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Macrocycles incorporating sulphur and *nido*-carborane cages: reactivity towards Rh(III) and Ir(III). Molecular structures of $[Ir(C_5Me_5)Cl(7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10})]$ and $[Rh(C_5Me_5)Cl(7,8\text{-}\mu\text{-}(S(CH_2CH_2(OCH_2CH_2)_3)S)\text{-}7,8\text{-}C_2B_9H_{10})]$

Clara Viñas [a], M. Rosa Cirera [b], Francesc Teixidor [a,*], Raikko Kivekäs [c], Reijo Sillanpää [d], Joan Llibre [b]

[a] *Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, E-08193 Bellaterra, Spain*
[b] *Sociedad Española de Carburos Metálicos, SA Passeig de la Zona Franca, 14-20, 08038 Barcelona, Spain*
[c] *University of Helsinki, Department of Chemistry, PO Box 55, FIN 00014 Helsinki, Finland*
[d] *University of Turku, Department of Chemistry, FIN 20014 Turku, Finland*

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Abstract

The carboranyl bonded dithioether $[7,8\text{-}\mu\text{-}(S(CH_2)_2S)\text{-}7,8\text{-}C_2B_9H_{10}]^-$, $[n6S2]^-$, and $[7,8\text{-}\mu\text{-}(S(CH_2CH_2(OCH_2CH_2)_3)S)\text{-}7,8\text{-}C_2B_9H_{10}]^-$, $[n15S2]^-$, are better metal-coordinating than their organic analogues. Reaction of $[NMe_4][n6S2]$ with $[M_2(C_5Me_5)_2Cl_4]$ (M = Rh, Ir) produces $[M(C_5Me_5)Cl(n6S2)]$ (M = Rh, Ir) and reaction of $[NMe_4][n15S2]$ with $[Rh_2(C_5Me_5)_2Cl_4]$ produces $[Rh(C_5Me_5)Cl(n15S2)]$. The carboranyl dithioether ligands are able to remove one chloride ligand from the metal's coordination sphere, which is interpreted as if the negative charge of the cluster partly resides on thioether. The crystal structure of $[Rh(C_5Me_5)Cl(n15S2)]$ and $[Ir(C_5Me_5)Cl(n6S2)]$ have been solved. The ligands behave in a chelating mode providing two coordinating sites to the metal, the other three being provided by the carbocyclic ligand and the remaining one by the chloride. The length of the spacer connecting the two thioether groups produces significant geometrical differences in the metal's surrounding specially in what concerns the S–M–S angle and the dihedral angle between the planes S(1), Ir, S(2) and S(1), S(2), C(7) and C(8). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Boron compounds; Rhodium compounds; Iridium compounds; Thioether

1. Introduction

Ligand derivatives of 7,8-dithio-7,8-dicarba-*nido*-undecaborate(−1), $[nxS2]^-$, where n stands for the anionic fragment, $[7,8\text{-}C_2B_9H_{10}]^-$, x indicates the number of atoms forming the *exo*-cycle cluster, and S2 indicates two sulphur atoms connected to both cluster carbon atoms, have been thoroughly studied in our group [1,2]. A relevant characteristic of these ligands is the enhanced bonding capacity of the thioether groups as compared to organic thioether. This enhancement is interpreted as if the negative charge of the cluster partly resides on the thioether [3]. An example is the ready substitution of Cl^- by these ligands from a metal's coordination sphere [4], contrary to organic dithioether ligands that require the previous removal of the chloride ligand by precipitating agents like $AgPF_6$ [5].

Our previous efforts had been directed towards the reaction of these ligands with transition metal complexes leading to new ones containing in their coordination sphere neutral ligands like PPh_3, COD or halogen atoms. No indication on the reactivity of these $[nxS2]^-$ ligands towards complexes incorporating carbocyclic ligands had been reported.

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* Corresponding author. Tel.: +34 3 5801853; fax: +34 3 5805729; e-mail: teixidor@icmab.es

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On the other hand ligand substitution reactions on pentamethylcyclopentadienyl–rhodium and –iridium complexes are of considerable importance [6], especially in view of the utility of these complexes for many reaction types [7]. Examples of mixed thioether/cyclopentadienyl Rh(III) and Ir(III) complexes are, however scarce and up to now no structural details have been reported in the literature.

This led us to study the reaction of $[nxS2]^-$ ligands with $[M_2(C_5Me_5)_2Cl_4]$ (M = Rh, Ir) and $x = 6, 15$. Here we report the synthesis of these complexes and the crystal structures of $[Rh(C_5Me_5)Cl(n15S2)]$ and $[Ir(C_5Me_5)Cl(n6S2)]$.

