Sandwich iridium complexes with the monoanionic carborane ligand [9-SMe_2-7,8-$C_2B_9H_{10}$]$^-$

*D. A. Loginov, M. M. Vinogradov, D. S. Perekalin, Z. A. Starikova, K. A. Lyssenko, P. V. Petrovskii, and A. R. Kudinov**

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5085. E-mail: arkudinov@ineos.ac.ru

The reaction of the [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)$IrBr_2$]$_2$ complex with Tl[Tl(η-7,8-$C_2B_9H_{11}$)] afforded the iridacarborane compound (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(η-7,8-$C_2B_9H_{11}$). The cationic complex [Cp*Ir(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]$^+PF_6^-$ (**5**·PF_6, Cp* is pentamethylcyclopentadienyl) was synthesized by the reaction of [Cp*$IrCl_2$]$_2$ with Na[9-SMe_2-7,8-$C_2B_9H_{10}$]. The structures of (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(η-cod) (cod is 1,5-cyclooctadiene) and **5**·PF_6 were established by X-ray diffraction.

Key words: iridium, metallacarboranes, sandwich compounds.

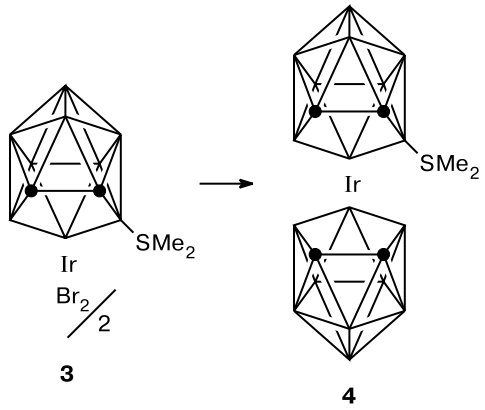
The carborane ligand [9-SMe_2-7,8-$C_2B_9H_{10}$]$^-$ (**1**) is isolobal with the cyclopentadienide anion and has the same charge. Therefore, complexes with **1** are close analogs of metallocenes. The sandwich compounds (η-9-SMe_2-7,8-$C_2B_9H_{10}$)$_2$Fe (see Ref. 1) and (ring)M(η-9-SMe_2-7,8-$C_2B_9H_{10}$), where (ring)M = (C_5R_5)Fe,[2,3] (C_4Me_4)Co,[3,4] CpNi,[5] (C_5R_5)Ru,[5,6] or (arene)Ru,[7,8] have been characterized earlier. The reaction of the cyclooctadiene complexes (η-9-SMe_2-7,8-$C_2B_9H_{10}$)M(η-cod) (M = Rh or Ir; cod is 1,5-cyclooctadiene) with hydrohalic acids afforded the dinuclear halide metallacarborane complexes [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)MX_2]$_2$ (X = Cl, Br, or I)[9—11] analogous to the known [Cp*MCl_2]$_2$ compounds (Cp* is pentamethylcyclopentadienyl). These rhodium complexes were used for the synthesis of other derivatives containing the (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh fragment.[10]

In the present study, we synthesized sandwich iridium complexes with ligand **1** and established the structures of (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(η-cod) (**2**) and [Cp*Ir(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]PF_6 by X-ray diffraction.

Results and Discussion

We found that the reaction of the [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)$IrBr_2$]$_2$ complex (**3**) with Tl[Tl(η-7,8-$C_2B_9H_{11}$)] yielded the iridium complex (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(η-7,8-$C_2B_9H_{11}$) (**4**) containing simultaneously the mono- and dianionic carborane ligands (Scheme 1). Earlier, this approach has been used for the synthesis of the rhodium complex (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(η-7,8-$C_2B_9H_{11}$).[10]

Scheme 1



Reagents: Tl[Tl(η-7,8-$C_2B_9H_{11}$)], MeCN.

