1.64 (m, 2H, H_{7-exo}, H_{8-exo}), 1.22 (m, 2H, H_{7-endo}, H_{8-endo}), −4.40 (m, 1H, H_{6-endo}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C; 100.61 MHz; J(Rh,C), Hz): 135.0 (C_6H_4-*ipso*), 128.5, 127.6 (C_6H_4), 87.5 (d, J = 8, C_2, C_5), 63.4 (C_1, C_6) 42.7 ((CH_2)$_2$$C_6H_4$), 34.1 ($C_7$, C_8), 29.3 (C_3, C_4). ^{11}B ($CDCl_3$, 25 °C; 128.33 MHz; J(B,H), Hz): 3.0 (d, 1B, J = 137), −0.1 (d, 1B, J = 144), −2.9 (d, 2B, J = 142), −8.1 (d, 2B, J = 142), −11.1 (d, 1B, J = 144), −13.0 (d, 2B, J = 158).

Preparation of [*closo*-3-(η^3-C_8H_{13})-1,2-μ-(*ortho*-xylylene)-3,1,2-$RhC_2B_9H_9$] (11). (a) To a mixture of **4** (67 mg, 0.242 mmol) and **10** (50 mg, 0.101 mmol) taken as solids was added via syringe 10 mL of degassed benzene. The resulting mixture was stirred for 36 h at room temperature. The brown solution was placed on a chromatographic column and was eluted with a 1:1 benzene/*n*-hexane mixture. The wide red band was collected to give, after evaporation, **11** (64 mg, 72% yield) as a dark red crystalline solid. (b) Compound **9** (50 mg, 112 mmol) was dissolved in 5 mL of methylene chloride and was then left to stand at room temperature for 4 h. The resulting deep red solution was filtered through a short silica gel column to give, after evaporation, **11** (49 mg, 98%) as a deep red crystalline solid. IR spectrum (KBr, cm^{-1}): 2551 ν(B−H). ^{1}H NMR ($CDCl_3$, 25 °C; 400.13 MHz; J(H,H), Hz): 7.16 (m, 2H, C_6H_4), 7.00 (m, 2H, C_6H_4), 5.88 (q, 2H, J = 8.5, H_1, H_3), 4.44 (t, 1H, J = 7.4, H_2), 3.89 (d, 2H, J = 16.7, (CH_2)$_2$$C_6H_4$), 3.79 (d, 2H, J = 16.7, (CH_2)$_2$$C_6H_4$), 2.04 (m, 2H, H_{4-exo}, H_{8-exo}), 1.55 (m, 3H, H_{5-exo}, H_{6-exo}, H_{7-exo}), 1.27 (m, 2H, H_{5-endo}, H_{7-endo}), 1.09 (m, 1H, H_{6-endo}), −0.21 (m, 2H, H_{4-endo}, H_{8-endo}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C; 100.61 MHz): 131.02 (C_6H_4-*ipso*), 129.62, 127.90 (C_6H_4), 105.30 (C_2), 84.41 (C_1, C_3), 42.67 ((CH_2)$_2$$C_6H_4$), 30.83 ($C_4$, C_8), 30.14 (C_5, C_7), 22.92 (C_6). ^{13}C NMR ($CDCl_3$, 25 °C; 100.61 MHz; J(C,H), Hz): 131.61 (s, C_6H_4-*ipso*), 130.28 (d, J = 162, C_6H_4), 128.67 (d, J = 163, C_6H_4), 105.99 (d, J = 164, C_2), 85.12 (d, J = 160, C_1, C_3), 76.00 ($C_{carb.}$), 43.31 (t, J = 133, (CH_2)$_2$$C_6H_4$), 31.52 (t, J = 126, C_4, C_8), 30.78 (t, J = 128, C_5, C_7), 22.92 (t, J = 132, C_6). ^{11}B NMR ($CDCl_3$, 25 °C; 128.33 MHz;

Table 2. Crystal Data, Data Collection and Structure Refinement Parameters for 5

formula	$C_{18}H_{30}B_9Ir$
molecular weight	535.91
cryst color, habit	yellow needle
temperature, K	110(1)
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	7.659(1)
b, Å	16.045(2)
c, Å	16.740(2)
β, deg.	97.726(3)
V, Å^3	2038.5(5)
Z	4
$d_{calc.}$, g cm^{-3}	1.746
difractometer	SMART 1000 CCD
scan mode	ω and φ
$2\theta_{max}$, deg	56
μ(Mo Kα, λ = 0.71073 Å), cm^{-1}	65.51
absorption corr	SADABS
transmn factors, min./max.	0.376/0.825
no. of collected reflns	21 591
no. of unique reflns (R_{int})	5057 (0.0312)
no. of obsvd reflns ($I > 2\sigma(I)$)	4362
no. of params	344
R_1 (on F for obsd reflns)[a]	0.0317
wR_2 (on F^2 for all reflections)[b]	0.0805

[a] $R_1 = \sum||F_o| - |F_d||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

J(B,H), Hz): 3.73 (d, 1B, $J = 144$), −3.26 (d, 3B, $J = 153$), −11.06 (d, 3B, $J = 143$), −19.03 (d, 2B, $J = 158$). Anal. Calcd for $C_{18}H_{30}B_9Rh$: C, 48.41; H, 6.72; B, 21.78. Found: C, 48.47; H, 6.78; B, 21.74.

Crystal Data Collection and Structure Refinement Parameters for Complex 5. Details of crystal data, data collection, and the structure refinement of compound **5** are presented in Table 2. The structure has been solved by direct methods and refined by full-matrix least-squares technique against F^2 with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The SAINT[29] and SHELXTL-97[30] program packages were used throughout the calculations.

(29) *SMART* V5.051 and *SAINT* V5.00, Area detector control and integration software; Bruker AXS Inc.: Madison, WI 53719, 1998.

(30) Sheldrick, G. M. *SHELXTL-97*, V5.10, Program for crystal structure refinement; Bruker AXS Inc.: Madison, WI 53719, 1997.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond lengths and angles for **5**. The room-temperature 2D [^{1}H−^{1}H]-EXSY spectrum of **5**. The room-temperature 2D [^{1}H−^{1}H]-COSY and [^{13}C−^{1}H]-HETCOR spectra of **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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