2. Results and discussion

The direct reaction of $[NMe_4][7,8\text{-}\mu\text{-}(S(CH_2)_2S)\text{-}7,8\text{-}C_2B_9H_{10}]$, $[NMe_4][n6S2]$ with the binuclear complexes $[M_2(C_5Me_5)_2Cl_4]$ (M = Rh, Ir) and $[NMe_4][7,8\text{-}\mu\text{-}(S(CH_2CH_2(OCH_2CH_2)_3)S)\text{-}7,8\text{-}C_2B_9H_{10}]$, $[NMe_4][n15S2]$, with the complex $[Rh_2(C_5Me_5)_2Cl_4]$ in ethanol were performed and the complexes $[Rh(C_5Me_5)Cl(n6S2)]$ (**1**), $[Rh(C_5Me_5)Cl(n15S2)]$ (**2**), and $[Ir(C_5Me_5)Cl(n6S2)]$ (**3**) were obtained. Reactions of $[Rh_2(C_5Me_5)_2Cl_4]$ with chelating organic dithioethers (e.g. 1,4-dithiacyclohexane, 2,5-dithiahexane) have been performed before [5], but the direct synthesis was not possible. It was required the preparation of tris-solvent complexes $[Rh(C_5Me_5)(sol)_3]^{2+}$ by the reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with $AgPF_6$ in the presence of weakly binding ligands like MeCN, py or thf. In few occasions the direct reaction took place but it was necessary a 12–27-fold excess of dithioether for the reaction to occur [5]. For the $[nxS2]^-$ ligands reported here, the presence of the anionic cluster directly bonded to the thioether permits the easy replacement of the chloride ligands from the Rh(III) or Ir(III) coordination sphere.

These $[nxS2]^-$ ligands present different modes of bonding to the metal. They behave as chelating through the sulphur atoms [1,4] or tricoordinating through the two sulphur atoms and the B(3)–H [8,9]. The $^1H\{^{11}B\}$-NMR spectra of the complexes (**1**)–(**3**) display resonances at −2.7 ppm corresponding to the BHB resonances. This rules out the possibility of an interaction with the C_2B_3 open face. The $^1H\{^{11}B\}$-NMR spectra do not present any resonance which can be assigned to a B–H–M, so a tricoordinating *exo-nido* coordination is not indicated. The $^{11}B\{^1H\}$-NMR spectra of the (**1**)–(**3**) complexes are different from those of the free ligands, suggesting that the $[nxS2]^-$ ligands are coordinated to the metal in a chelating *exo-nido* coordination through the two sulphur atoms. The $^{11}B\{^1H\}$-NMR pattern for the $[n6S2]^-$ ligand is 2:1:2:2:1:1 while in complex (**1**) the pattern is 1:2:1:2:1:1:1, and in (**3**) is 1:2:1:1:1:1:1:1. For ligand $[n15S2]^-$ the $^{11}B\{^1H\}$-NMR pattern is 2:1:2:2:1:1 while in complex (**2**) is 2:2:3:1:1. The resonance at 1.8 ppm in the $^1H\{^{11}B\}$-NMR spectra of all three complexes corresponds to the methyl groups of the C_5Me_5 ligand. The chemical analysis support in all cases the stoichiometry $[M(C_5Me_5)Cl(nxS2)]$.

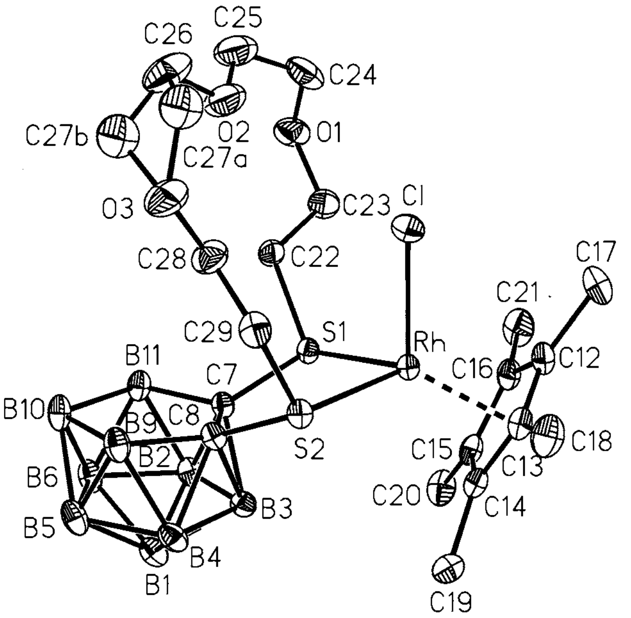

Fig. 1. Perspective view of $[Rh(C_5Me_5)Cl(n15S2)]$ showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Previous structural studies of chelated $[nxS2]^-$ metal complexes show that usually the metal is placed *anti* [1,4,8–10,13] with regard to the C_2B_3 open face but there exists also the possibility of a *syn* disposition [2,9,11].

