Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 680 (2003) 111–123

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

First agostic *closo*-metallacarboranes with η^3-cyclooctenyl type ligand: synthesis and structural characterization of *closo*-3-[η^3-(*endo*-1,5-dimethylcycloocten-1-yl)]-1,2-μ-(1′,2′-xylylene)-3,1,2-$IrC_2B_9H_9$ and its isomerization to *closo*-3-[η^3-(*exo*-1-methylene-5-methylcyclooctene-1-yl)]-1,2-μ-[η^2-(1′,2′-xylylene)]-3,1,2-$IrC_2B_9H_9$

Alexander V. Safronov, Tatiana V. Zinevich, Fedor M. Dolgushin, Evgenii V. Vorontsov, Oleg L. Tok, Igor T. Chizhevsky [1],*

A. N. Nesmeyanov Institute of Organoelement Compounds RAS, Inorganic Chemistry, 28 Vavilov Street, GSP-1, 119991 Moscow, Russian Federation

Received 3 March 2003; received in revised form 24 March 2003; accepted 26 March 2003

Dedicated to Professor M. Frederick Hawthorne on the occasion of his 75th birthday in recognition of his outstanding contributions to polyhedral boron, metalla-cage-boron and carborane chemistry

---

Abstract

The reaction of a new iridium reagent $[Ir(\eta^4\text{-}1,5\text{-}Me_2COD)Cl]_2$ (**1**) with [*nido*-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-7,8-$C_2B_9H_{10}]^-K^+$ (**2**) in solution of C_6H_6–MeOH mixture or in C_6H_6 afforded either an agostic (C–H···Ir) *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-3,1,2-$IrC_2B_9H_9$ (**3**) along with *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-8-(EtO)-3,1,2-$IrC_2B_9H_8$ (**4**) or the only complex **3** in high yield. Complex **3** in dichloromethane solution is quantitatively converted to isomeric η^3-exo-allylic complex *closo*-3-[η^3-(1-*exo*-CH_2-5-MeC_8H_{12})]-1,2-μ-[η^2-(1′,2′-$CH_2C_6H_4CH_2$–)]-3,1,2-$IrC_2B_9H_9$ (**5**) for a few days. All new complexes **3**, **4** and **5** were characterized by single-crystal X-ray diffraction studies, which confirmed the existence of an agostic C–H···Ir interaction in **3** and revealed a weak η^2-coordination of the metal atom with one of the aromatic bonds of *ortho*-xylylene cage substituent in **5**. The normal and low-temperature ^{1}H- and $^{13}C/^{13}C\{^1H\}$-NMR spectra as well as 2D COSY/HETCOR NMR data obtained for the studied complexes are discussed in details.

Keywords: *closo*-Metallacarboranes; Iridium; Agostic (C–H···Ir) interaction; Allylic ligand isomerization; NMR spectroscopy; X-ray diffraction

---

1. Introduction

Although the first 12-vertex *closo*-metallacarboranes of both rhodium and iridium were discovered by Hawthorne and co-worker almost simultaneously as early as 1974 [1], in the subsequent years iridium complexes received much less attention [2–4] than their rhodium congeners. As to 12-vertex mononuclear complexes belonging to hydrocarbon-containing *closo*-iridacarborane family, (η-L)$_n$-*closo*-$IrC_2B_9H_{11}$ (L = carbocyclic diene/dienyl, olefin or allyl ligands), until very recently [5], those of our knowledge were limited to a single representative with η^5-Cp* ligand at the iridium

---

* Corresponding author. Tel.: +7-095-1359334; fax: +7-095-1355085.

E-mail address: chizbor@ineos.ac.ru (I.T. Chizhevsky).

[1] One of the authors of this paper (I.T.C.) was really lucky to work within the group of Professor Hawthorne for about year-and-a-half and participate in implementation of his interesting ideas. There is no doubt that these years had a standing effect on all my subsequent work that would have shaped differently had I not been feeling the watchful eye and relentless help of my demanding teacher and kind friend ever since.

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00215-8

vertex [3]. At the same time, numerous related *closo*-rhodacarboranes with η-carbocyclic ligands were reported [6], some of them being extensively studied as catalysts or catalyst precursors in homogeneous catalysis [7].

The preparative efforts targeting *closo* 12-vertex iridium systems suffer from a fairly limited choice of convenient synthetic routes for introducing of π-hydrocarbon ligands into the *closo*-iridacarborane framework [3,8]. This is, presumably, due to much shorter supply of hydrocarbon-containing iridium reagents, as compared with those of rhodium congeners, which could be used in traditional ligand-exchange reactions with in situ generated dicarbollide dianions (usually through a base degradation of the parent C_2B_{10}-*closo*-carboranes). While searching for more reliable preparative method for platinum metal *closo*- and/or *exo*-*nido*-metallacarboranes with η-carbocyclic ligands, we have recently developed a simple one-pot procedure which is based on the reaction of dimeric μ-halide diene-metal complexes $[M(\eta^4\text{-diene})Cl]_2$ (M = Rh, Ir) with K^+ salts of isomeric *nido*-carborane monoanions $[nido\text{-}7,n\text{-R,R}'\text{–}C_2B_9H_{10}]^-$ ($n = 8$ or 9; R, R′ = H, Alk, ArAlk) [5]. This method allowed in one step to prepare a series of new *closo*-rhodacarboranes with η-carbocyclic ligands of π-allyl and π-allylolefin types and a few related *closo*-iridacarboranes [5,9] in modest to high yields. It seemed, probable, therefore, that under these very mild conditions, which exclude the use of either strong bases or acids (reagents are usually treated in solution of benzene–ethanol mixture at ambient temperature [5]), syntheses of other novel *closo*-(η-carbocycle)iridacarboranes could be expected.

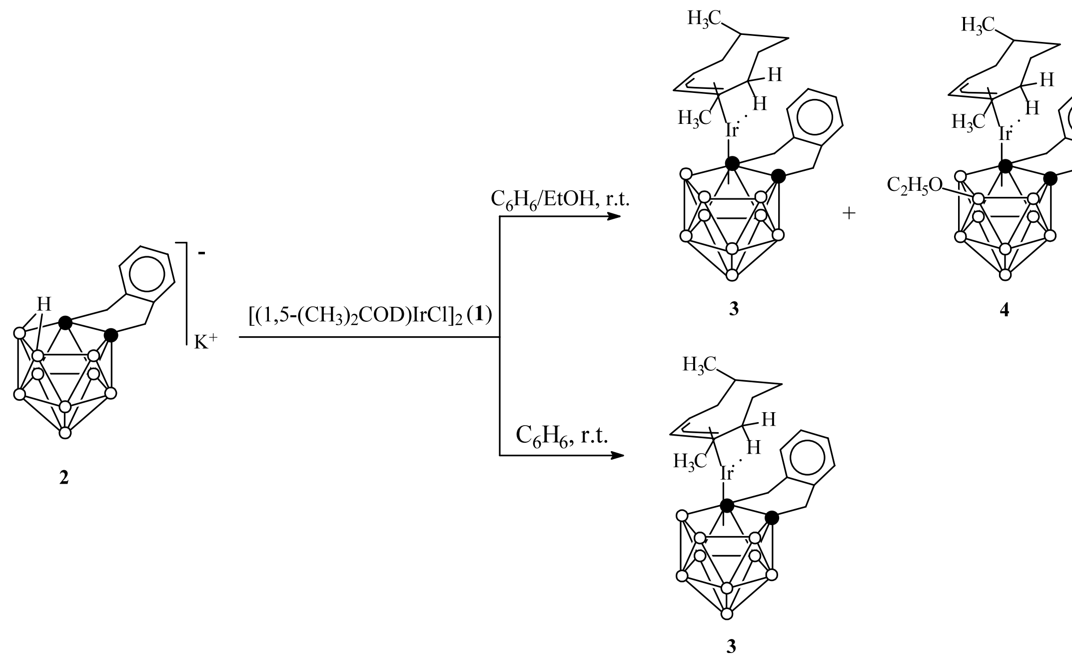
The results reported here are based on the development of this approach and, in particular, involved the reaction of a new μ-halide iridium dimer $[Ir(\eta^4\text{-}1,5\text{-}Me_2COD)Cl]_2$ (**1**, where COD = cycloocta-1,5-diene) with sterically crowded *nido*-carborane derivative $[nido\text{-}7\text{-}R^1\text{-}8\text{-}R^2\text{-}7,8\text{-}C_2B_9H_{10}]^-K^+$ (**2**, where R^1, R^2 = μ-1′,2′-$CH_2C_6H_4CH_2$–) which produced an agostic (C–H···Ir) *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-3,1,2-$IrC_2B_9H_9$ (**3**) as a principal product, along with ethoxy-cage-substituted species *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-8-(EtO)-3,1,2-$IrC_2B_9H_8$ (**4**) as a minor product. This paper also describes the rearrangement of complex **3** which occurs slowly in dichloromethane solution at ambient temperature to form η^3-*exo*-allylic isomer *closo*-3-[η^3-(1-*exo*-CH_2-5-MeC_8H_{12})]-1,2-μ-[η^2-(1′,2′-$CH_2C_6H_4CH_2$–)]-3,1,2-$IrC_2B_9H_9$ (**5**). Also presented are single-crystal X-ray diffraction studies of complexes **3**, **4** and **5**, which confirmed their overall geometry and revealed some peculiar structural details of these molecules, specifically the existence of an agostic C–H···Ir interaction in **3**, and a weak η^2-coordination of the metal atom with one of the aromatic bonds of *ortho*-xylylene cage substituent in **5**.

