Structures of cationic metallacarborane complexes $[(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})\text{Ni}(\mu\text{-Cp})\text{Ni}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})]^+$ and $[\text{Cp*Ru}(\text{Me}_2\text{S-C}_2\text{B}_9\text{H}_{10})\text{RuCp*}]^+$

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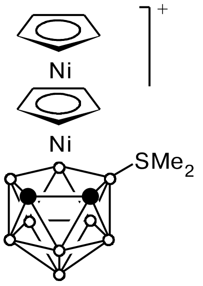
The structures of the metallacarborane cations $[(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})\text{Ni}(\mu\text{-Cp})\text{Ni}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})]^+$ (**2**) and $[\text{Cp*Ru}(\text{Me}_2\text{S-C}_2\text{B}_9\text{H}_{10})\text{RuCp*}]^+$ (**4b**) were established by X-ray diffraction analysis. These results confirmed the triple-decker structure proposed for complex **2** earlier, whereas complex **4b** proved to be 13-vertex dimetallacarborane rather than the triple-decker complex, as has been suggested earlier.

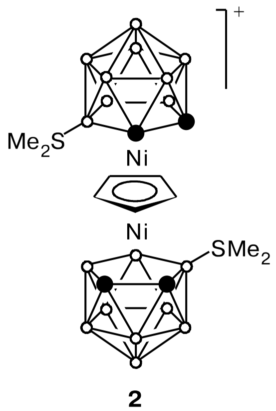
Key words: metallacarboranes, nickel, ruthenium, triple-decker complexes.

Earlier,[1] we have studied the electrophilic reactions of metallacarboranes $(\text{C}_5\text{R}_5)\text{M}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})$ (M = Ni, Ru; R = H, Me) with cationic metal complex fragments. The reactions of nickelacarborane $\text{CpNi}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})$ with the $[\text{CpNi}]^+$ and $[(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})\text{Ni}]^+$ cations afforded triple-decker nickel complexes **1** and **2**, respectively. In the cited study,[1] the structures of triple-decker ruthenium complexes **3a,b** have been assigned to the products of the reactions of ruthenacarborane $\text{Cp*Ru}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})$ with the $[(\text{C}_5\text{R}_5)\text{Ru}]^+$ fragments (R = H, Me).

In the present study, the triple-decker structure of nickel complex **2** was confirmed by X-ray diffraction analysis. However, the X-ray study demonstrated that the ruthenium-containing complexes have, in fact, structures of 13-vertex dimetallacarboranes **4a,b**.



1



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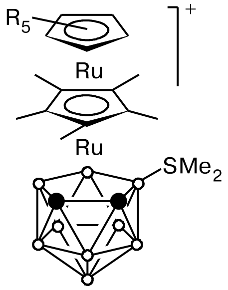
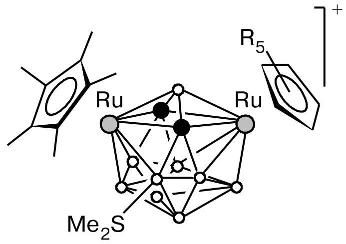


3a,b



4a,b

R = H (**a**), Me (**b**)

Results and Discussion

The structure of triple-decker cation **2** (*meso* form) is shown in Fig. 1. Selected bond lengths are given in Table 1. In the crystal, the cation occupies a special position, *viz.*, an inversion center, which coincides with the center of the cyclopentadienyl ligand. The planes of the five-membered rings bound to the nickel atoms are almost coplanar ($\text{C}_2\text{B}_3/\text{C}_5$ dihedral angle is 3.5°). Due to the presence of the center of symmetry, the cyclopentadienyl ligand is disordered over two positions. The dihedral angle between the planes of the cyclopentadienyl ligand in these positions is 180°, the Cp ring in both conformers adopting an eclipsed conformation with respect to one of the C_2B_3 rings (torsion angle is 5°) and a staggered conformation with respect to another C_2B_3 ring (Fig. 2). The distances

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† Deceased.