However, an analogous reaction of **3** with Cp*Li in tetrahydrofuran did not produce the expected (cyclopentadienyl)iridacarborane complex [Cp*Ir(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]$^+$ (**5**). An attempt to synthesize cation **5** by the reaction of the solvate complex [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(Me_2CO)$_3$]$^+$ (which was generated from **3** by elimination of the bromide ions under the action of a silver salt in acetone) with C_5Me_5H also failed.* Nevertheless, we succeeded in preparing complex **5** by the reaction of [Cp*$IrCl_2$]$_2$ with the sodium salt of carborane anion **1** (Scheme 2).** Earlier, we have used analogous

* Earlier, this method has been successfully used for the synthesis of the rhodium complex [Cp*Rh(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]$^+$.[10]

** Cation **5** was isolated as a salt with the PF_6^- anion.

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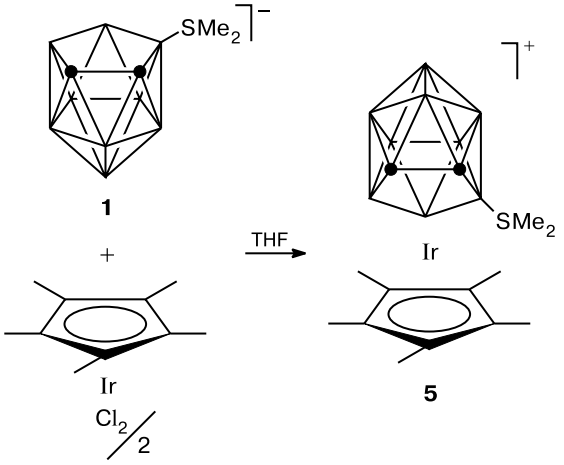
reactions of $[Cp^*RhCl_2]_2$ and $[(arene)RuCl_2]_2$ with **1** for the synthesis of $[Cp^*Rh(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^+$ (see Ref. 10) and $[(arene)Ru(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^+$, respectively.[7]

Scheme 2



Compounds **4** and **5** · PF_6 are colorless crystalline compounds, which are stable in air both in the solid state and as solutions in CH_2Cl_2 and Me_2CO. Their structures were confirmed by elemental analysis and ^1H and ^{11}B NMR spectroscopy (Table 1). The ^1H NMR spectrum of complex **4** shows four signals for the CH protons of two carborane ligands. The nonequivalence of the CH protons in the unsubstituted carborane ligand is, apparently, associated with slow rotation of this ligand on the NMR time scale. An analogous situation has been observed earlier for the rhodium analog $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}7,8\text{-}C_2B_9H_{11})$.[10]

Compounds **2** and **5** · PF_6 were studied by X-ray diffraction. The structures of complex **2** and cation **5** are shown in Figs 1 and 2, respectively. Selected bond lengths for these complexes and the related compound $Cp^*Ir(7,8\text{-}C_2B_9H_{11})$[12] are given in Table 2. In complex **2**, the distance between the iridium atom and the C_2B_3 plane (Δ_1) is 1.655(2) Å. The pentagonal C_2B_3 face adopts an envelope conformation with the C(7) atom deviating from the C(8)—B(9)—B(10)—B(11) plane by 0.062(6) Å. In cation **5**, the distance Δ_1 (1.598(4) Å) is substantially shorter than that in **2**, and the C_2B_3 face is planar. The observed differences are, apparently, associated with

Table 1. ^1H and $^{11}B\{^1H\}$ NMR spectroscopic data for complexes **4** and **5** in $(CD_3)_2CO$

Compound	δ	
	^1H	$^{11}B\{^1H\}$
4	2.76 (s, 6 H, SMe_2); 4.40 (br.s, 1 H, carb. CH); 4.46 (br.s, 1 H, carb. CH); 4.62 (br.s, 1 H, carb. CH); 5.23 (br.s, 1 H, carb. CH)	−24.3 (1 B); −23.4 (1 B); −20.4 (2 B); −18.5 (1 B); −17.7 (1 B); −12.0 (1 B); −8.7 (4 B); −7.7 (2 B); −4.6 (1 B, B(9)); −1.9 (1 B); 0.2 (1 B); 1.4 (1 B); 4.5 (1 B)
5	2.29 (s, 15 H, Cp*); 2.74 (s, 6 H, SMe_2); 4.30 (br.s, 1 H, carb. CH); 5.15 (br.s, 1 H, carb. CH)	−25.2 (1 B); −21.9 (1 B); −21.0 (1 B); −13.3 (1 B); −10.1 (1 B); −6.8 (1 B); −6.0 (1 B, B(9)); −2.1 (1 B); −1.3 (1 B)