2. Results and discussion

2.1. Synthesis and characterization of complexes *3*, *4*, and their iridium-diene precursor $[Ir(\eta^4\text{-}1,5\text{-}Me_2COD)Cl]_2$ (*1*)

By slightly modifying procedure published for the known dimeric complex $[Ir(\eta^4\text{-}COD)Cl]_2$ starting from the 1,5-dimethylcycloocta-1,5-diene and $H_2IrCl_6 \cdot 6H_2O$ [10] we have succeeded in preparation of a new hydrocarbon-containing iridium reagent $[Ir(\eta^4\text{-}Me_2C_8H_{10})Cl]_2$ (**1**) as analytically pure pale yellow microcrystalline solid in 62% yield. According to the recently reported general procedure [5], the reaction between **1** and *nido*-carborane **2** in C_6H_6–EtOH (4:1) mixture at ambient temperature for 30 min afforded a 10:1 mixture of complexes **3** and **4** with the combined 71% yield (Scheme 1). The mixture of complexes obtained was then successfully separated into individual compounds **3** and **4** by column chromatography on silica gel. If solvents C_6H_6–EtOH for the reaction were taken in a 1:4 ratio, complexes **3** and **4** were formed in a 7:1 ratio. When this reaction was carried out in solution of pure benzene instead of C_6H_6–EtOH mixture, complex **3** was found to be the only reaction product obtained in 89% yield.

The low-temperature ^1H- and $^{13}C\{^1H\}$-NMR spectra are characteristic of **3** having the η^3-cyclooctenyl type ligand with *endo*-methallyl portion of the ring coordinated by the iridium atom. One of the most reliable indication for that is the observation of two medium-field allylic resonances of an equal intensity at 5.14 (br. d) and 4.59 ppm (q-like signal) in the ^1H-NMR spectrum (−73 °C, CD_2Cl_2) of **3**. Besides, there are two resonances at 2.33 and 0.78 ppm each of 3H relative intensity area originating from the non-equivalent methyl groups of which one at 0.78 ppm has revealed as a doublet with $^3J(H,H) = 5.6$ Hz and can thus be assigned to the methyl group of an aliphatic part of the carbocyclic ligand, but the other at 2.33 ppm, which is observed as a singlet, can apparently be attributed to the methyl group of the allylic unit. The carborane cage *ortho*-xylylene substituent gives rise to the two sets of resonances arising from bridging methylene groups and aromatic protons, and in particular, there are two AB patterns of equal intensities with the doublet components centered at 4.20 and 3.58 ppm ($J_{AB} = 16.8$ Hz) and 4.04 and 3.90 ppm ($J_{AB} = 16.8$ Hz) along with the three phenyl proton multiplets of a 2:1:1 intensity ratio at 7.11 (2H), 7.01 (1H) and 6.91 (1H) ppm, respectively. An essentially noteworthy feature of the spectrum is the presence of a unique high-field resonance at −2.80 ppm.



Scheme 1.

Since this resonance shows unusually downfield shift as compared with those of a typical iridium–hydride complexes [11], and represents a single proton via integration, we suggested the presence in **3** of an agostic interaction between the iridium atom and one of the *endo*-C–H bond of the carbocyclic ligand at adjacent position to the allylic unit. We note, at the observation temperature (−73 °C), the ^{1}H-NMR spectrum is clearly consistent with **3** having a 'static' agostic structure where no molecular symmetry plane exists.

The lack of symmetry in the molecule **3** is also established by the low-temperature $^{13}C\{^{1}H\}$-NMR spectrum which showed 20 separate resonances of which 10 ($1C+3CH+4CH_2+2CH_3$) account for the carbocyclic ligand. A combination of the low-temperature DEPT $^{13}C\{^{1}H\}$-NMR and a 2D [$^{1}H-^{13}C$] heteronuclear correlation (HETCOR) spectroscopy was used to assign ^{13}C and ^{1}H resonances of **3**. Thus, the resonance of the carbon atom involving in the C–H···Ir agostic interaction which is observed at $\delta(^{13}C)$ 33.8 ppm was clearly assigned as such from the [$^{1}H-^{13}C$]-HETCOR spectrum where a strong cross peak connecting that resonance with the proton resonance at −2.80 ppm has been found. We have also examined the low-temperature (−73 °C) ^{13}C-NMR spectrum of **3** as it is well known that the low value of ^{1}J(C,H) observed for sp^{3} carbons is diagnostic indicator of C–H···M agostic interactions [12,13]. As can be seen from Fig. 1, the only carbon resonance of **3**, namely at 33.8 ppm (marked by a star), displays as doublet of doublets in the proton-coupled spectrum which is apparently due to non-equivalency of two hydrogen atoms attached to this carbon atom wherein one is involved in the agostic interaction with the iridium center. The observed values for coupling constants ^{1}J(C,H) of 132 and 104 Hz found from this signal clearly indicate that, as expected, the 'static' agostic structure for **3** to be existed at this temperature. Since typical values for $^{1}J(C,H_{ag})$ for static agostic systems are usually in the range of 60–90 Hz and very seldom are above of 100 Hz [13], the agostic C–H···Ir interaction in **3** appeared to be rather weak and this has been proven to be the case on analysis of an X-ray structural data of **3** (vide infra).

The ^{1}H- and $^{13}C\{^{1}H\}$-NMR spectra of **4** are very similar to those of **3**, except for much better resolution observed for the aliphatic part in the ^{1}H-NMR spectrum. This allowed us to assign all basic aliphatic signals of the carbocyclic ligand of **4** with use of its normal temperature [$^{1}H-^{1}H$]-COSY spectrum. As in the ^{1}H-NMR spectrum of **3**, a unique high-field resonance is also observed for **4**, but in this case it appears somewhat downfield, at δ −1.09 ppm. A set of two related resonances observed at δ 3.23 ppm [br. dq, $^{3}J(H,H)=6.8$ Hz, 2H] and δ 0.92 ppm [t, $^{3}J(H,H)=6.8$ Hz, 3H] has provided additional structural details of **4**. Due to quite characteristic multiplicity of these resonances and the observed values of ^{3}J(H,H), these could reasonably be attributed to ethoxy group. Taking into account that in the proton-coupled ^{11}B-NMR spectrum of **4** one resonance from a set of nine has revealed as a sharp singlet at $\delta(^{11}B)$ +4.0 ppm, in contrast with that of **3**, where all resonances observed were doublets, we have concluded that ethoxy group in **4** is attached to one of the cage boron atoms. In order to determine at what particular boron atom this substituent is located, an X-ray diffraction study of **4** was undertaken which, similar

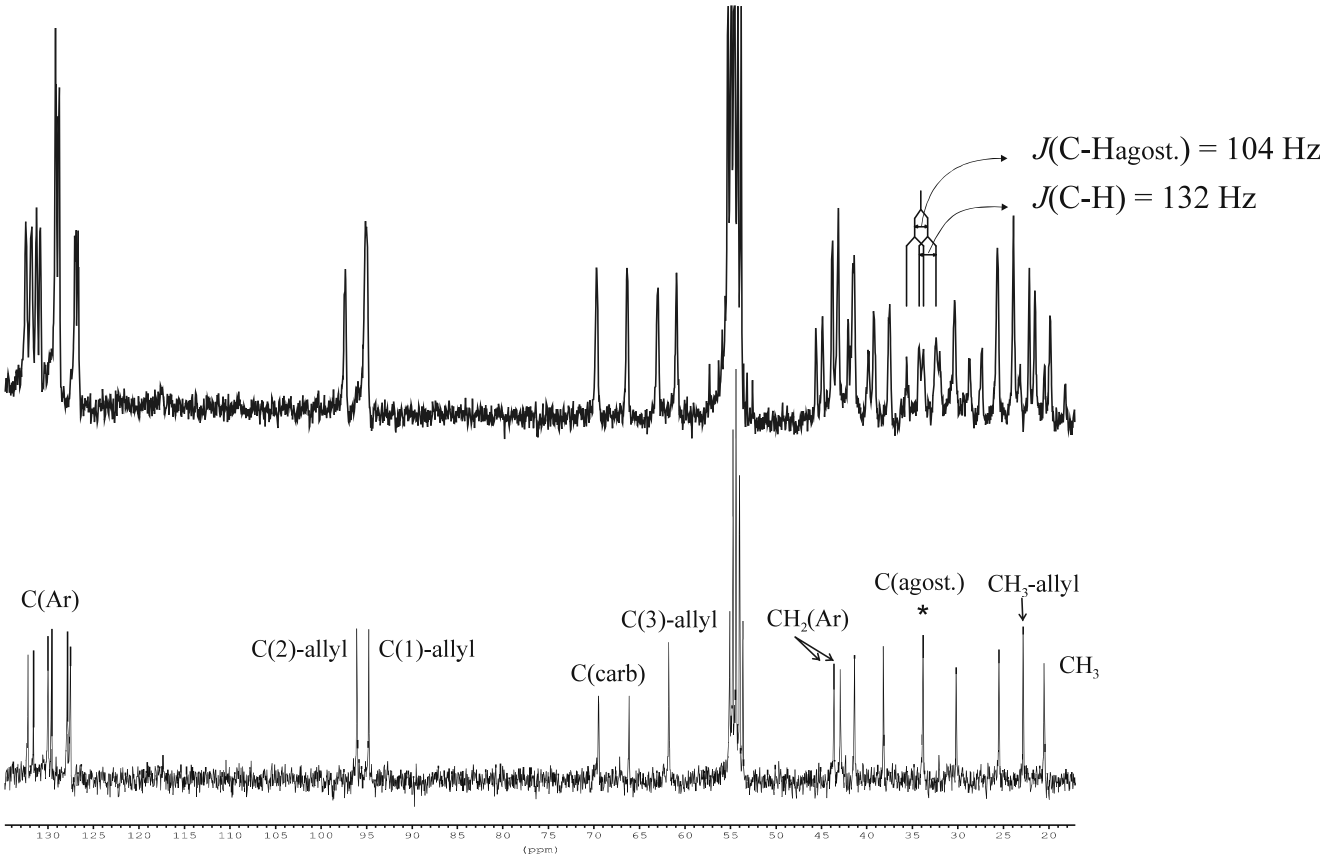


Fig. 1. Low-temperature (−73 °C, CD_2Cl_2) 100.61 MHz ^{13}C- (top) and $^{13}C\{^1H\}$-NMR (bottom) spectra of **3** showing the values of $J(^1H,^{13}C)$ coupling of C(8) carbon resonance (marked by a star).

to other known examples of alkoxy-cage-substituted metallacarboranes [14], unambiguously positioned an ethoxy group at the B(8) atom of the carborane cage. An ORTEP representation of the molecular structure of **4** is shown in Fig. 2 and selected bond distances and angles are given in Table 1. However, because of the major disorder found in crystal of **4**, the precision of the X-ray structural results is rather low that prevents from of fine geometrical details of molecule **4** including those of the structural fragment involved in agostic C–H···Ir interaction.