Crystals of $[Rh(C_5Me_5)Cl(n15S2)]$ were grown from acetone. The molecular structure is shown in Fig. 1,

Table 1
Crystallographic data for $[Rh(C_5Me_5)Cl(n15S2)]$ (2) and $[Ir(C_5Me_5)Cl(n6S2)]$ (3)

Chemical formula	$C_{20}H_{41}B_9ClO_3RhS_2$	$C_{14}H_{29}B_9ClIrS_2$
Formula weight	629.30	586.43
a (Å)	11.2538(12)	8.497(2)
b (Å)	14.0980(11)	19.655(4)
c (Å)	10.6875(13)	13.874(4)
α (°)	104.017(8)	90
β (°)	118.316(8)	97.83(3)
γ (°)	84.816(9)	90
V (Å^3)	1447.7(3)	2295.5(10)
Z	2	4
Space group	$P\bar{1}$ (no.2)	$P2_1/n$ (no.14)
Temperature (°C)	21	21
λ (Å)	0.71069	0.71069
$D_{calc.}$ (g cm^{-3})	1.444	1.697
μ (cm^{-1})	849	16.13
R_1^a	0.0269	0.0387
wR_2^b	0.0747	0.0858

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

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^2$) for $[Rh(C_5Me_5)Cl(n15S2)]$

Atom	*x*	*y*	*z*	U_{eq}
Rh	7265(1)	6819(1)	−972(1)	27(1)
Cl	9561(1)	6859(1)	795(1)	50(1)
S(1)	6768(1)	8419(1)	−5(1)	29(1)
S(2)	6475(1)	6251(1)	448(1)	30(1)
O(1)	10244(2)	10001(2)	2523(3)	60(1)
O(2)	10786(3)	8469(3)	4444(3)	88(1)
O(3)	9422(3)	6726(2)	4647(3)	71(1)
B(1)	2997(3)	8008(3)	19(4)	40(1)
B(2)	4125(3)	8826(2)	97(4)	34(1)
B(3)	4230(3)	7569(2)	−555(3)	32(1)
B(4)	3869(3)	6927(2)	469(4)	38(1)
B(5)	3628(4)	7788(2)	1815(4)	42(1)
B(6)	3790(4)	9002(2)	1589(4)	40(1)
C(7)	5662(3)	8261(2)	732(3)	28(1)
C(8)	5530(3)	7227(2)	971(3)	29(1)
B(9)	5206(4)	7246(2)	2301(4)	38(1)
B(10)	5086(3)	8540(2)	3062(3)	42(1)
B(11)	5484(3)	9141(2)	1942(3)	35(1)
C(12)	7947(3)	6150(2)	−2616(3)	39(1)
C(13)	7031(3)	5507(2)	−2640(3)	36(1)
C(14)	5741(3)	5981(2)	−3066(3)	35(1)
C(15)	5902(3)	6926(2)	−3231(3)	36(1)
C(16)	7290(3)	7048(2)	−2900(3)	38(1)
C(17)	9362(4)	5919(3)	−2368(4)	58(1)
C(18)	7286(4)	4479(2)	−2439(4)	53(1)
C(19)	4459(3)	5490(2)	−3394(3)	47(1)
C(20)	4828(3)	7648(2)	−3783(3)	50(1)
C(21)	7876(4)	7922(3)	−3005(4)	59(1)
C(22)	8233(3)	9034(2)	1621(3)	39(1)
C(23)	9161(3)	9475(3)	1238(4)	56(1)
C(24)	11384(4)	9456(3)	3273(5)	69(1)
C(25)	11531(4)	9279(3)	4656(5)	78(1)
C(26)	11087(5)	8106(3)	5661(4)	85(1)
C(27a) # 1	10763(5)	7035(4)	5359(6)	75(2)
C(27b) # 2	10050(2)	7582(12)	5740(2)	75(2)
C(28)	8555(3)	6985(3)	3303(3)	53(1)
C(29)	7796(3)	6065(2)	2200(3)	41(1)

Site occupation parameters: # 1 = 0.833(8); # 2 = 0.167(8).
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

crystal data are listed in Table 1, final atomic parameters are given in Table 2, and selected bond distances and angles are reported in Table 3.

In $[Rh(C_5Me_5)Cl(n15S2)]$ the rhodium(III) atom has a three leg piano stool coordination. The carborane cluster is coordinated to the metal by the two sulphur atoms, and the remaining sites are occupied by the C_5Me_5 ring and the Cl atom. The macrocycle fragment is partly disordered because the C(27) atom is divided in two positions C(27a) and C(27b) with 83.3(8)% and 16.7(8)% occupancies. The macrocycle extends towards the cluster's open face, in such a way that the rhodium atom is *anti* with regard to the C_2B_3 open face and occupies the farthest possible position with respect to the cluster's open face, avoiding any possible interaction.

The ligand's conformation is the expected one for the free ligand to reduce the sulphur lone pairs π open face electrons interaction to an energy minimum. This suggest that the most stable ligand conformer establishes the ligand conformation in this complex.