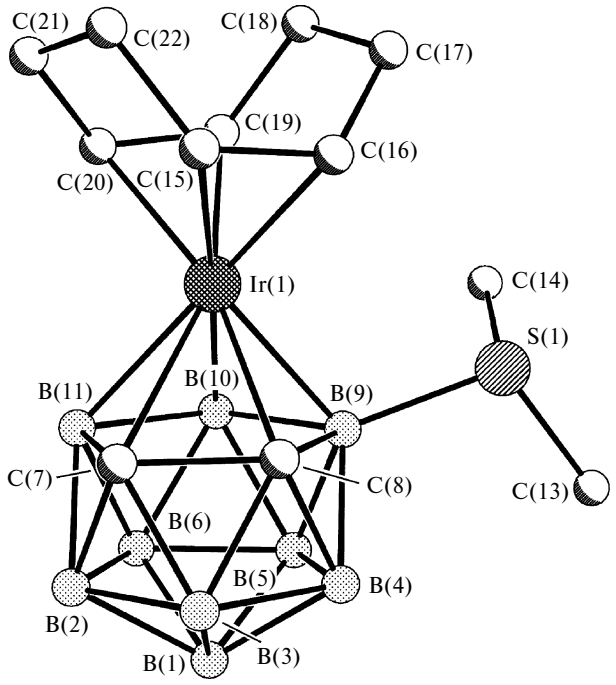


Fig. 1. Structure of complex **2**.

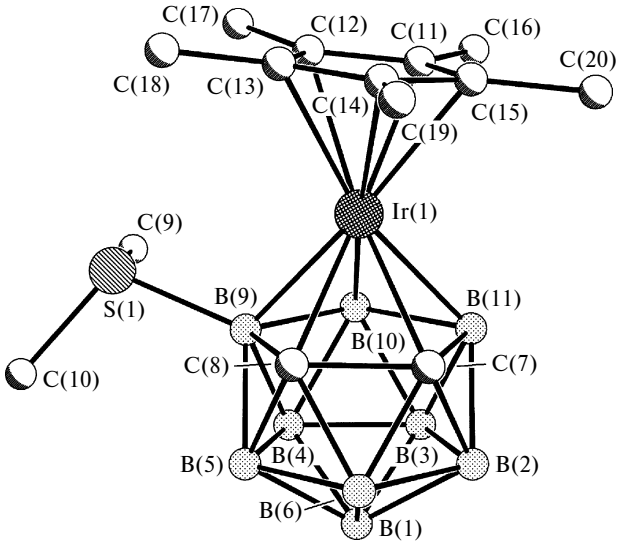


Fig. 2. Structure of cation **5**.

Table 2. Selected bond length (Å) in complexes **2**, **5**·PF_6, and Cp*Ir(7,8-$C_2B_9H_{11}$)[12]

Bond	**2**	**5**·PF_6	Cp*Ir(7,8-$C_2B_9H_{11}$)
Ir(1)—C(7)	2.273(3)	2.169(7)	2.17
Ir(1)—C(8)	2.164(3)	2.154(7)	2.16
Ir(1)—B(9)	2.198(4)	2.178(8)	2.18
Ir(1)—B(10)	2.239(4)	2.211(8)	2.21
Ir(1)—B(11)	2.256(4)	2.200(8)	2.14
Ir(1)—C(L)*	2.163(3) (C(15))	2.169(7) (C(11))	2.16
	2.157(3) (C(17))	2.204(7) (C(12))	2.22
	2.120(3) (C(19))	2.228(7) (C(13))	2.23
	2.117(4) (C(20))	2.217(7) (C(14))	2.20
	—	2.193(7) (C(15))	2.16
C(7)—C(8)	1.655(5)	1.64(1)	1.62
C(7)—B(11)	1.701(5)	1.76(1)	1.76
C(8)—B(9)	1.752(5)	1.70(1)	1.72
B(9)—B(10)	1.799(5)	1.82(1)	1.78
B(10)—B(11)	1.834(6)	1.82(1)	1.88
B(9)—S(1)	1.887(4)	1.919(8)	—

* L is a ligand.

higher symmetry and stronger π-donating ability of the Cp* ligand compared to cyclooctadiene.

The most distinguishing structural feature of complex **2** is that the Ir(1)—C(7) and Ir(1)—C(8) bond lengths are substantially different (by 0.109(3) Å). A shortening of the Ir(1)—C(8) bond is, apparently, attributed to the *trans*-effect of the C(19)—C(20) double bond of the cyclooctadiene ligand. The Ir(1)—C(19) and Ir(1)—C(20) bonds (aver. 2.118 Å) are substantially shorter than the Ir(1)—C(15) and Ir(1)—C(16) bonds (aver. 2.160 Å). In addition, the C(19)—C(20) bond (1.439(5) Å) in the cyclooctadiene ligand is 0.01 Å longer than the C(15)—C(16) bond (1.429(5) Å). An analogous situation was observed in the related rhodium and palladium complexes.[13] Coordination of the metal atom by the Cp* ligand, unlike coordination by the cyclooctadiene ligand, does not lead to such a large difference in the length of the M—C(7) and M—C(8) bonds. In cation **5**, as well as in the related rhodium,[10] ruthenium,[6] and iron[2] complexes, these bond lengths differ by no more than 0.03 Å.