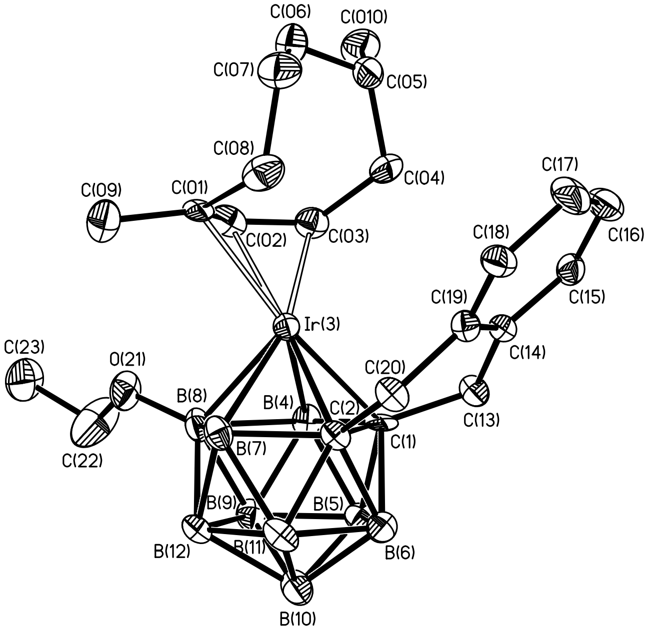


Fig. 2. ORTEP representation of the molecular structure of **4** with thermal ellipsoids drawn at 30% probability level.

On the other hand, an X-ray diffraction study of a single crystal **3** (grown from CH_2Cl_2–n-hexane), where all hydrogen atoms were directly located from the difference Fourier map, and their position parameters were refined, provided firmly confirmation of the presence of an agostic C–H···Ir interaction in the complexes obtained. First of all, as found in the solid-state structure of **3** (see Fig. 3 for an ORTEP representation of its molecular structure and Table 1 for the selected bond distances and angles), and in accord with the existence of the π-allyl system in this molecule, the C–C distances within the allylic portion of the ring (C(01)–C(02) and C(02)–C(03) of 1.408(13) and 1.426(13) Å, respectively) proved to be noticeably shorter than any other aliphatic C–C distances in the ring, which range from 1.508(16) to 1.559(13) Å. However, unlike typical π-allyl complexes, where the

Table 1
Selected bond lengths (Å) and angles (°) for complexes **3**, **4** and **5**

	3	**4**	**5**
Bond lengths			
Ir(3)–C(1)	2.146(9)	2.10(2)	2.142(3)
Ir(3)–C(2)	2.222(8)	2.17(2)	2.146(4)
Ir(3)–B(4)	2.190(10)	2.18(1)	2.190(4)
Ir(3)–B(7)	2.133(12)	2.20(1)	2.182(5)
Ir(3)–B(8)	2.125(11)	2.19(1)	2.144(5)
Ir(3)–C(01)	2.192(8)	2.26(3)	2.187(4)
Ir(3)–C(02)	2.163(8)	2.11(3)	2.176(4)
Ir(3)–C(03)	2.160(8)	2.21(3)	
Ir(3)···C(04)	3.11(1)	3.08(3)	
Ir(3)···C(08)	2.66(1)	2.72(3)	
Ir(3)–H(08B)	2.22(8)		
Ir(3)–C(09)			2.142(4)
Ir(3)–C(14)			2.792(4)
Ir(3)–C(19)			2.785(4)
C(1)–C(2)	1.641(12)	1.68(2)	1.734(5)
C(1)–C(13)	1.491(11)	1.53(2)	1.515(5)
C(2)–C(20)	1.536(12)	1.51(2)	1.526(5)
C(13)–C(14)	1.537(11)	1.51(1)	1.513(5)
C(14)–C(15)	1.383(11)	1.41(1)	1.388(6)
C(14)–C(19)	1.373(11)	1.40(1)	1.410(6)
C(15)–C(16)	1.392(11)	1.39(1)	1.384(7)
C(16)–C(17)	1.358(12)	1.39(2)	1.373(9)
C(17)–C(18)	1.383(13)	1.40(2)	1.368(8)
C(18)–C(19)	1.390(12)	1.33(1)	1.396(6)
C(19)–C(20)	1.525(13)	1.51(1)	1.508(6)
C(01)–C(02)	1.408(13)	1.39(2)	1.407(6)
C(01)–C(08)	1.508(16)	1.53(2)	1.499(6)
C(01)–C(09)	1.523(13)	1.46(2)	1.408(7)
C(02)–C(03)	1.426(13)	1.42(3)	1.505(7)
C(03)–C(04)	1.531(12)	1.54(2)	1.524(7)
C(04)–C(05)	1.541(12)	1.54(2)	1.533(8)
C(05)–C(06)	1.524(14)	1.50(3)	1.536(8)
C(05)–C(010)	1.504(15)	1.50(2)	1.533(8)
C(06)–C(07)	1.510(14)	1.50(3)	1.521(9)
C(07)–C(08)	1.559(13)	1.53(2)	1.545(7)
Bond angles			
C(1)–C(13)–C(14)	115.1(8)	111.3(8)	109.0(3)
C(15)–C(14)–C(13)	116.7(7)	116.0(7)	121.1(4)
C(18)–C(19)–C(20)	116.5(8)	117.8(8)	121.0(4)
C(19)–C(20)–C(2)	113.7(7)	116.8(8)	109.1(3)
C(02)–C(01)–C(08)	120.4(10)	119(2)	121.6(4)
C(02)–C(01)–C(09)	120.8(10)	121(2)	116.4(4)
C(08)–C(01)–C(09)	116.9(10)	120(2)	121.6(4)
C(01)–C(02)–C(03)	120.4(9)	128(2)	123.9(4)
C(02)–C(03)–C(04)	130.3(9)	126(1)	115.4(4)
C(01)–C(08)–C(07)	115.5(10)	112(1)	108.8(4)

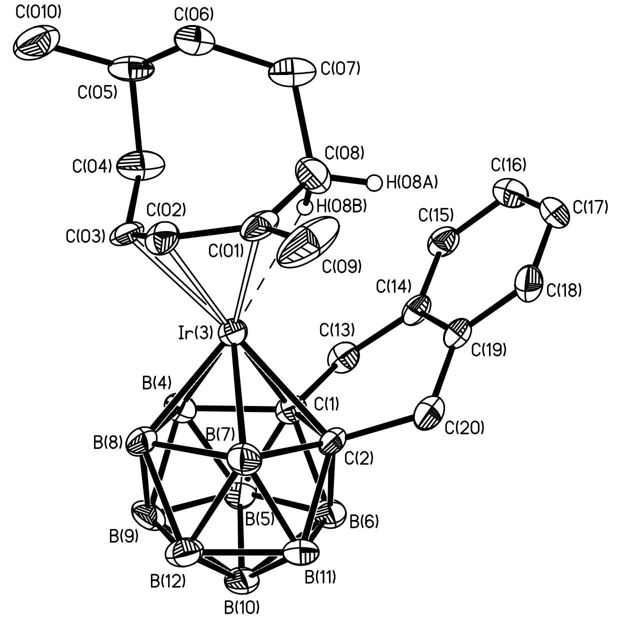


Fig. 3. ORTEP representation of the molecular structure of **3** with thermal ellipsoids drawn at 30% probability level. The hydrogen atoms are omitted for clarity except for the hydrogen atoms at C(08).

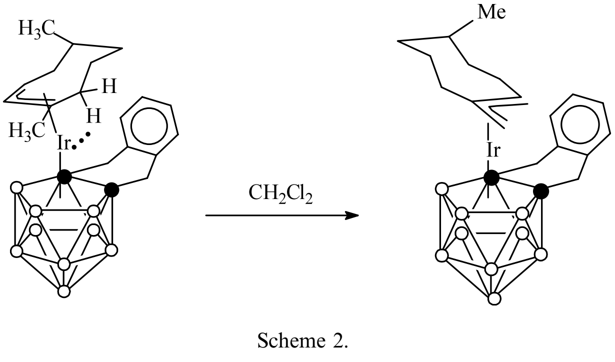
metal atom is usually closer to the allylic center carbon atom than to the two terminal ones [15], in molecule **3** both Ir–C(02) and Ir–C(03) distances (2.163(8) and 2.160(8) Å) are essentially equal while the third Ir–C(01) separation, 2.192(8) Å, is slightly longer. This is, presumably, the result of the steric effect caused by methyl substituent at the allylic unit of the C_8-ring. Similar variations of M–C distances in case of substituted allyl coordination was found in the dimeric π-allylpalladium chloride complex $[PdCl(\eta^3\text{-}C_{10}H_{16}Cl)]_2$ [16] which has the same *endo*-methallyl portion of the carbocyclic ligand. To detect an agostic C–H···Ir interaction in **3** some structural points should be considered. It is apparent from the overall geometry of **3** that the shortening of Ir···H(08B) distance of up to 2.22(8) Å coupled with much closer Ir···C(08) separation of 2.66(1) as compared with that of Ir···C(04), 3.11(1), are both the result of the attractive Ir···H(08B) interaction. Also significant are differences in deviation of C(08) and C(04) atoms with respect to the plane of allyl moiety (0.53 and 0.90 Å, respectively) as well as differences in bond lengths of C(01)–C(08) of 1.508(16) and C(03)–C(04) of 1.531(12) Å which, apparently, arise from the same reason, because of the C–H(08B)···Ir interaction. A similar, but more pronounced, trend in asymmetry of the allyl units have been observed in several known agostic η^3-cyclooctenyl organometallic complexes of transition metals [17]. Finally, the comparison of the Ir···H(08B) separation found in **3** with those of the typical metal–hydrogen separations in the agostic groups (usually ranging from 1.8 to 2.2 Å [13]) leads to the conclusion that the agostic interaction in **3** is relatively weak.