The Rh–S(1), Rh–S(2) distances of 2.3797(7) Å and 2.3954(7) Å indicate that the cluster is coordinating in a symmetrical way. Excluding the partially disordered chain between the sulphur atoms, the molecule has a pseudo mirror plane that contains the Rh, B(1), B(3), B(10), Cl, C(12), and C(17) atoms. The distance between the cluster carbon atoms C(7)–C(8) is 1.571(3) Å being close to this in the sodium salt of the ligand 1.596(8) Å [1]. The distances of the five carbon atoms of the pentamethylcyclopentadienyl ring to Rh are quite similar. To say for Rh–C(12), Rh–C(13), Rh–C(14), Rh–C(15), and Rh–C(16) these are 2.216(3), 2.171(3), 2.189(3), 2.196(3), and 2.173(3) Å (average 2.191 Å), respectively, and thus the Rh–C distances are longer than in the compound $[Rh_2(C_5Me_5)_2Cl_4]$, in which the average is 2.128 Å [12].

Crystals of $[Ir(C_5Me_5)Cl(n6S2)]$ were grown from a mixture of CH_2Cl_2:EtOH (1:2). The structure is shown in Fig. 2, and crystal data, final atomic parameters, and selected distances and angles are listed in Tables 1, 4 and 5, respectively.

In $[Ir(C_5Me_5)Cl(n6S2)]$ the metal's coordination mode is similar to this in the Rh complex and thus the

Table 3
Selected bond lengths (Å) and angles (°) for $[Rh(C_5Me_5)Cl(n15S2)]$

Rh–C(12)	2.216(3)
Rh–C(13)	2.171(3)
Rh–C(14)	2.189(3)
Rh–C(15)	2.196(3)
Rh–C(16)	2.173(3)
Rh–Cl	2.3640(8)
Rh–S(1)	2.3797(7)
Rh–S(2)	2.3954(7)
S(1)–C(7)	1.813(2)
S(1)–C(22)	1.817(3)
S(2)–C(8)	1.807(3)
S(2)–C(29)	1.820(3)
C(7)–C(8)	1.571(3)
Cl–Rh–S(1)	96.68(3)
Cl–Rh–S(2)	93.89(3)
S(1)–Rh–S(2)	86.68(2)
C(7)–S(1)–Rh	106.30(8)
C(22)–S(1)–Rh	111.82(10)
C(7)–S(1)–C(22)	101.71(12)
C(8)–S(2)–Rh	106.97(8)
C(29)–S(2)–Rh	114.74(10)
C(8)–S(2)–C(29)	102.73(13)
B(3)–C(7)–S(1)	112.27(17)
C(8)–C(7)–S(1)	118.92(17)
B(11)–C(7)–S(1)	121.01(18)
B(3)–C(8)–S(2)	110.97(17)
C(7)–C(8)–S(2)	117.33(17)
B(9)–C(8)–S(2)	121.02(18)

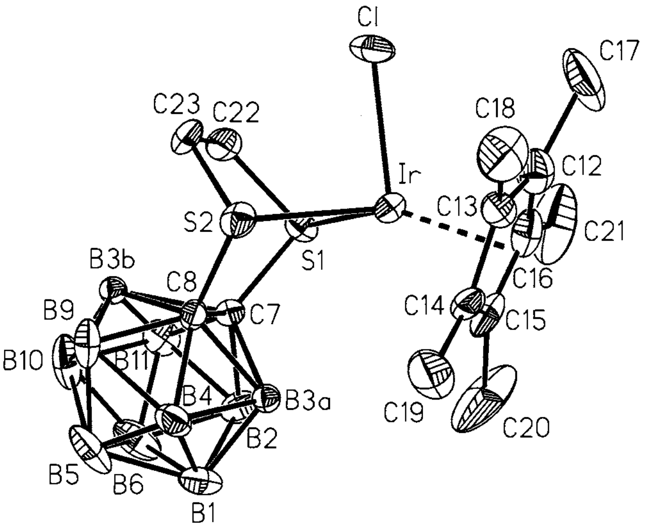

Fig. 2. Perspective view of [Ir(C_5Me_5)Cl(n6S2)] showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for [Ir(C_5Me_5)Cl(n6S2)]