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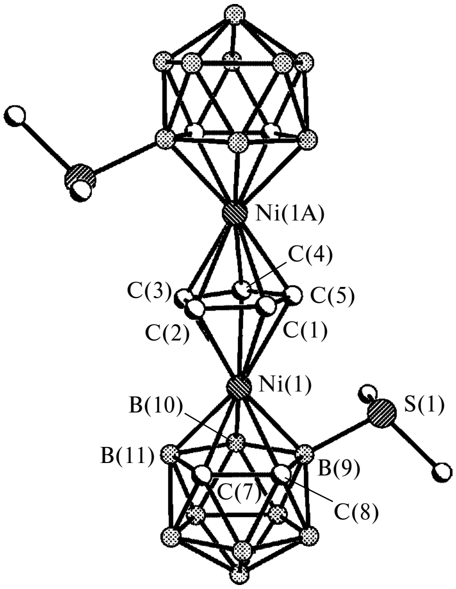

Fig. 1. Structure of the *meso* form of triple-decker nickelacarborane cation **2**. Disorder of the Cp ligand is omitted.

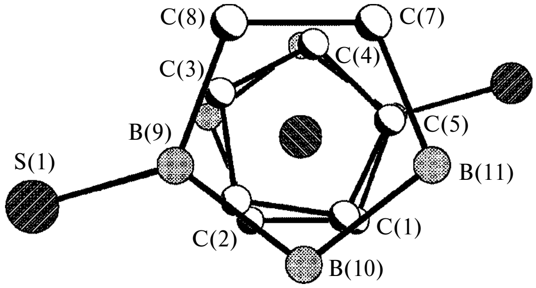

Fig. 2. Relative conformations of the C_5 and C_2B_3 rings in the *meso* form of cation **2**.

from the nickel atoms to the planes of the C_2B_3 rings (1.541 Å) are substantially shorter than those in the nickel bis(carboranyl) complexes *meso*- and *DD*/*LL*-Ni(η-9-Me_2S-7,8-$C_2B_9H_{10}$)$_2$, which we have studied recently (1.676—1.689 Å).* This fact indicates that the Ni—carborane ligand bonds in triple-decker complex **2** are stronger than those in Ni(η-9-Me_2S-7,8-$C_2B_9H_{10}$)$_2$ and agree well with the results of calculations at the extended Hückel theory level for the cyclopentadienyl analogs of these complexes. Actually, four additional electrons in the 34-electron triple-decker [CpNi(μ-Cp)NiCp]$^+$ cation occupy two nonbonding molecular orbitals, which could not cause substantial weakening of the Ni—Cp bond.[2] In the nickelocene, two additional electrons occupy two antibonding molecular orbitals resulting in weakening of this bond.[3]

Table 1. Selected bond lengths (*d*) in cation *meso*-**2**

Bond	*d*/Å	Bond	*d*/Å
Ni(1)—C(7)	2.108(3)	C(1)—C(2)	1.432(18)
Ni(1)—C(8)	2.115(3)	C(1)—C(5)	1.398(14)
Ni(1)—B(9)	2.113(4)	C(2)—C(3)	1.428(15)
Ni(1)—B(10)	2.136(4)	C(3)—C(4)	1.382(12)
Ni(1)—B(11)	2.122(4)	C(4)—C(5)	1.421(16)
Ni(1)—C(1)	2.088(10)	C(7)—C(8)	1.596(5)
Ni(1)—C(2)	2.222(12)	C(7)—B(11)	1.700(5)
Ni(1)—C(3)	2.174(10)	C(8)—B(9)	1.685(5)
Ni(1)—C(4)	2.184(11)	B(9)—B(10)	1.781(5)
Ni(1)—C(5)	2.202(11)	B(10)—B(11)	1.793(6)
S(1)—B(9)	1.905(4)		

The distances from the nickel atoms to the central Cp ligand in molecule **2** (1.850 Å) are substantially longer than those in [CpNi(μ-Cp)NiCp]$^+$ (1.788 Å),[4,5] which is indicative of weakening of the Ni—μ-Cp bond in complex **2**. This is associated with both weakening of back donation due to the electron-withdrawing effect of the carborane ligand and the fact that the symmetry of the frontier MOs in the [(9-Me_2S-7,8-$C_2B_9H_{10}$)Ni]$^+$ fragment is less suitable compared to those in the [CpNi]$^+$ fragment for efficient overlapping with MOs of the cyclopentadienyl anion.