In this context it should be noted, that for the two crystallographically studied *closo*-rhodacarboranes with η^3-cyclooctenyl ligand, *closo*-3-(η^3-C_8H_{13})-1,2-Me_2-3,1,2-$RhC_2B_9H_9$ [6a] and *pseudocloso*-3-(η^3-C_8H_{13})-1-SPh-2-Ph-3,1,2-$RhC_2B_9H_9$ [7c], which are somewhat related to **3**, the NMR spectroscopy as well as X-ray diffraction studies provided no indication for the existence of an agostic C–H···Rh interaction, and, therefore, the Rh(III) atom in these molecules was postulated to attain 16-electron rather than 18-electron configuration. While other agostic (C–H···Rh) metallacarborane complexes of the *closo*-(π,σ-carbocycle) type are known [6b,6g,6h,9], 18-electron complex **3** is at present the first *closo*-metallacarborane species with the η^3-cyclooctenyl type ligand in which an agostic C–H···Ir interaction was fully documented by a combination of NMR and X-ray diffraction studies.

2.2. Rearrangement of 3 into isomeric complex 5. NMR characterization and single crystal X-ray diffraction structure of 5

Complex **3** was found to be sufficiently stable in the solid-state and could also be stored indefinitely in solution of chlorinated solvents at temperature below −40 °C for a long time. However, at room temperature it becomes quite reactive and undergoes irreversible transformation ($t_{1/2} \sim 3$ days at room temperature) to afford a new species formulated as *closo*-3-[η^3-(1-*exo*-CH_2-5-MeC_8H_{12})]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-3,1,2-$IrC_2B_9H_9$ (**5**). By stirring of **3** in solution of dry CH_2Cl_2 for 1 week at 22 °C followed by column chromatography on silica gel complex **5** could be obtained in 93% yield (Scheme 2).

An examination of the normal temperature ^1H- and $^{13}C\{^1H\}$-NMR and a 2D [$^1H-^1H$]-COSY combined with a 2D [$^1H-^{13}C$]-HETCOR (Fig. 4) spectra allowed to determine the structure of **5**. In the ^1H-NMR spectrum of **5** in CD_2Cl_2 no signals attributable to either agostic or terminal metal hydrides were observed in the high-field region of up to −20 ppm, which was indicative that **5** did not retain an agostic structure of its precursor, complex **3**. At the same time, the ^1H-NMR spectrum exhibits two characteristic doublets which have quite different chemical shifts of 4.67 and 1.54 ppm and identical small coupling constants $^2J(H,H)_{gem} = 2.4$ Hz which is typical of *syn–anti* protons of methylene group in the exocyclic η^3-allylmetal [6c,18] and other η-enylmetal complexes [19]. Another outer side allylic proton also appears in aliphatic part of the spectrum as a doublet of doublets with $^2J(H,H) = 9.6$ and 4.8 Hz, and is coincidentally overlapped with one of the aliphatic resonances of the carbocyclic ligand. The assignment made for the proton resonances of the carbocyclic *exo*-allyl portion has been achieved from the [$^1H-^{13}C$]-HETCOR spectrum of **5**, where one cross peak connects carbon resonance at 58.4 ppm (*exo*-CH_2) and two proton resonances at 4.67 (H_{syn}) and 1.54 ppm (H_{anti}), and another cross peak connects carbon resonance at 86.2 ppm (*exo*-CH_2CCH–) to the doublet of doublets of overlapped proton signals centered at 1.66 ppm. At last, central allylic carbon resonance at 119.2 ppm, predictably, does not share a cross peak with any observable proton signals. The remaining assignments of ^1H- and ^{13}C-NMR spectra of **5** are given in Section 3.



Scheme 2.

If complex **5** indeed is a neutral mononuclear species of the above formula, then there should be one additional uncharged two-electron-donor ligand attached to the metal vertex to attain its 18-electron configuration. The overall geometry of **5** determined by an X-ray diffraction study (see Fig. 5 for an ORTEP representation of the structure and Table 1 for the selected bond distances and angles) confirmed the pseudooctahedral 18-electron configuration of the Ir(III) atom in this molecule. The iridium atom in **5** is quite symmetrically bound to the planar C_2B_3 face of the *nido*-carborane cage which occupies, formally, three facial coordination sites [Ir–C(1) and Ir–C(2) of 2.142(3) and 2.146(4) Å, respectively, and Ir–B(*avg*), 2.172(5) Å]. The *exo*-allylic η^3-carbocyclic ligand occupies two additional coordination sites around the metal center and, as expected, the η^3-bonding mode for the allylic unit is unsymmetrical. The Ir–C(09) separation of 2.142(4) Å proved to be considerably shorter than the two other distances Ir–C(01) of 2.187(4) and Ir–C(02) of 2.176(4) Å. At the same time, the C(01)–C(02) and C(01)–C(09) bond lengths in the η^3-coordinated *exo*-allyl moiety are quite identical, 1.407(6) and 1.408(7) Å, respectively. Nearly, the same structural picture can be seen in many of the known η^3-benzyl [20] and β-pinene-based η^3-*exo*-allylic complexes [21] wherein the shortest M–C bond is the one involving to the *exo*-cyclic carbon atom. On the other hand, in earlier studied *closo*-rhodacarboranes with $\eta^{2,3}$-methylennorbornadienyl type ligands, *closo*-3,3-($\eta^{2,3}$-$C_7H_7CH_2$)-1,2-R_2-3,1,2-$RhC_2B_9H_9$ (where R = H [7b], R = Me [6c]) as well as in their cationic η^5-cyclopentadienyl analogues [($\eta^{2,3}$-$C_7H_7CH_2$)Rh(η^5-C_5H_5)]$^+$[PF_6]$^-$ [18b] these distances between metal atom and *exo*-cyclic carbon atom were found to be longer than any other bond distances in the metal–allyl systems. It is interesting to note that the remaining ligand site in **5** proved to be occupied by the *ortho*-xylylene cage substituent functioning in this case as a weak chelating η^2-ligand. Indeed, the relatively short distance between the iridium atom and the midpoint of the C(14)=C(19) bond of 2.698 Å consistent with the presence of such specific interaction in **5**. This is

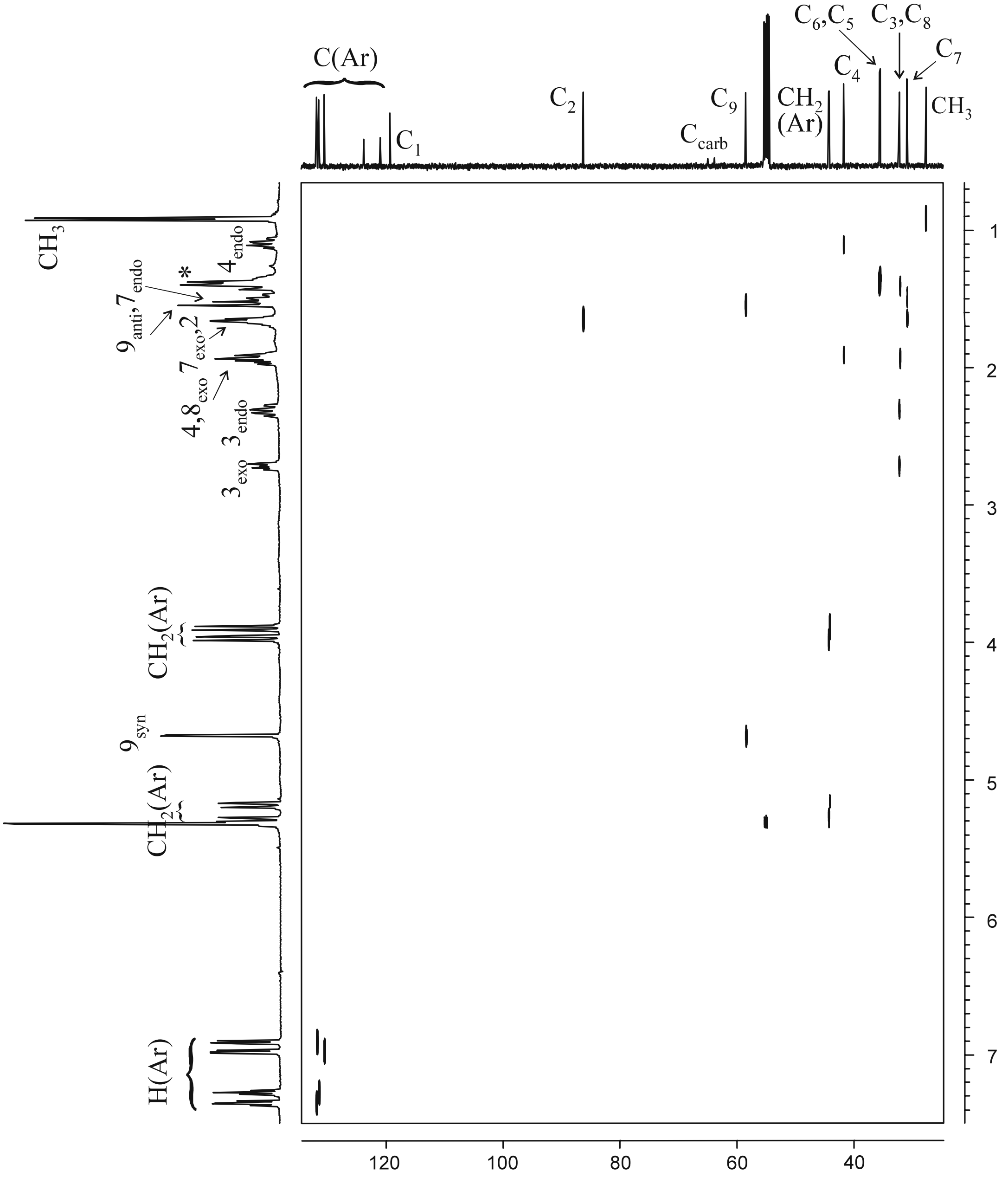


Fig. 4. 500.13 MHz 2D ($^1H-^{13}C$) heteronuclear correlated spectrum of **5** in CD_2Cl_2 solution at 23 °C showing the assignment of the carbon and proton resonances. The spin–spin relationships among resonances at 2.71 ($H_{3\text{-}exo}$), 2.31 ($H_{3\text{-}endo}$), 1.93 ($H_{4\text{-}exo}$), and 1.66 (H_2-all) ppm were proved by double-irradiation experiments. Complex multiplet arising from $H_{8\text{-}endo}$, $H_{6\text{-}exo/endo}$ and H_5 is marked by a star.