Atom	*x*	*y*	*z*	U_{eq}
Ir	10225(1)	2327(1)	6391(1)	34(1)
Cl	12527(2)	2324(1)	5570(1)	74(1)
S(1)	9186(1)	3270(1)	5424(1)	39(1)
S(2)	11210(1)	3310(1)	7294(1)	45(1)
B(1)	6495(7)	4115(4)	7609(4)	63(2)
B(2)	6520(6)	3969(3)	6362(4)	53(2)
B(3a) #3	7663(8)	3485(4)	7266(5)	32(1)
B(3b) #4	9456(18)	4691(8)	6535(11)	32(1)
B(4)	8475(7)	4002(3)	8200(4)	52(2)
B(5)	7759(10)	4828(3)	7935(5)	84(3)
B(6)	6511(9)	4809(4)	6774(5)	76(2)
C(7)	8424(5)	3853(2)	6257(3)	34(1)
C(8)	9508(5)	3872(2)	7278(3)	34(1)
B(9)	9673(8)	4640(3)	7744(5)	62(2)
B(10)	8462(10)	5152(3)	6893(5)	80(3)
B(11)	7710(7)	4601(3)	5903(4)	55(2)
C(12)	10389(7)	1198(3)	6234(4)	63(2)
C(13)	10690(5)	1394(2)	7217(3)	44(1)
C(14)	9350(5)	1716(2)	7531(3)	45(1)
C(15)	8148(5)	1730(3)	6631(4)	67(2)
C(16)	8912(7)	1398(3)	5878(4)	64(2)
C(17)	11453(10)	771(3)	5680(5)	122(3)
C(18)	12212(6)	1202(3)	7850(5)	83(2)
C(19)	9232(8)	1918(3)	8554(4)	96(2)
C(20)	6448(7)	1901(4)	6616(8)	192(5)
C(21)	8021(10)	1295(4)	4850(5)	147(3)
C(22)	11015(6)	3744(3)	5376(4)	63(2)
C(23)	12071(6)	3771(3)	6356(4)	64(2)

Site occupation parameters: #3 = 0.704(7); #4 = 0.297(7).
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Selected bond lengths (Å) and angles (°) for [Ir(C_5Me_5)Cl(n6S2)]

Ir–C(12)	2.235(6)
Ir–C(13)	2.170(5)
Ir–C(14)	2.194(5)
Ir–C(15)	2.183(5)
Ir–C(16)	2.205(5)
Ir–Cl	2.3938(15)
Ir–S(1)	2.3863(12)
Ir–S(2)	2.3923(13)
S(1)–C(7)	1.810(4)
S(1)–C(22)	1.821(5)
S(2)–C(8)	1.818(4)
S(2)–C(23)	1.819(6)
C(7)–C(8)	1.581(5)
Cl–Ir–S(1)	89.88(5)
Cl–Ir–S(2)	90.05(5)
S(1)–Ir–S(2)	75.12(4)
C(7)–S(1)–Ir	105.67(14)
C(22)–S(1)–Ir	99.53(16)
C(7)–S(1)–C(22)	94.6(2)
C(8)–S(2)–Ir	105.27(13)
C(23)–S(2)–Ir	99.99(18)
C(8)–S(2)–C(23)	94.9(2)
B(3a)–C(7)–S(1)	116.5(3)
C(8)–C(7)–S(1)	111.8(3)
B(11)–C(7)–S(1)	121.7(3)
B(3a)–C(8)–S(2)	116.7(3)
C(7)–C(8)–S(2)	111.3(3)
B(9)–C(8)–S(2)	121.9(3)

metal is in a three leg piano stool coordination. The carborane cluster is coordinated in a symmetric way because the Ir–S(1), Ir–S(2) distances are 2.3863(12) and 2.3923(13) Å. These distances are slightly longer than the previously reported Ir(III)–S(thioether) distances of 2.349(2) and 2.376(2) Å found in [$IrO_2(C_2B_9H_{10}S_2Me)(PPh_3)_2$] [13]. The molecule has a pseudo mirror plane that includes the atoms Ir, B(1), B(10), Cl, C12, and C(17), and the disordered B(3) atom positions B(3a) and B(3b). The distance from the Ir atom to the five carbon atoms of the pentamethylcyclopentadienyl ring do not differ much, being 2.235(6), 2.170(5), 2.194(5), 2.183(5), and 2.205(5) Å for Ir–C(12), Ir–C(13), Ir–C(14), Ir–C(15), Ir–C(16), (average 2.213 Å), respectively. In [$Ir_2(C_5Me_5)_2Cl_4$] the average of the Ir–C bond length is 2.132 [14].

Contrarily to the Rh complex, the *nido* cage presents two orientations in [Ir(C_5Me_5)Cl(n6S2)] because B(3) is situated in two positions (B(3a) 70.4(7)% and B(3b) 29.6(7)%), as mentioned above. When B(3) is in position a the metal is *anti* with regard to the C_2B_3 open face and the ethylene group extends towards the cluster's open face.

As before, the ligand conformation is the one for a free ligand to reduce the sulphur lone pairs-π open face electrons interaction to an energy minimum. This suggest that the most stable ligand conformer establishes the ligand conformation in this complex in 70.4(7)% contrarily to the complex (**2**) that establishes this ligand conformation in 100%. Thus, the ethylene fragment permits that the metal can be *syn* with regard to the open face in 29.6(7)% when B(3) is in position b. Comparable disordering of B(3) atom and *anti* and *syn* conformations of the carborane cage have been reported for Ag(I) and Ru(II) complexes [2,9]. For the *syn* conformer the observed B(10)–B(3b) distance of 1.38(2) Å is obviously too short. However, the shapes of the displacement ellipsoids for atoms B(1), B(5), B(6), B(9), and B(10) indicate, that probably all the atoms of the carborane cage, except the cluster carbons, have two close positions (a and b), but the data did not allow their refinements. Thus the observed short B(3b)–B(10) distance is not real.