Earlier,[6] we have found that the reactions of the acetonitrile complexes [(C_5R_5)Ru(MeCN)$_3$]$^+$ with the ruthenacarborane anion [Cp*Ru(η-7,8-$C_2B_9H_{11}$)]$^-$ are accompanied by the electrophilic insertion of the [(C_5R_5)Ru]$^+$ fragments into the cage to form 13-vertex diruthenacarboranes (C_5R_5)Ru($C_2B_9H_{11}$)RuCp* (**5a,b**). The structure of complex **5b** was confirmed by X-ray diffraction analysis. It was reasonable to assume that the analogous reaction of [(C_5R_5)Ru(MeCN)$_3$]$^+$ with neutral ruthenacarborane Cp*Ru(η-9-Me_2S-7,8-$C_2B_9H_{10}$) would afford cationic diruthenacarboranes **4a,b** rather than triple-decker complexes **3a,b**, whose structures we have initially erroneously assigned to these reaction products (by analogy with the [(C_5R_5)Ru(μ-Cp*)RuCp*]$^+$ cations, which were prepared by the reactions of [(C_5R_5)Ru]$^+$ with decamethylruthenocene[7,8]). Actually, the ^{1}H and ^{11}B NMR spectra of cations **4a,b** are similar to the spectra of compounds **5a,b**. The CH protons of the cage appear as broad singlets at δ −0.03, −0.84 (**4a**) and −0.72, −1.41 (**4b**) similar to those in the spectra of **5a** (δ −0.67) and **5b** (δ −1.27). These signals are abnormally shifted upfield compared to the corresponding signals for the starting 12-vertex ruthenacarboranes Cp*Ru(η-9-Me_2S-7,8-$C_2B_9H_{10}$) (δ 3.32, 2.67) and [Cp*Ru(η-7,8-$C_2B_9H_{11}$)]$^-$ (δ 2.72). The ^{11}B NMR spectra of both types of the diruthenacarborane complexes show very characteristic narrow low-field signals (δ 96.40 (**4a**), 97.75 (**4b**), 95.10 (**5a**), and 97.03 (**5b**)), which are assigned to the bridging boron atom having the lowest coordination number. It is known[9] that the low-field signals are characteris-

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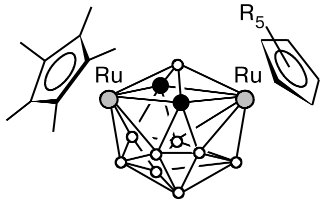
* The results of this study will be published elsewhere.

tic of low coordinated boron vertices, particularly, if they are adjacent to the metal atoms. Finally, the structures of cations **4a,b** were unambiguously confirmed by the results of X-ray diffraction study of the $[\mathbf{4b}]^+[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$ salt.*



5a,b

R = H (**a**), Me (**b**)

The structure of cation **4b** is shown in Fig. 3. Selected bond lengths are given in Table 2. The cation has a structure of 13-vertex *closo*-diruthenacarborane. The Cp* ring bound to the Ru(1) atom is disordered over two positions with occupancies of 0.4 and 0.6. Both ruthenium atoms are linked to the C_2B_4 faces, the $\{C_2B\}$ fragment serving as a bridge between the metal atoms. The distances from the ruthenium atoms to the bridging B(1) atom (2.030(4) and 2.071(4) Å; aver., 2.05 Å) are substantially shorter than all other Ru—B distances (2.168(7)—2.235(7) Å; aver., 2.21 Å). The long Ru···Ru distance (3.543(1) Å) is indicative of the absence of a direct interaction between the metal atoms. On the whole, cation **4b** is structurally similar to uncharged complex **5b**, and the presence of the Me_2S group has only a slight effect on the bond lengths in the cage. The largest elongation (by 0.048 Å) is observed for the C(2)—B(5) bond, which is involved in a direct contact with the B(4) atom bound to the Me_2S group.