The structure of cation **5** is, as a whole, similar to the structure of the neutral Cp*Ir(7,8-$C_2B_9H_{11}$) complex.[12] In both compounds, the bonds are similar in length (see Table 2). However, the bond lengths in the neutral complex were determined with low accuracy (0.011—0.030 Å), which did not allow us to perform an in-depth comparison. The distance Δ_1 in Cp*Ir(7,8-$C_2B_9H_{11}$) (1.579 Å) is 0.02 Å shorter than that in **5**, which can be considered as evidence for stronger binding of the dicarbollide dianion compared to anion **1**. The distance between the metal atom and the C_2B_3 plane in the rhodium complex [Cp*Rh(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]$^+$ (1.625 Å)[10] is also longer than that in Cp*Rh(7,8-$C_2B_9H_{11}$) (1.596 Å).[12]

The distance between the iridium atom and the plane of the Cp* ligand (Δ_2) in cation **5** (1.833(3) Å) is somewhat longer than that in [Cp*IrCp]$^+$ (1.80 Å),[14] which can be attributed to a weaker back donation due to the stronger accepting character of ligand **1** compared to Cp^-. The angle between the Cp* ring and the C_2B_3 plane is 5.5°. In the unsubstituted Cp*Ir(η-7,8-$C_2B_9H_{11}$) complex, the corresponding angle is 7.6°.[12] The SMe_2 group in **5** is twisted by 49.1(3)° out of the C_2B_3 plane so that both Me groups are oriented in the direction opposite to the iridium atom. The Ir(1)—B(9)—S(1)—C(9) and Ir(1)—B(9)—S(1)—C(10) torsion angles are 97.9(4)° and −158.4(4)°, respectively. The same orientation of the SMe_2 group was observed in [Cp*Rh(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]$^+$ (see Ref. 10) and Cp*M(η-9-SMe_2-7,8-$C_2B_9H_{10}$) (M = Fe (see Ref. 2) or Ru (see Ref. 6)). However, the orientation of this group in molecule **2** is substantially different. This group is twisted out of the C_2B_3 plane by 57.0(2)°. The Ir(1)—B(9)—S(1)—C(13) and Ir(1)—B(9)—S(1)—C(14) torsion angles are −179.2(2) and −74.3(2)°, respectively. In analogous rhodium and palladium complexes,[13] the orientation of the SMe_2 group is similar to that in complex **2**. The difference in the orientation of this group in complex **2** and cation **5** is, apparently, attributed to the steric effect of five methyl groups of the Cp* ligand.

Experimental

The reactions were carried out under argon with the use of anhydrous solvents, which were prepared according to standard procedures. All operations associated with isolation of the reaction products were performed in air. The starting compounds Na[**1**],[1] **2**, **3**,[11] Tl[Tl(η-7,8-$C_2B_9H_{11}$)],[15] and [Cp*$IrCl_2$]$_2$ (see Ref. 16) were synthesized according to known procedures. The ^{1}H NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz for ^{1}H and 128.38 MHz for ^{11}B).

(9-Dimethylsulfonio-7,8-dicarbollyl)(7,8-dicarbollyl)iridium, (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Ir(η-7,8-$C_2B_9H_{11}$) (4). Acetonitrile (5 mL) was added to a mixture of complex **3** (70 mg, 0.064 mmol) and Tl[Tl(η-7,8-$C_2B_9H_{11}$)] (87 mg, 0.161 mmol). The reaction mixture was stirred for 48 h and filtered through a layer of SiO_2 (5 cm). The solvent was removed *in vacuo* and the residue was dissolved in acetone (2 mL). Then petroleum ether (6 mL) was added, the resulting dark oily precipitate was separated by centrifugation, and petroleum ether (10 mL) was added. The white precipitate that formed was filtered off and dried *in vacuo*. Complex **4** was obtained as a white solid compound in a yield of 40 mg (60%). Found (%): C, 17.25; H, 5.68; B, 34.86.