Comparison of the structures of [Rh(C_5Me_5)Cl(n15S2)] and [Ir(C_5Me_5)Cl(n6S2)] reveals that the bond lengths are very similar in the coordination spheres. Despite of the similar coordination modes of the carborane, pentamethylcyclopentadienyl and chloro ligands, there are considerable differences in the bond angle values as well as in the geometry of the two complexes originating from the different size of the organic chain between the sulphur atoms.

As reported earlier [9], the dihedral angle ω (between the planes S(1), M, S(2) and S(1), S(2), C(7), C(8)) and geometry of the S,S′-substituted carborane ligand can be modified in [RuCl(nxS2)(PPh_3)$_2$] complexes by changing the length of the link between the sulphur atoms. In the present Rh and Ir complexes no agostic B(3)–H–M bond can be formed as the coordination spheres of the metals are satisfied. The short ethylene bridge between the sulphur atoms makes the carborane ligand very rigid, and thus in the Ir complex the S–M–S angle is very closed 75.12(4)°. In the Rh complex the considerably longer chain between the S atoms allows a much greater S–M–S angle of 86.68(2)° to be formed. The chain length influences also into the shape of the molecules. In the Ir complex the dihedral angle between the planes S(1), Ir, S(2) and S(1), S(2), C(7), C(8) is 48.3(1)°, while in the Rh complex the relevant value is only 18.1(1)°. Further differences between the two structures can be noticed in the intramolecular distances. There are no very short interligand contacts in the Rh complex and thus the pentamethylcyclopentadienyl anion has enough space to take the energetically suitable orientation when coordinating to Rh. Contrarily to the Rh complex, the Ir complex is more crowded, and quite short interatomic contact distances can be noticed. So it seems that first of all the available space for the pentamethylcyclopentadienyl moiety influences its orientation and the Cl atom in the two complexes. Accordingly, the dihedral angle between the planes S(1), M, S(2) and C(12), C(13), C(14), C(15), C(16) is 52.64(7)° in the Rh complex and 62.4(2)° in the Ir complex.

3. Experimental section

3.1. General methods

Ligands [NMe_4][7,8 - μ - (S(CH_2)$_2$S) - 7,8 - $C_2B_9H_{10}$], [NMe_4][n6S2] and [NMe_4][7,8-μ-(S-CH_2CH_2(OCH_2-CH_2)$_3$S)-7,8-$C_2B_9H_{10}$)], [NMe_4][n15S2] [15] and complexes [M_2(C_5Me_5)$_2Cl_4$] (M = Rh [16], Ir [17]) were synthesised by published procedures. Ethanol was of reagent quality. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed in our analytical laboratory by using a Perking Elmer 240B microanalyzer. IR spectra (KBr disk) were measured on a Nicolet 710-FT spectrophotometer. The $^1H\{^{11}B\}$-NMR and $^{11}B\{^1H\}$-NMR spectra were recorded on a Bruker ARX-300 instrument.

3.2. Synthesis of [Rh(C_5Me_5)Cl(n6S2], (**1**)

To a deoxygenated boiling ethanol solution (8 ml) containing [NMe_4][n6S2] (48 mg, 0.16 mmol) was added [Rh_2(C_5Me_5)$_2Cl_4$] (50 mg, 0.08 mmol) and the mixture was refluxed for 4 h. A yellow solid was separated by filtering the warm mixture. The solid was washed with water, warm ethanol and diethyl ether to yield an analytically pure solid [Rh(C_5Me_5)Cl(n6S2)] (**1**). Yield 50 mg (64%). Anal. Calc. for $C_{14}H_{29}B_9ClRhS_2$: C, 33.82; H, 5.88; S, 12.90. Found: C, 33.57; H, 5.55; S, 12.70. IR (KBr), υ (cm^{-1}): 2537 (B–H). $^1H\{^{11}B\}$-NMR (300 MHz, $(CD_3)_2CO$, 25°C, TMS): $\delta = -2.8$ (br, 1H, B–*H*–B), 1.8 (s, 15H, C*–*Me*), 3.4 (m, *2H*, $-CH_2^{a}$), 3.8 (m, 2H, $-CH_2^{b}$). $^{11}B\{^1H\}$-NMR (96 MHz, $(CD_3)_2CO$, 25°C, $BF_3\cdot Et_2O$): $\delta = -12.2$ (1B), -15.2 (2B), -18.9 (1B), -20.8 (2B), -25.1 (1B), -35.3 (1B), -40.5 (1B).