The crystal structure of the $[\mathbf{4b}]^+[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$ complex is characterized by a rather unusual packing. As can be seen from the projection shown in Fig. 4, the cations and anions form layers parallel to the crystallographic *cb* plane, the cationic and anionic "dimers" alternating in these layers. The layers are shifted with respect to each other in such a way that each anionic dimer is surrounded by four cationic dimers. Analysis of the intermolecular contacts demonstrated that weak specific CH...HB interactions (H...H, 2.29 Å; C—H—H, 165°) are present only in the anionic dimers.

To summarize, the structures of cations **2** and **4b** were unambiguously established by X-ray diffraction analysis. The triple-decker structure of nickel complex **2** was confirmed. By contrast, the structure of ruthenium complex **4b** was demonstrated to differ from the structure, which has been initially assigned based on the NMR spectroscopic data. This fact demonstrates once again the importance of X-ray diffraction analysis for establishing the structures of new types of organometallic compounds.

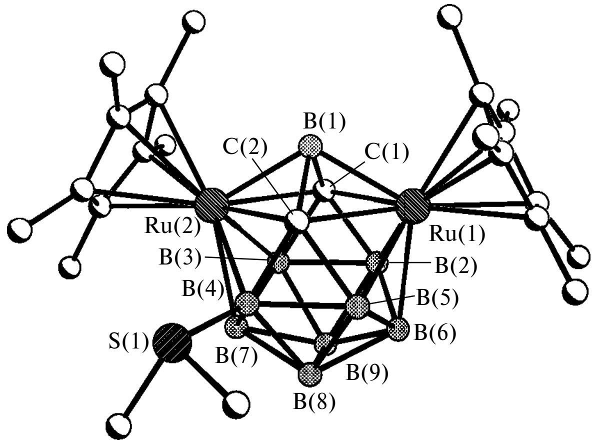


Fig. 3. Structure of diruthenacarborane cation **4b**. Disorder of the Cp* ligand is omitted.

Table 2. Selected bond lengths (*d*) in cation **4b**

Bond	*d*/Å
Ru(1)—C(1)	2.207(5)
Ru(1)—C(2)	2.214(5)
Ru(1)—B(1)	2.030(4)
Ru(1)—B(2)	2.215(7)
Ru(1)—B(5)	2.168(7)
Ru(1)—B(6)	2.235(7)
Ru(2)—C(1)	2.192(5)
Ru(2)—C(2)	2.235(5)
Ru(2)—B(1)	2.071(4)
Ru(2)—B(3)	2.202(6)
Ru(2)—B(4)	2.209(7)
Ru(2)—B(7)	2.221(6)
C(1)—B(1)	1.688(7)
C(1)—B(2)	1.664(8)
C(1)—B(3)	1.661(8)
C(2)—B(1)	1.654(6)
C(2)—B(4)	1.650(8)
C(2)—B(5)	1.712(8)
B(2)—B(3)	1.833(9)
B(2)—B(6)	1.788(10)
B(2)—B(9)	1.780(11)
B(3)—B(7)	1.763(9)
B(3)—B(9)	1.787(10)
B(4)—B(5)	1.854(9)
B(4)—B(7)	1.808(9)
B(4)—B(8)	1.767(9)
B(5)—B(6)	1.812(9)
B(5)—B(8)	1.808(9)
B(7)—B(8)	1.807(9)
B(7)—B(9)	1.772(9)
B(6)—B(8)	1.799(10)
B(6)—B(9)	1.767(10)
B(8)—B(9)	1.760(10)
S(1)—B(4)	1.907(7)

Experimental

All reactions were carried out under argon using anhydrous solvents. The NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz for ^1H and 128.38 MHz for ^{11}B). The $[\mathbf{2}]^+[PF_6]^-$,[1] $Cp^*Ru(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})$,[1] and $[Cp^*RuCl]_4$ [10] complexes were synthesized according to procedures described earlier. The $Tl[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]$ salt was prepared analogously to $[NMe_4][Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]$ [11] with the use of TlOAc instead of $[NMe_4]Cl$.