also reflected in elongation of the C(14)=C(19) bond [1.410(6) Å] as compared with other carbon–carbon bonds in the C_6-ring of the *ortho*-xylylene substituent, span the range from 1.368(8) to 1.396(6) Å. It is noteworthy, that there is also a major difference in the dispositions of *ortho*-xylylene cage substituents with regard to the carborane cage in **3** and **5**. The angle between the normals to the least-square planes defined by the eight *ortho*-xylylene carbon atoms and by the C_2B_3 plane of the carborane cage for complex **5** (78.6°) is much greater than those found in **3** (48.8°) or in the related *closo*-3,3-$(PPh_3)_2$-3-H-1,2-μ-(1,2-$CH_2C_6H_4CH_2$–)-3,1,2-$RhC_2B_9H_9$ (38.7°) [22]. At the same time, this angle in **5** is close to those found in species belonging to a group of *exo*–*nido* complexes, *exo*-*nido*-6,10-[$(PPh_3)(PCy_3)$Rh]-6,10-μ-$(H)_2$-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-7,8-$C_2B_9H_8$ (81.0°) [22] and *exo*-*nido*-5,6,10-[$Cl(PPh_3)_2$Os]-5,6,10-μ-$(H)_3$-10-H-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-7,8-$C_2B_9H_6$ (81.9°) [23], where no steric repulsive interaction between the *ortho*-xylylene group and the metal-containing moiety located at the *exo*-position can be expected. All these structural features, taken together, are evidences for the presence of a weak metal-to-*ortho*-xylylene η^2-coordination in

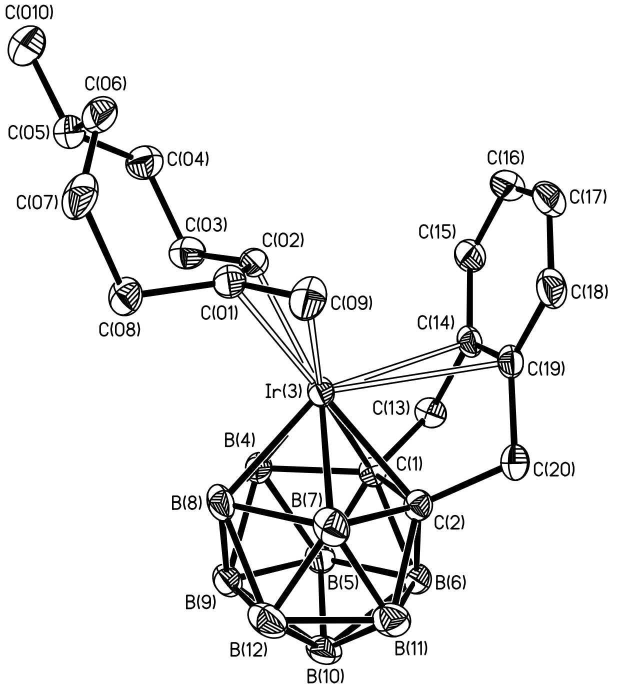


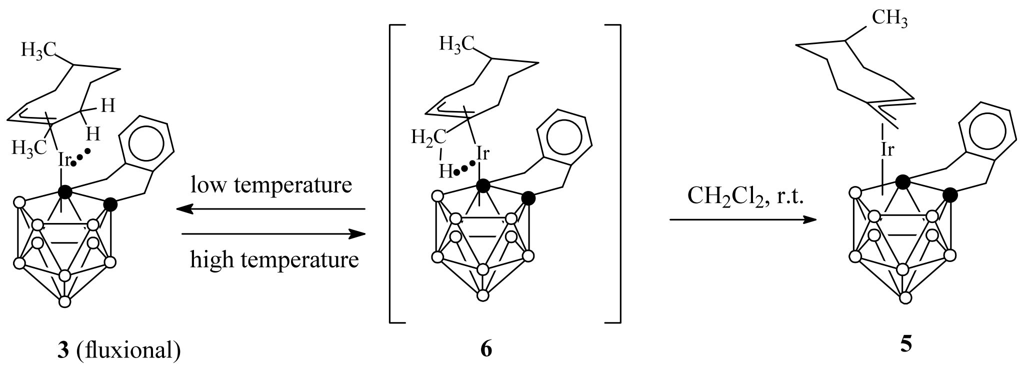
Fig. 5. ORTEP representation of the molecular structure of **5** with thermal ellipsoids drawn at 30% probability level. The hydrogen atoms are omitted for clarity.

complex **5** which, in fact, effectively stabilizes the iridium center providing thus two additional electrons for attaining 18-electron configuration in its valence shell.

The convincing evidence for the presence of a η^2-coordinated *ortho*-xylylene group in **5** in the solution has also been obtained from the comparison of $^{13}C\{^1H\}$-NMR spectra of **5** with those of **3** and **4**. In the same way as with complex **3** (see above), a combination of the DEPT $^{13}C\{^1H\}$-NMR and a 2D [$^1H-^{13}C$]-HETCOR spectroscopy was used to assign ^{13}C resonances in the spectrum of **5**. In the low-field part of the $^{13}C\{^1H\}$-NMR spectra of **3** and **4** there are sets of six non-equivalent carbon resonances arising from the C_6-ring of *ortho*-xylylene group with *ipso*-carbon resonances reduced in intensity and located at lowest field at 132.2 and 131.6 ppm for **3** and 132.3 and 131.7 ppm for **4**, respectively. The $^{13}C\{^1H\}$-NMR spectra of **5** displayed also six resonances for the C_6-ring of *ortho*-xylylene group of which two arising from *ipso*-carbon atoms proved to be shifted considerably upfield [$\delta(^{13}C)$, 123.6 and 120.8 ppm] as compared with those for **3** and **4**. Such shielding of *ipso*-carbon resonances in **5** appears unexpectedly strong and can, definitely, be considered as an argument demonstrating the presence of coordination of the iridium atom to the aromatic bond of *ortho*-xylylene group, namely to C(14)=C(19). Although, a variety of structural types of di- and monocarbon *closo*-metallacarboranes with different chelating alkene-containing groups attached to the cage ligand have been reported [24], we believe that complex **5** represents the first metallacarborane, where *ortho*-xylylene cage substituent plays the role of η^2-coordinating ligand for the *closo*-metallacarborane framework.

In the reaction pathway leading to rearrangement of **3** into **5** one may reasonably propose the existence of an equilibrium between **3** and one more agostic complex **6** (Scheme 3) through which an irreversible conversion of **3** to the final product **5** might occur by an [1,2]-allyl or [1,4]-hydrogen shift mechanism via hydrido-diene intermediate species. However, no direct evidence for an equilibrium between these two agostic complexes have been obtained on studying the low-temperature ^1H-NMR spectrum of **3**, where product **5** was the only new observable species formed in trace quantities, most probably, during the time of sample preparation. It is explained if either the equilibrium shifts predominantly towards complex **3** at lower temperature, whereas **6** is predominant at high-temperature or the intermediate species **6** is very short-lived and could not be observed by NMR spectroscopy under conditions used. Preliminary examination of a variable temperature ^1H-NMR spectra of **3** in the range of −73 to +57 °C showed this species became fluxional at temperature above −33 °C (Fig. 6). However, its higher temperature dynamic behavior appeared to be complex and may be a result of several rapid intramolecular hydride migration processes manifested in the apparent symmetry of the η^3-metallyl coordination in the range from +25 to +57 °C. Indeed, as the temperature is raised above −33 °C, signals originated from non-equivalent methylene groups (two individual AB systems) and aromatic protons of *ortho*-xylylene substituent which remained separated in the low-temperature spectra become broadened and eventually coalesce, finally giving rise to an equivalency of aromatic protons H(15) and H(18), as well as protons of the two bridging methylene groups that appear now in spectrum as one AB system. Moreover, the allylic resonances of **3** at 5.14 and 4.59 ppm as well as the agostic hydrogen peak at −2.80 ppm have also revealed dynamic behavior, finally disappearing at +25 and +57 °C, respectively, into the base line. It has also been found that the temperature strongly influences the rate of formation of product **5**, whose concentration is markedly increasing under conditions of fast exchange, at temperature above +50 °C. As can be seen from the reversed spectrum of **3** (Fig. 6), the conversion of **3** to **5** is, apparently, irreversible process. This, in fact, precluded the observation of the high-temperature limiting spectrum of **3**, and, therefore, more appropriate fluxional iridium or rhodium species closely related to **3** will be required for detailed study of this dynamic process. We currently plan further experimentation to attempt to find the requested model.

In summary, we have extended the family of the known agostic metallacarboranes by preparing two



Scheme 3.