3.3. Synthesis of [Rh(C_5Me_5)Cl(n15S2)], (**2**)

Following the procedure described above, deoxygenated boiling ethanol (10 ml) containing [NMe_4][n15S2] (66 mg, 0.16 mmol) and [Rh(C_5Me_5)Cl_2]$_2$ (50 mg, 0.08 mmol) was refluxed for 2 h to yield a yellow solid [Rh(C_5Me_5)Cl(n15S2)]. Yield 63 mg (64%). Anal. Calc. for $C_{20}H_{41}B_9ClO_3RhS_2$: C, 38.17; H, 6.57; S, 10.19. Found: C, 38.37; H, 6.33; S, 9.92. IR (KBr), υ (cm^{-1}): 2542 (B–H). $^1H\{^{11}B\}$-NMR (300 MHz, $(CD_3)_2CO$, 25°C, TMS): $\delta = -2.8$ (br, 1H, B–*H*–B), 1.8 (s, 15H, C*–*Me*), 3.1 (m, 4H, $-CH_2$), 3.6 (m, 4H, $-CH_2$), 3.9 (m, 4H, $-CH_2$), 4.3 (m, 4H, $-CH_2$). $^{11}B\{^1H\}$-NMR (96 MHz, $(CD_3)_2CO$, 25°C, $BF_3\cdot Et_2O$): $\delta = -10.5$ (2B), -15.1 (2B), -16.5 (3B), -29.4 (1B), -34.6 (1B). A yellow crystal suitable for X-ray analysis was grown from acetone.

3.4. Synthesis of [Ir(C_5Me_5)Cl(n6S2)], (3)

Following the procedure described above, deoxygenated boiling ethanol (8 ml) containing [NMe_4][n6S2] (92 mg, 0.14 mmol) and [Ir(C_5Me_5)Cl_2]$_2$ (50 mg, 0.07 mmol) was refluxed for 3 h to yield a yellow solid [Ir(C_5Me_5)Cl(n6S2)]. Yield 54 mg, (61%). Anal. Calc. for $C_{14}H_{29}B_9ClIrS_2$: C, 28.67; H, 4.98; S, 10.93. Found: C, 28.48; H, 5.02; S, 10.67. IR (KBr), υ (cm^{-1}): 2538 (B–H). ^{1}H{^{11}B}-NMR (300 MHz, $(CD_3)_2CO$, 25°C, TMS): $\delta = -2.7$ (br, 1H, B–*H*–B), 1.8 (s, 15H, C*–*Me*), 3.8 (m, 2H, –CH_2^a), 4.2 (m, 2H, –CH_2^b). ^{11}B{^{1}H}-NMR (96 MHz, $(CD_3)_2CO$, 25°C, $BF_3 \cdot Et_2O$): $\delta = -8.0$ (1B), -11.9(2B), -14.8 (1B), -16.1 (1B), -17.3 (1B), -21.5 (1B), -30.8 (1B), -36.2 (1B). A yellow crystal suitable for X-ray analysis was grown from a mixture of CH_2Cl_2:EtOH (1:2).

3.5. X-ray structure determinations of [Rh(C_5Me_5)Cl(n15S2)] or (2) and [Ir(C_5Me_5)Cl(n6S2)] or (3)

Single-crystal data collections for both compounds were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo–K_α radiation. The unit cell parameters for both compounds were determined by least-squares refinement of 25 carefully centred reflections. Both data obtained were corrected for Lorentz and polarization effects and for dispersion. Corrections for empirical absorption (ψ scan) were also applied. A total of 5394 and 4300 reflections giving 5111 and 4042 unique reflections ($R_{\mathrm{int}} = 0.0106$ and 0.0356) were collected by $\omega/2\theta$ scan mode ($2\theta_{\mathrm{max}} = 50°$) for **2** and **3**, respectively.

Both structures were solved by direct methods by using the SHELXS86 program [18] and least-squares refinements and all subsequent calculations were performed using the SHELX-97 program system [19].

For complex **2**, refinement of all non-hydrogen atoms with anisotropic displacement parameters revealed a residual peak of 1.00 e Å^{-3} at the vicinity of C(27) indicating that C(27) occupies two positions, labelled C(27a) and C(27b). Refinement resulted site occupation parameters 0.833(8) for C(27a) and 0.167(8) for C(27b). In final cycles, C(27a) and C(27b) were refined with isotropic but rest of the non-hydrogen atoms with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at the fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters. Partially occupied hydrogen atoms were not positioned.

For complex **3**, refinement of all non-hydrogen atoms with anisotropic displacement parameters revealed a residual peak of 1.38 e Å^{-3} at the C_2B_3 open face and at a distance of 1.4 Å from B(10) indicating that B(3) occupies two positions, labelled B(3a) and B(3b). Refinement resulted site occupation parameters 0.704(7) for B(3a) and 0.296(7) for B(3b). B(3a) and B(3b) were refined with isotropic but rest of the non-hydrogen atoms with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at the fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters. Partially occupied bridging hydrogen atoms were not positioned. Maximum and minimum residual electron densities of 1.346 and –1.126 e Å^{-3} were at the vicinity of Ir.