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* For the salts of cation **4b** with the PF_6^-, BF_4^-, and BPh_4^- anions, we failed to grow single crystals suitable for X-ray diffraction study. The $[\mathbf{4b}]^+[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$ salt was prepared by the reaction of $Cp^*Ru(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})$ with $[Cp^*RuCl]_4$ in THF in the presence of $Tl[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]$. Due to the generation of the highly reactive $[Cp^*Ru(THF)_n]^+$ cations, the insertion reaction proceeds at room temperature.

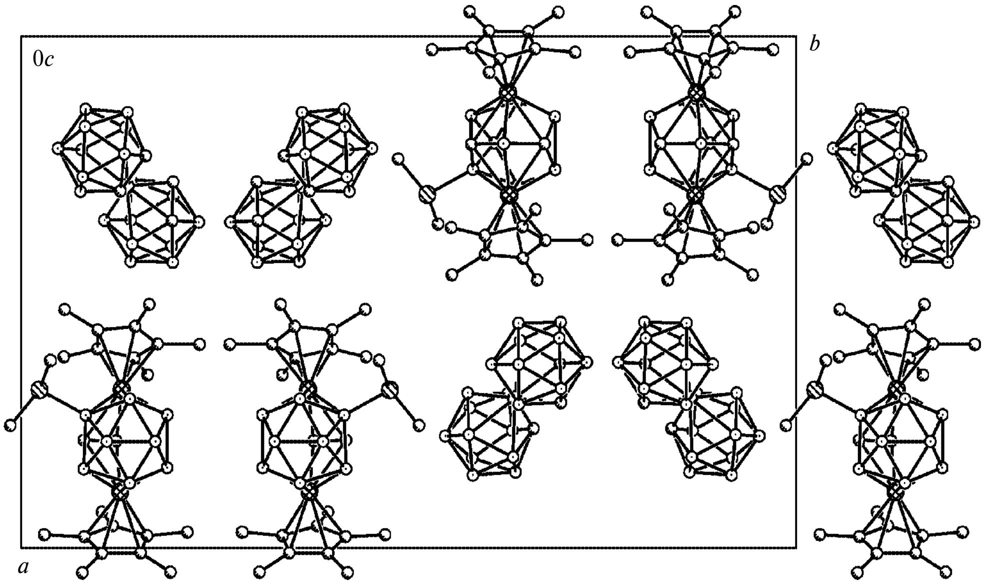

Fig. 4. Crystal structure of $[\mathbf{4b}]^+[\mathrm{Co}(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$ projected onto the *ac* plane.

Table 3. Main crystallographic characteristics and details of the refinement of $[\mathbf{2}]^+[PF_6]^-$ and $[\mathbf{4b}]^+[\mathrm{Co}(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$

Parameter	$[\mathbf{2}]^+[PF_6]^-$	$[\mathbf{4b}]^+[\mathrm{Co}(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]^-$
Molecular formula	$C_{13}H_{37}B_{18}F_6Ni_2PS_2$	$C_{28}H_{68}B_{27}CoRu_2S$
M	714.52	989.82
Crystal system	Monoclinic	
Space group	*C*2/*c*	*P*2$_1$/*c*
Z (*Z*′)	4 (0.5)	4 (1)
a/Å	21.621(4)	17.998(3)
b/Å	12.475(3)	27.925(5)
c/Å	14.413(3)	9.573(2)
β/deg	124.63(3)	99.736(4)
V/Å^3	3198.8(11)	4742.0(14)
d_{calc}/g cm^{-3}	1.484	1.386
μ/cm^{-1}	14.02	10.43
F(000)	1448	2008
$2\theta_{\max}$/deg	60	60
Number of measured reflections (R_{int})	15801 (0.0379)	36931 (0.0888)
Number of independent reflections	4655	13716
Number of observed reflections	2964	4492
Number of parameters in refinement	282	544
R_1	0.0554	0.0638
wR_2	0.1536	0.1205
GOOF	1.065	1.062
Residual electron density (min/max)/e · Å^{-3}	1.54/–0.69	1.20/–0.43