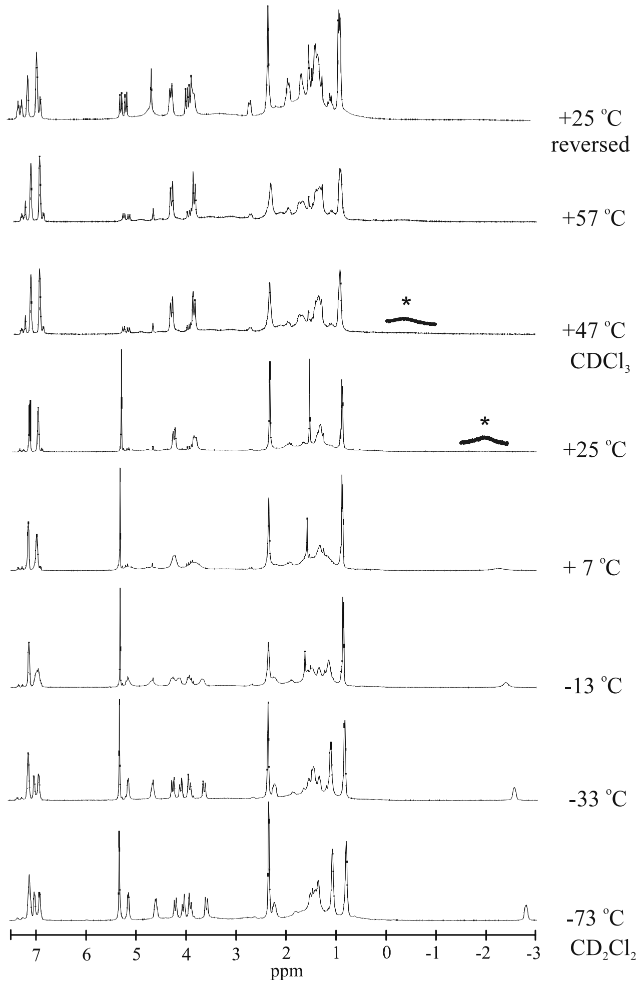


Fig. 6. 400.13 MHz variable-temperature ^1H-NMR spectra of **3** in CD_2Cl_2 solution from −73 to +25 °C and in $CDCl_3$ solution at +47, +57 and +25 °C (reversed). The assignments are given in Section 3; an agostic hydrogen ($H_{8\text{-}endo}$) resonance at +25 and +47 °C is marked by a star.

novel complexes *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-3,1,2-$IrC_2B_9H_9$ (**3**) and its ethoxy-cage-substituted analog *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-8-(EtO)-3,1,2-$IrC_2B_9H_8$ (**4**). Complex **3** is at present the first such species with η^3-cyclooctenyl type ligand in which an agostic C–H···Ir interaction is fully confirmed by a combination of NMR and X-ray diffraction data. In addition, we have studied an interesting intramolecular rearrangement of an agostic complex **3** into isomeric *exo*-allyl complex *closo*-3-[η^3-(1-*exo*-CH_2-5-MeC_8H_{12})]-1,2-μ-[η^2-(1′,2′-$CH_2C_6H_4CH_2$–)]-3,1,2-$IrC_2B_9H_9$ (**5**) wherein a weak η^2-coordination of the iridium atom with one of the aromatic bonds of *ortho*-xylylene cage substituent has been revealed both in solution and solid-state by $^{13}C\{^1H\}$-NMR spectroscopy and X-ray diffraction studies, respectively.

3. Experimental

3.1. General consideration

All reactions and manipulations except for column chromatography were carried out in atmosphere of dry Ar using Schlenk techniques. Solvents used were reagent grade and were freshly distilled from appropriate drying agents under an Ar atmosphere before use. Starting reagents 1,5-dimethylcycloocta-1,5-diene and $H_2IrCl_6\cdot 6H_2O$ were purchased from Aldrich and Fluka, respectively, and used as received; *closo*-1,2-μ-(1′,2′-xylylene)-1,2-$C_2B_{10}H_{10}$ [25] was prepared and further degraded to form **2** [26] according to the literature methods. The ^1H-, ^{11}B/$^{11}B\{^1H\}$- and ^{13}C/$^{13}C\{^1H\}$-NMR as well as room- and low-temperature 2D correlation spectra were recorded on a Bruker AMX-400 (^1H at 400.13, ^{13}C at 100.61, and ^{11}B at 128.33 MHz) and Bruker DRX-500 (^1H at 500.13, ^{13}C at 125.76 MHz) spectrometers. IR spectra were obtained on Carl-Zeiss M-82 spectrometer and Nicolet Magma-IR-750 IR FT spectrometer (KBr pellets). Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

*3.2. Preparation of [(1,5-dimethylcycloocta-1,5-diene)IrCl]$_2$ (**1**)*

To a stirred solution of $H_2IrCl_6 \cdot 6H_2O$ (1.1 g, 2.14 mmol) in 5 ml of degassed water and 2 ml of *i*-PrOH was added 1.1 ml of 1,5-dimethylcycloocta-1,5-diene. The resulting suspension was stirred at ambient temperature (0.5 h), then heated up to 80 °C (internal thermometer), and the mixture generated was stirred additionally for 3 h. After cooling to room temperature (r.t.), the mother liquid was removed by pipette from the bright orange oil formed and 5 ml of C_2H_5OH was added to the residue. The resulting mixture was stored at 0 °C overnight; the precipitated solid material was filtered, then washed with 2 ml of water and 2 ml of ice-cold C_2H_5OH and thoroughly dried in vacuo, affording 0.48 g (62% yield) of pale yellow crystalline **1**. IR (Nujol mull, cm^{-1}): 258 (ν_{Ir-Cl}); ^{1}H-NMR [CDCl$_3$, 400.13 MHz, J (Hz), 23 °C]: δ 4.21 (dd, $J_1 = 7.0$, $J_2 = 2.4$, 2H, vinylic CH), 2.19, 1.84 (m, each 2H, methylene CH), 1.60 (s, 6H, CH$_3$), 1.45, 1.29 (m, each 2H, methylene CH). Anal. Calc. for $C_{20}H_{32}Ir_2Cl_2$: C, 32.99; H, 4.39; Cl, 9.76. Found: C, 33.53; H, 4.45; Cl, 9.74%.

*3.3. Preparation of closo-3-[η^3-(endo-1,5-Me$_2$COD)]-1,2-μ-(1′,2′-CH$_2$C$_6$H$_4$CH$_2$–)-3,1,2-IrC$_2$B$_9$H$_9$ (**3**) and closo-3-[η^3-(endo-1,5-Me$_2$COD)]-1,2-μ-(1′,2′-CH$_2$C$_6$H$_4$CH$_2$–)-8-(EtO)-3,1,2-IrC$_2$B$_9$H$_8$ (**4**)*

a) To a stirred solution of **2** (0.09 g, 0.326 mmol) in 1 ml of absolute C_2H_5OH was added reagent **1** (0.10 g, 0.138 mmol) as a solid in one portion, and to a resulting suspension was added 4 ml of absolute C_6H_6 via syringe. After 0.5 h of vigorous stirring the bright orange reaction mixture was evaporated to dryness under reduced pressure and the crude material obtained was treated by column chromatography on 70–230 mesh silica gel using a CH_2Cl_2–*n*-hexane (1:2) mixture as eluent. The wide orange band which eluted first was collected to give after evaporation 0.10 g (65%) of complex **3** as slowly solidifying red oil. Anal. Calc. for $C_{20}H_{34}B_9Ir$: C, 42.59; H, 6.03; B, 17.25. Found: C, 42.99; H, 5.99; B, 17.28%. IR (KBr, cm^{-1}): 2551(ν_{B-H}). ^{1}H-NMR [CD$_2$Cl$_2$, 400.13 MHz, J (Hz), −73 °C]: δ 7.11 (m, 2H, C$_6$H$_4$-*m*), 7.01 (br. d, 1H, C$_6$H$_4$-*o*), 6.91 (br. d, 1H, C$_6$H$_4$-*o*), 5.14 (br. d, ^3J(H$_2$,H$_3$) = 7.2, 1H, H$_2$-allylic), 4.59 (br. q-like, $J = 7.2$, 1H, H$_3$-allylic), 4.20 (d, $J_{AB} = 16.8$, 1H, $-C\mathit{H_A}H_BC_6H_4CH_2-$), 4.04 (d, $J_{AB} = 16.8$, 1H, $-CH_2C_6H_4C\mathit{H_A}H_B-$), 3.90 (d, $J_{AB} = 16.8$, 1H, $-CH_2C_6H_4CH_A\mathit{H_B}-$), 3.58 (d, $J_{AB} = 16.8$, 1H, $-CH_A\mathit{H_B}C_6H_4CH_2-$), 2.33 (s, 3H, CH$_3$-allylic), 2.22 (m, 1H, H$_4$-*exo*), 1.8–1.06 (m+m, 7H, methylene C*H*), 0.78 (d, 3H, ^3J(H,H) = 5.6, CH$_3$), −2.80 (br. s, 1H, H$_8$-*endo*); ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 106.61 MHz, −73 °C): 132.2, 131.6 (C$_{aryl}$-*ipso*), 130.0, 129.6, 127.8, 127.5 (C$_{aryl}$), 96.0 (C$_2$-allylic), 94.7 (C$_1$-allylic), 69.5, 66.1 (C$_{cluster}$), 61.7 (C$_3$-allylic), 43.6, 42.9 [C$_6$H$_4$(CH$_2$)$_2$], 41.3 (C$_4$), 38.2 (C$_5$), 33.8 (C$_8$), 30.1 (C$_6$ or C$_7$), 25.5 (C$_7$ or C$_6$), 22.8 (CH$_3$-allylic), 20.5 (CH$_3$); ^{13}C-NMR (CD$_2$Cl$_2$, 106.61 MHz, $J = {}^1J$(C,H) (Hz), −73 °C): δ 132.2, 131.6 (C$_{aryl}$-*ipso*), 130.0 (d, $J = 161$, C$_{aryl}$), 129.6 (d, $J = 154$, C$_{aryl}$), 127.8 (d, $J = 163$, C$_{aryl}$), 127.5 (d, $J = 161$, C$_{aryl}$), 96.0 (d, $J = 167$, C$_2$-allylic), 94.8 (C$_1$-allylic), 69.5, 66.1 (C$_{cluster}$), 61.7 (d, $J = 153$, C$_3$-allylic), 43.6 (t, $J = 136$, [C$_6$H$_4$(CH$_2$)$_2$]), 42.9 (t, $J = 130$, [C$_6$H$_4$(CH$_2$)$_2$]), 37.3 (t, $J = 140$, C$_5$), 33.8 (dd, $J = 132$, ^1J(C,H$_{ag}$) = 104, C$_8$), 30.2 (t, $J = 121$, C$_6$ or C$_7$), 25.5 (t, $J = 128$, C$_7$ or C$_6$), 22.8 (q, $J = 126$, CH$_3$-allylic), 20.5 (q, $J = 124$, CH$_3$); ^{11}B-NMR [CDCl$_3$, 128.33 MHz, $J = {}^1J$(B,H) (Hz), 23 °C]: δ 2.6 (d, 1B, $J = 140$), −5.5 (br. d, 2B, $J \sim 150$), −10.5 (d, 1B, $J = 144$), −14.1 (d, 3B, $J = 132.5$), −20.5 (d, 2B, $J = 144$). The second orange band was also eluted with the same mixture of solvent to afford after evaporation 0.01 g (6%) of complex **4** as semi-solid orange material which was characterized by spectroscopic data. IR (KBr, cm^{-1}) 2545 (ν_{B-H}). ^{1}H-NMR [CDCl$_3$, 400.13 MHz, J (Hz), 23 °C]: δ 7.2–6.8 (m, 4H, C$_6$H$_4$), 4.95 (br. d, ^1J(H$_2$,H$_3$) = 7.6, 1H, H$_2$-allylic), 4.87 (br. q-like, $J = 7.6$, 1H, H$_3$-allylic), 4.30 (d, $J_{AB} = 16.8$, 1H, $-C\mathit{H_A}H_BC_6H_4CH_2-$), 4.14 (d, $J_{AB} = 16.8$, 1H, $-CH_2C_6H_4C\mathit{H_A}H_B-$), 3.97 (d, $J_{AB} = 16.8$, 1H, $-CH_2C_6H_4CH_A\mathit{H_B}-$), 3.78 (d, $J_{AB} = 16.8$, 1H, $-CH_A\mathit{H_B}C_6H_4CH_2$), 3.23 (br. d q-like, $J_d \sim 26.8$, Jq ~ 6.8, 2H, CH$_3$CH_2O), 2.38 (s, 3H, CH$_3$-allylic), 2.10 (m, 1H, H$_{4\text{-}exo}$), 1.55 (m, 1H, H$_{6\text{-}exo}$), 1.41 (br. m, 2H, H$_5$, H$_{8\text{-}exo}$), 1.27 (br. m, 2H, H$_{4\text{-}endo}$, H$_{7\text{-}exo}$), 1.08 (m, 2H, H$_{6\text{-}endo}$, H$_{7\text{-}endo}$), 0.92 (t, ^3J(H,H) = 6.8, 3H, CH_3CH$_2$O), 0.90 (d, ^3J(H,H) = 7.6, 3H, CH$_3$), −1.09 (br. s, 1H, H$_{8\text{-}endo}$); ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 125.76 MHz, −30 °C): 132.3, 131.7 (C$_{aryl}$-*ipso*), 130.8, 130.5, 128.5, 128.1 (C$_{aryl}$), 102.6 (C$_2$-allylic), 92.9 (C$_1$-allylic), 69.6 (C$_{cluster}$), 65.8 (C$_3$-allylic), 64.3 (CH$_3$$CH_2$O), 62.7 (C$_{cluster}$), 44.2, 43.8 [C$_6H_4$($CH_2$)$_2$], 41.3 (C$_4$), 39.0 (C$_5$), 33.2 (C$_8$), 31.0 (C$_6$ or C$_7$), 30.6 (CH$_3$CH$_2$O), 30.4 (C$_7$ or C$_6$), 27.5 (CH$_3$-allylic), 23.6 (CH$_3$); ^{11}B-NMR [CDCl$_3$, 128.33 MHz, $J = {}^1J$(B,H) (Hz), 23 °C]: δ 4.0 (s, 1B, B$_8$), −1.1 (d, 1B, $J = 147$), −5.0 (d, 1B, $J = 152$), −8.1 (d, 1B, $J = 145$), −14.5 (d, 1B, $J = 159$), −16.2 (d, 1B, $J = 148$), −20.5 (br. d, 1B, $J = 165$), −22.6 (d, 2B, $J = 121$). When analogous reaction of **2** (0.09 g, 0.326 mmol) with **1** (0.10 g, 0.138 mmol) was carried out in solvents C$_6$H$_6$–EtOH taken in a 1:4 ratio, complexes **3** and **4**, after the same work up procedure, were obtained in 72 and 12% yields, respectively. Crystals of **4** suitable for X-ray diffraction experiment were obtained from solution of $CHCl_3$ by slow evaporation.