3.6. Supplementary data

Tables including crystal data and structure refinement, interatomic distances and angles, positional and thermal parameters for hydrogen atoms, anisotropic displacements parameters for non-hydrogen atoms and least-squares planes for **2** and **3** are available.

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References

[1] (a) F. Teixidor, C. Viñas, J. Rius, C. Miravitlles, J. Casabó, Inorg. Chem. 29 (1990), 149. (b) F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó, J. Organomet. Chem. 43 (1994) 153. (c) F. Teixidor, J. Rius, C. Miravitlles, C. Viñas, Ll. Escriche, E. Sanchez, J. Casabó, Inorg. Chim. Acta 176 (1990) 61.

[2] F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó, Inorg. Chem. 33 (1994) 1756.

[3] C. Viñas, J. Pedrajas, J. Bertran, F. Teixidor, R. Kivekäs, R. Sillanpää, Inorg. Chem. 36 (1997) 2482.

[4] (a) F. Teixidor, A. Romerosa, C. Viñas, J. Rius, C. Miravitlles, J. Casabó, J. Chem. Soc. Chem. Commun. (1991) 192. (b) F. Teixidor, J. Casabó, C. Viñas, E. Sanchez, Ll. Escriche, R. Kivekäs, Inorg. Chem. 30 (1991) 3053.

[5] M.J.H. Russell, C. White, A. Yates, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1978) 849.

[6] (a) J.J. Garcia, H. Torrens, H. Adams, N.A. Bailey, P.M. Maitlis, J. Chem. Soc. Chem. Commun. (1991) 74. (b) J.J. Garcia, H. Torrens, H. Adams, N.A. Bailey, A. Shacklady, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1993) 1529. (c) P. Cornago, C. Escolástico, M.D. Santa Maria, et al., J. Organomet. Chem. 467 (1994) 293. (d) D. Drommi, C.G. Arena, F. Nicolò, G. Bruno, F. Faraone, J. Organomet. Chem. 485 (1995) 115. (e) J.A. Bailey, S.L. Grundy, S.R. Stobart, Inorg. Chim. Acta 243 (1996) 47. (f) D. Carmona, F.J. Lahoz, L.A. Oro, M.P. Lamata, F. Viguri, E. San José, Organometallics 15 (1996) 2961. (g) D.M. Heinekey, A.S. Hinkle, J.D. Close, J. Am. Chem. Soc. 118 (1996) 5353. (h) J. Chen, L.M. Daniels, J. Angelici, Organometallics 15 (1996) 1223 and references therein. (i) R.D. Simpson, W.J. Marshall, Organometallics 16 (1997) 3719. (j) F. Teixidor, M.R.

Cirera, C. Viñas, R. Kivekäs, R. Sillanpää, J. Llibre, New J. Chem. (in press).
[7] (a) P.M. Maitlis, Acc. Chem. Res. 11 (1978) 301 and references therein. (b) A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352. (c) J.K. Hoyano, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3723. (d) D.S. Glueck, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 111 (1989) 2719. (e) W.D. Jones, R.M. Chin, J. Am. Chem. Soc. 116 (1994) 198. (f) D.A. Dobbs, R.G. Bergman, Organometallics 13 (1994) 4594. (g) J.C.M. Ritter, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 2580.
[8] F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó, J. Chem. Soc. Chem. Commun. (1992) 1281.
[9] F. Teixidor, J.A. Ayllón, C. Viñas, R. Kivekäs, R. Sillanpää, J. Casabó, Organometallics 13 (1994) 2751.
[10] (a) F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, J. Casabó, Inorg. Chem. 33 (1994) 2645. (b) R. Kivekäs, R. Sillanpää, F. Teixidor, C. Viñas, E. Sanchez, Acta. Chim. Scand. 48 (1994) 113.
[11] F. Teixidor, J.A. Ayllón, C. Viñas, J. Rius, C. Miravitlles, J. Casabó, J. Chem. Soc. Chem. Commun. (1992) 1279.
[12] M.R. Churchill, S.A. Julis, F.J. Rotella, Inorg. Chem. 16 (1977) 1137.
[13] F. Teixidor, J.A. Ayllón, C. Viñas, R. Sillanpää, R. Kivekäs, J. Casabó, Inorg. Chem. 33 (1994) 4815.
[14] M.R. Churchill, S.A. Julis, Inorg. Chem. 16 (1977) 1488.
[15] F. Teixidor, A.M. Romerosa, J. Rius, C. Miravitlles, J. Casabó, C. Viñas, E. Sanchez, J. Chem. Soc. Dalton Trans. (1990) 525.
[16] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1989) 229.
[17] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1989) 230.
[18] G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, University of Gottingen, Germany, 1986.
[19] G.M. Sheldrick, SHELX-97, Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.