7-Dimethylsulfonio-3,5-bis(pentamethylcyclopentadienyl)-3,5-diruthena-2,4-dicarbatridecaborane(1+)bis(dicarbollide)cobalt(1–), $[\mathbf{Cp^*Ru(Me_2S\text{-}C_2B_9H_{10})RuCp^*}][\mathbf{Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2}]$, $[\mathbf{4b}]^+[\mathbf{Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2}]^-$. A mixture of $[\mathrm{Cp^*RuCl}]_4$ (27 mg, 0.1 mg-equiv.), $\mathrm{Tl[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]}$ (53 mg, 0.1 mmol), $\mathrm{Cp^*Ru(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})}$ (43 mg, 0.1 mmol), and THF (5 mL) was stirred for 6 h, during which the color of the mixture changed from pale- to dark-red. Then the reaction mixture was concentrated to dryness. The residue was extracted with CH_2Cl_2 and eluted through a short (5—10 cm) silica gel column. The red fraction was concentrated to ~2 mL and then diethyl ether (20 mL) was added. The precipitate that formed was filtered off and dried *in vacuo* to give an air-stable bright-red solid compound, which is readily soluble in acetone, CH_2Cl_2, and THF. The yield was 67 mg (68%). Found (%): C, 34.19; H, 6.73; B, 29.30. $C_{28}H_{68}B_{27}CoRu_2S$. Calculated (%): C, 33.97; H, 6.92; B, 29.49. ^{1}H NMR (acetone-d$_6$), δ: –1.10 and –0.40 (both br.s, 1 H each, carb. CH); 1.69 and 1.76 (both s, 15 H each, C_5Me_5); 2.46 and 2.79 (both s, 3 H each, SMe_2); 3.93 (br.s, 4 H, $[\mathrm{Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2}]^-$, carb. CH). ^{11}B{^{1}H} NMR (acetone-d$_6$), δ: 96.56, 34.98, 30.15, 19.43, 13.59, 13.32 ($BSMe_2$), –1.89, –9.73 (1 : 1 : 1 : 2 : 1 : 1 : 1 : 1, cation **4b**); 5.51, 0.77, –6.13, –6.98, –17.98, –23.62 (2 : 2 : 4 : 4 : 4 : 2, $[\mathrm{Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2}]^-$).

X-ray diffraction study. Crystals were grown by slow diffusion in a two-layer system containing Et_2O and a solution of the complex in $MeNO_2$ ($[\mathbf{2}]^+[PF_6]^-$, –10 °C) or CH_2Cl_2 ($[\mathbf{4b}]^+[\mathrm{Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2}]^-$, 20 °C). X-ray diffraction data were collected on a three-circle SMART CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning technique) at 120 K. The main crystallographic parameters and characteristics of the refinement are given in Table 3. The semi-empirical absorption correction was applied based on equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic displacement parameters for nonhydrogen atoms. Analysis of difference electron density maps demonstrated that the central cyclopentadienyl fragment in the structure of cation **2** is disordered over two positions with equal occupancies. It should be noted that the disorder is retained in the noncentrosymmetric space group *Cc*. One of the Cp* groups in cation **4b** is also disordered over two positions with occupancies of 0.6 and 0.4. The position of the Cp* ligand with an occupancy of 0.4 was refined isotropically. The coordinates of the hydrogen atoms, except for the hydrogen atoms of the Cp* groups, were revealed from difference electron density maps and refined using the riding model. All calculations were carried out with the use of the SHELXTL PLUS 5.0 program package.[12]

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