b) To a mixture of **1** (0.05 g, 0.069 mmol) and **2** (0.045 g, 0.163 mmol) flushed with Ar was added 5 ml of absolute C_6H_6, and the resulting orange solution was stirred for 40 min. The reaction mixture was placed on a short silica gel column and the single orange band eluted with C_6H_6–*n*-hexane mixture (1:1) was collected to give after evaporation 0.07 g (89%) slowly solidifying red oil, which from examination of ^1H-NMR spectrum was deduced to be pure complex **3**. Crystals suitable for single-crystal X-ray diffraction study were grown from a solution of **3** in CH_2Cl_2–*n*-hexane mixture (1:2).

3.4. *Preparation of closo-3-[η^3-(1-exo-CH_2-5-MeC_8H_{12})]-1,2-μ-[η^2-(1′,2′-$CH_2C_6H_4CH_2$–)]-3,1,2-$IrC_2B_9H_9$ (5)*

0.1 g (0.177 mmol) of **3** dissolved in 10 ml of dry methylene chloride was left to stand at r.t. for a week. The reaction mixture was then treated by column chromatography on 230–400 mesh silica gel using CH_2Cl_2–*n*-hexane mixture (1:4) as eluent to give after evaporation 0.093 g (93%) of **5** as red crystalline solid. Anal. Calc. for $C_{20}H_{34}B_9Ir$: C, 42.59; H, 6.03; B, 17.25. Found: C, 42.74; H, 5.97; B, 17.05%. IR (KBr, cm^{-1}) 2549 (ν_{B-H}). ^1H-NMR [CD_2Cl_2, 500.13 MHz, J (Hz), 25 °C]: δ 7.34 (br. t, 1H, C_6H_4-*m*), 7.27 (br. t, 1H, C_6H_4-*m*), 6.97 (br. d, 1H, C_6H_4-*o*), 6.90 (br. d, 1H, C_6H_4-*o*), 5.28 (d, $J_{AB} = 15.2$, 1H, –$CH_AH_BC_6H_4CH_2$–), 5.18 (d, $J_{AB} = 15.1$, 1H, –$CH_2C_6H_4CH_AH_B$–), 4.67 (d, $J_{gem} = 2.4$, 1H, $H_{9\text{-}syn}$), 3.96 (d, $J_{AB} = 15.2$, 1H, –$CH_AH_BC_6H_4CH_2$–), 3.89 (d, $J_{AB} = 15.1$, 1H, –$CH_2C_6H_4CH_AH_B$–), 2.71 (br. dt, $J_d = 14.6$, $J_t = 5.6$, 1H, $H_{3\text{-}exo}$), 2.31 (br. q-like, $J_q = 12.4$, 1H, $H_{3\text{-}endo}$), 1.93 (m, 2H, $H_{4\text{-}exo}$, $H_{8\text{-}exo}$), 1.66 (dd+m, $J_{d-1} = 9.6$, $J_{d-2} = 4.8$, 2H, H_2-allylic, $H_{7\text{-}exo}$), 1.54 (d, $J_{gem} = 2.3$, 1H, $H_{9\text{-}anti}$), 1.49 (m, 1H, $H_{7\text{-}endo}$), 1.39 (m, 4H, $H_{8\text{-}endo}$, $H_{6\text{-}exo}$, $H_{6\text{-}endo}$, H_5), 1.09 (br. q-like, $J_q = 12.5$, 1H, $H_{4\text{-}endo}$), 0.91 (d, $J = 6.6$, CH_3); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 125.76 MHz, 20 °C): 131.8 (C_{aryl}-*m*), 131.7 (C_{aryl}-*o*), 131.4 (C_{aryl}-*m*), 130.5 (C_{aryl}-*o*), 123.6 (C_{aryl}-*ipso*), 120.8 (C_{aryl}-*ipso*), 119.2 (C_1-allylic), 86.2 (C_2-allylic), 64.8, 63.7 ($C_{cluster}$), 58.4 (C_9-allylic), 44.2 [$C_6H_4(CH_2)_2$], 44.0 [$C_6H_4(CH_2)_2$], 41.6 (C_4), 35.5 (C_6), 35.4 (C_5), 32.1 (C_3), 32.0 (C_8), 30.8 (C_7), 27.6 (CH_3); ^{11}B-NMR [$CDCl_3$, 128.33 MHz, $J = {}^1J$(B,H) (Hz), 23 °C]: δ 4.5 (d, 1B, $J =$

Table 2
Crystal data, data collection and structure refinement parameters for **3**, **4** and **5**

Complex	**3**	**4**	**5**
Empirical formula	$C_{20}H_{34}B_9Ir$	$C_{22}H_{38}B_9IrO$	$C_{20}H_{34}B_9Ir$
Molecular weight	563.96	608.01	563.96
Temperature (K)	293(2)	293(2)	293(2)
Radiation	Mo–K_α, $\lambda = 0.71073$ Å		
Crystal habit	prism	prism	prism
Crystal dimensions (mm)	0.25 × 0.20 × 0.20	0.20 × 0.20 × 0.10	0.30 × 0.20 × 0.10
Crystal system	orthorhombic	triclinic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	10.473(2)	7.731(2)	7.851(2)
b (Å)	14.532(3)	9.312(2)	9.430(2)
c (Å)	15.171(5)	9.531(2)	16.013(3)
α (°)		73.50(3)	84.33(3)
β (°)		81.44(3)	79.81(3)
γ (°)		76.52(3)	81.34(3)
V (Å^3)	2308.9(9)	637.2(2)	1150.3(4)
Z	4	1	2
D_{calc} (g cm^{-3})	1.622	1.584	1.628
μ (Mo–K_α) (cm^{-1})	57.88	52.52	58.09
Diffractometer	Siemens P3/PC	Enraf Nonius CAD4	
Scan mode	$\theta-2\theta$	$\theta-5/3\theta$	$\theta-5/3\theta$
θ_{max} (°)	30	30	30
Absorption correction	ψ-scan	ψ-scan	ψ-scan
Min/max transmission factors	0.178/0.236	0.316/0.466	0.279/0.500
No. collected reflections	3783	3949	7097
No. unique reflections (R_{int})	3783(0.0000)	3698(0.0446)	6650(0.0158)
No. observed reflections ($I > 2\sigma(I)$)	2521	3575	5845
R_1 (on F for observed reflections) [a]	0.0376	0.0310	0.0278
wR_2 (on F^2 for all reflections) [b]	0.0635	0.0772	0.0757

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma\, w(F_o^2)^2\}^{1/2}$.