$C_6H_{27}B_{18}IrS \cdot 0.75(CH_3)_2CO$. Calculated (%): C, 17.64; H, 5.65; B, 34.64.

(9-Dimethylsulfonio-7,8-dicarbollyl)(pentamethylcyclopentadienyl)iridium hexafluorophosphate, [Cp*Ir(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]PF_6 (5 · PF_6). A solution of Na[9-SMe_2-7,8-$C_2B_9H_{10}$] in THF (1.3 mL of a 0.16 *M* solution, 0.208 mmol) was added to a suspension of the $[Cp^*IrCl_2]_2$ complex (72 mg, 0.090 mmol) in THF (5 mL). The reaction mixture was stirred for 72 h. The solvent was removed *in vacuo* and the solid residue was extracted with warm water (50—70 °C, 2×5 mL). Then an excess of an aqueous NH_4PF_6 solution was added. The white precipitate that formed was filtered off, washed with water, and dried *in vacuo*.

Table 3. Crystallographic data and details of the structure refinement for compounds **2** and **5** · PF_6

Parameter	**2**	**5** · PF_6
Molecular formula	$C_{12}H_{28}B_9IrS$	$C_{14}H_{31}B_9F_6IrPS$
M	512.89	665.91
Space group	$P\bar{1}$	$P2_1/n$
T/K	110	163
a/Å	6.9949(7)	15.192(4)
b/Å	8.4718(9)	9.621(3)
c/Å	16.122(2)	16.449(5)
α/deg	100.964(2)	—
β/deg	93.254(2)	99.16(2)
γ/deg	107.397(2)	—
V/Å^3	888.4(2)	2374(1)
Z	2	4
d_{calc}/g cm^{-3}	1.917	1.863
Color, crystal shape	Colorless platelet	
Crystal dimensions/mm	0.40×0.25×0.15	0.45×0.30×0.20
Diffractometer	Bruker SMART	Syntex $P2_1$
Radiation	Mo-K_α (λ = 0.71073)	
μ/cm^{-1}	76.31	58.29
Absorption correction	DIFABS	—
Scan mode	φ − ω	θ/2θ
$2\theta_{max}$/deg	60.0	50.0
Total number of reflections	10703	4100
Number of independent reflections (R_{int})	5137 (0.0246)	3931 (0.0431)
Number of reflections with $I > 2\sigma(I)$	4843	3389
R_1 (based on *F* for reflections with $I > 2\sigma(I)$)	0.0282	0.0519
wR_2 (based on F^2 for all reflections)	0.0739	0.1155
Number of parameters in refinement	316	289
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = 1/3(F_0^2 + 2F_c^2)$	
a	0.0500	0.0808
b	0.6000	24.6974
GOOF	1.078	1.008
F(000)	494	1288
Residual electron density (max/min)/e Å^{-3}	4.262/−2.173	4.142/−3.284

After reprecipitation with diethyl ether from CH_2Cl_2, complex **5** · PF_6 was obtained as a solid white compound in a yield of 87 mg (71%). Found (%): C, 25.27; H, 4.61; B, 14.71. $C_{14}H_{31}B_9F_6IrPS$. Calculated (%): C, 25.25; H, 4.69; B, 14.61.

X-ray diffraction study of complexes 2 and 5 · PF_6. Colorless platelet crystals of **2** and **5** · PF_6 were grown by slow diffusion in a two-layer system, *viz.*, a solution of the complex in a CH_2Cl_2—petroleum ether (**2**) or CH_2Cl_2—Et_2O (**5** · PF_6) mixture. The crystallographic data, characteristics of X-ray data collection, and details of the structure solution and refinement are given in Table 3. The structures were solved by direct methods. All nonhydrogen atoms were located from difference Fourier maps and refined against F^2_{hkl} with anisotropic displacement parameters. The hydrogen atoms in the carborane fragment were located from difference Fourier maps and refined isotropically. Other hydrogen atoms were placed in geometrically calculated positions and refined using the riding model with $U(H) = nU(C)$, where $U(C)$ is the equivalent thermal parameter of the corresponding pivot carbon atom, $n = 1.2$ for CH and CH_2 groups, and $n = 1.5$ for Me groups. All calculations were carried out using the SHELXTL PLUS 5 program package.[17] The atomic coordinates, displacement parameters, and complete data on geometric parameters were deposited with the Cambridge Structural Database.

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