146), −4.3 (d, 1B, $J = 164$), −6.7 (d, 1B, $J = 146$), −7.8 (d, 1B, $J = 157$), −13.1 (d, 1B, $J = 168$), −14.5 (d, 2B, $J = 145$), −21.0 (d, 1B, $J = 154$), −21.8 (d, 1B, $J = 148$). Crystals suitable for single-crystal X-ray diffraction study were grown from a diluted solution of **5** in CH_2Cl_2–n-hexane mixture (1:1) at +4 °C.

3.5. *X-ray crystallography*

Crystal data and the details of data collection and structure refinement parameters for complexes **3**, **4** and **5** are given in Table 2. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms.

In crystal structure of **4**, all atoms of complex are disordered due to the center of symmetry (the superposition of the carborane and cyclooctenyl ligands). The refinement of this structure in the $P1$ space group as well as the careful analysis of the cell dimensions (the possible duplication of cell parameters) have not lead to any improvement. The H atoms of CH_2 group participating in the agostic C–H···Ir interaction in **3** were located in difference syntheses and refined in isotropic approximation; the remaining H atoms in **3** as well as all H atoms in **4** were placed geometrically and included in the structure factor calculation in the riding motion approximation. All H atoms in **5** were located in difference syntheses and refined in isotropic approximation. Absolute structure for **3** was defined by Flack parameter [27] refinement ($x = -0.04(2)$). The SHELXTL-97 program package [28] was used throughout the calculations, which were carried out on an IBM PC.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 204971–73, for complexes **3**–**5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We acknowledge the financial support of Russian Foundation for Basic Research (Grants Nos 03-03-32651 and 00-15-97359). The authors are grateful to E.G. Kononova for recording IR spectra of complexes.

References

[1] T.E. Paxson, M.F. Hawthorne, J. Am. Chem. Soc. 96 (1974) 4674.

[2] (a) J.A. Doi, R.G. Teller, M.F. Hawthorne, J. Chem. Soc. Chem. Commun. (1980) 81;
(b) T.B. Marder, R.T. Baker, J.A. Long, J.A. Doi, M.F. Hawthorne, J. Am. Chem. Soc. 103 (1981) 2988;
(c) J.A. Doi, E.A. Mizusawa, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 23 (1984) 1482;
(d) J.A. Walker, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 24 (1985) 2688.

[3] X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy, K. Nestor, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1990) 681.

[4] J.C. Jeffery, P.A. Jelliss, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1993) 1083.

[5] T.V. Zinevich, A.V. Safronov, E.V. Vorontsov, P.V. Petrovskii, I.T. Chizhevsky, Russ. Chem. Bull. 9 (2001) 1702.

[6] See for instance: (a) D.M. Speckman, C.B. Knobler, M.F. Hawthorne, Organometallics 4 (1985) 426;
(b) D.M. Speckman, C.B. Knobler, M.F. Hawthorne, Organometallics 4 (1985) 1692;
(c) L.I. Zakharkin, I.T. Chizhevsky, G.G. Zhigareva, P.V. Petrovskii, A.V. Polyakov, A.I. Yanovsky, J. Organomet. Chem. 358 (1988) 449;
(d) Z.G. Lewis, A.J. Welch, J. Organomet. Chem. 438 (1992) 353;
(e) J.C. Jeffery, F.G.A. Stone, I. Topaloglu, Polyhedron 12 (1993) 319;
(f) N.L. Douek, A.J. Welch, J. Chem. Soc. Dalton Trans. (1993) 1917;
(g) I.T. Chizhevsky, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem. 536–537 (1997) 51 (short review);
(h) T.V. Zinevich, P.V. Petrovskii, F.M. Dolgushin, A.I. Yanovsky, I.T. Chizhevsky, Russ. Chem. Bull. 3 (2001) 504.

[7] (a) B. Pirotte, A. Felekidis, M. Fontaine, A. Demonceau, A.N. Noels, J. Delarge, I.T. Chizhevsky, T.V. Zinevich, I.V. Pisareva, V.I. Bregadze, Tetrahedron Lett. 34 (1993) 1471;
(b) A. Felekidis, M. Goblet-Stachow, J.F. Liégeois, B. Pirotte, J. Delarge, A. Demonceau, M. Fontaine, A.N. Noels, I.T. Chizhevsky, T.V. Zinevich, V.I. Bregadze, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem. 536–537 (1997) 405;
(c) F. Teixidor, M.A. Flores, C. Viñas, R. Sillanpää, R. Kivekäs, J. Am. Chem. Soc. 122 (2000) 1963. For the latest review see: F. Teixidor, R. Núñez, M.A. Flores, A. Demonceau, C. Viñas, J. Organomet. Chem. 614–615 (2000) 48.

[8] P.T. Brain, M. Bühl, J. Cowie, Z.G. Lewis, A.J. Welch, J. Chem. Soc. Dalton Trans. (1996) 213.

[9] T.V. Zinevich, A.V. Safronov, F.M. Dolgushin, O.L. Tok, I.T. Chizhevsky, Russ. Chem. Bull. 11 (2001) 2254.

[10] G. Winkhaus, H. Singer, Chem. Ber. 99 (1966) 3610.

[11] (a) B. Buchmann, U. Piantini, W. von Philipsborn, A. Salzer, Helv. Chim. Acta 70 (1987) 1487;
(b) J.R. Sowa, Jr., R.J. Angelici, J. Am. Chem. Soc. 113 (1991) 2537;
(c) L.P. Szajek, J.R. Shapley, Organometallics 12 (1993) 3772;
(d) C. Bianchini, E. Farnetti, L. Glendenning, M. Graziani, G. Nardin, M. Peruzzini, E. Rocchini, F. Zanobini, Organometallics 14 (1995) 1489.

[12] (a) F.A. Cotton, T. Lacour, A.G. Stanislowski, J. Am. Chem. Soc. 96 (1974) 754;
(b) S.D. Ittel, F.A. Van-Catledge, J.P. Jesson, J. Am. Chem. Soc. 101 (1979) 6905.

[13] (a) M. Brookhart, M.L.H. Green, J. Organomet. Chem. 250 (1983) 395;
(b) M. Brookhart, M.L.H. Green, L.L. Wong, Prog. Inorg. Chem. 36 (1988) 1.

[14] D.F. Mullica, E.L. Sappenfield, F.G.A. Stone, Organometallics 14 (1994) 157.

[15] See for instance: (a) M.A. Esteruelas, M. Olivan, L.A. Oro, M. Schutz, E. Sola, H. Werner, Organometallics 11 (1992) 3659;
(b) J.A. Kaduk, A.T. Poulos, J.A. Ibers, J. Organomet. Chem. 127 (1977) 245;
(c) T.H. Talip, J.A. Ibers, J. Am. Chem. Soc. 101 (1979) 4201.

[16] E.E. Björkman, J.-E. Bäckvall, Acta Chem. Scand. A37 (1983) 503.

[17] (a) R.K. Brown, J.M. Williams, A.J. Schultz, G.D. Stucky, S.D. Ittel, R.L. Harlow, J. Am. Chem. Soc. 102 (1980) 981;
(b) T.V. Ashworth, D.C. Liles, E. Singleton, Organometallics 3 (1984) 1851.

[18] (a) A.C. Albéniz, P. Espinet, Y.-S. Lin, B. Martín-Ruiz, Organometallics 18 (1999) 3359;
(b) A.A. Koridze, I.T. Chizhevsky, P.V. Petrovskii, E.I. Fedin, N.E. Kolobova, L.A. Leites, V.G. Andrianov, Yu.T. Struchkov, J. Organomet. Chem. 206 (1981) 373.

[19] R.B. Cracknell, J.C. Nicholls, J.L. Spencer, Organometallics 15 (1996) 446.

[20] See for instance: (a) F.A. Cotton, M.D. LaPrade, J. Am. Chem. Soc. 25 (1968) 5419;
(b) J.R. Ascenso, Carrondo, M.A.A.F. De C.T., Carrondo, A.R. Dias, P.T. Gomes, M.F.M. Piedade, C.C. Romao, A. Revillon, I. Tkachenko, Polyhedron 8 (1989) 2449;
(c) H. Werner, M. Schäfer, O. Nürnberg, J. Wolf, Chem. Ber. 127 (1994) 27;
(d) M.D. Fryzuk, D.H. McConvolle, S.J. Rettig, J. Organomet. Chem. 445 (1993) 245.

[21] U. Burckhardt, V. Gramlich, P. Hofmann, R. Nesper, P.S. Pregosin, R. Salzmann, A. Togni, Organometallics 15 (1996) 3496.

[22] C.B. Knobler, T.B. Marder, E.A. Mizusawa, R.G. Teller, J.A. Long, P.E. Behnken, M.F. Hawthorne, J. Am. Chem. Soc. 106 (1984) 2990.

[23] G.D. Kolomnikova, P.V. Petrovskii, P.V. Sorokin, F.M. Dolgushin, A.I. Yanovsky, I.T. Chizhevsky, Russ. Chem. Bull. 4 (2001) 706.

[24] (a) C.W. Jung, R.T. Baker, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 102 (1980) 5782;
(b) M.S. Delaney, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 20 (1981) 1341;
(c) M.S. Delaney, R.G. Teller, M.F. Hawthorne, J. Chem. Soc. Chem. Commun. (1981) 235;
(d) S. Anderson, D.F. Mullica, E.L. Sappenfield, F.G.A. Stone, Organometallics 15 (1996) 1676;
(e) I.V. Pisareva, I.T. Chizhevsky, P.V. Petrovskii, E.V. Vorontsov, V.I. Bregadze, F.M. Dolgushin, A.I. Yanovsky, Inorg. Chim. Acta 280 (1998) 233;
(f) S. Du, D.D. Ellis, P.A. Jelliss, J.A. Kautz, J.M. Malget, F.G.A. Stone, Organometallics 19 (2000) 1983.

[25] D.S. Matteson, R.A. Davis, Inorg. Chem. 13 (1974) 859.

[26] M.F. Hawthorne, D.C. Young, P.M. Garrett, D.A. Owen, S.G. Schwerin, F.N. Tebbe, P.A. Wegner, J. Am. Chem. Soc. 90 (1968) 862.

[27] H.D. Flack, Acta Crystallogr. Sect. A 39 (1983) 876.

[28] G.M.Sheldrick, SHELXTL-97 V5.10, Bruker AXS Inc., Madison, WI-53719, USA, 1997.