Synthesis of the first metallacarborane triple-decker complexes with a central cyclopentadienyl ligand

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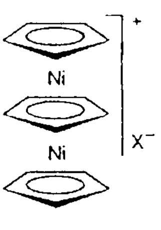
The previously unknown metallacarboranes $(\eta\text{-C}_5\text{R}_5)\text{Ru}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})$ (R = H or Me) and $(\eta\text{-C}_5\text{H}_5)\text{Ni}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})$ were prepared and used in the synthesis of the first metallacarborane triple-decker complexes with a central cyclopentadienyl ligand, *viz.*, $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu\text{-}\eta{:}\eta\text{-C}_5\text{Me}_5)\text{Ru}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})]\text{PF}_6$ (R = H or Me), $[(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})\text{Ni}(\mu\text{-}\eta{:}\eta\text{-C}_5\text{H}_5)\text{Ni}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})]\text{PF}_6$, and $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\mu\text{-}\eta{:}\eta\text{-C}_5\text{H}_5)\text{Ni}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})]\text{BF}_4$.

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

The synthesis of the first 34-electron triple-decker nickel complex with cyclopentadienyl ligands **1** was described in 1972.[1,2] In 1987, we developed a procedure for the synthesis of the previously unknown 30-electron cationic triple-decker complexes of the iron-group metals **2**,[3–5] which also contain exclusively cyclopentadienyl ligands.



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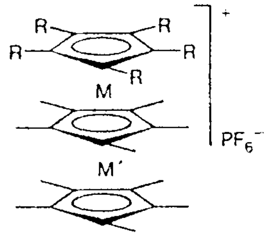

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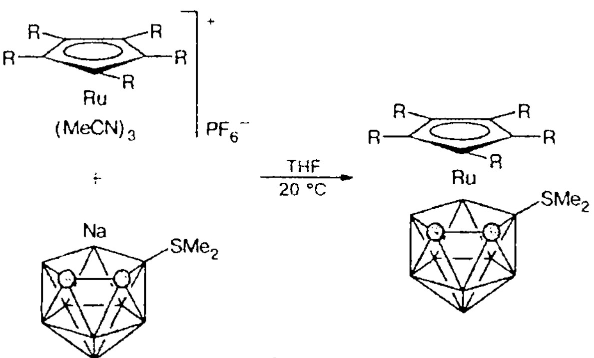
X = BF_4, PF_6

M = Fe; M′ = Fe, Ru, Os; R = H
M = Ru; M′ = Ru, Os; R = H, Me

In the present work, we report the synthesis of the first metallacarborane triple-decker complexes with a bridging cyclopentadienyl ligand. Metallacarborane triple-decker complexes which contain the 1,3-diborolyl ligand $\text{C}_3\text{B}_2\text{MeEt}_4$ in the bridging position have been described previously.[6–9] We used the $[\text{9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10}]^-$ anion as a carborane ligand in the synthesis of triple-decker complexes for the first time.[10–13] This monoanion, like the dianion $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$, is capable of forming π-complexes with transition metals. However, unlike the above-mentioned dianion, the monoanion under consideration resembles to a greater extent the $[\text{C}_5\text{H}_5]^-$ anion because they carry equal charges. Based on the $\text{Na}[\text{9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10}]$ salt (**3**),[13] we prepared cyclopentadienylmetallacarboranes $(\eta\text{-C}_5\text{R}_5)\text{M}(\eta\text{-9-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10})$ (M = Ru, R = H or Me; M = Ni, R = H), which were used in the synthesis of metallacarborane triple-decker complexes.

Ruthenacarboranes **4a,b**, which are carborane analogs of ruthenocenes, were synthesized by the reactions of compound **3** with the cationic trisacetonitrile ruthenium complexes $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\text{MeCN})_3]\text{PF}_6$ (R = H or Me) in tetrahydrofuran at 20 °C (Scheme 1).

Scheme 1



3

4a, R = H
4b, R = Me

Methylated compound **4b** was also formed in the reaction of compound **3** with $[(\eta\text{-C}_5\text{Me}_5)\text{RuCl}]_4$,* which had been prepared by reduction of $[(\eta\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$

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* When the present paper was in press, the synthesis of compound **4b** by the same method was reported in Ref. 20.

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Table 1. ^1H and $^{11}B\{^1H\}$ NMR spectral data for compounds **4a,b** and **5a,b** in CD_2Cl_2

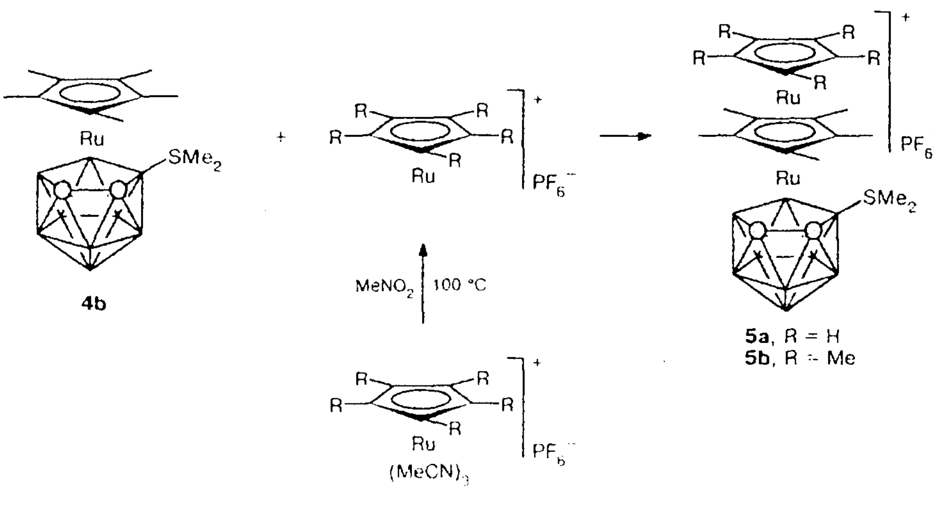
Compound	^1H, δ, J/Hz			$^{11}B\{^1H\}$, δ
	cage CH	SMe_2	C_5R_5	
4a	4.17 (br.s, 1 H); 3.60 (br.s, 1 H)	2.58 (s, 3 H); 2.41 (s, 3 H)	4.98 (s, 5 H, C_5H_5)	−4.38 (1 B, $BSMe_2$); −5.33 (1 B); −6.70 (1 B); −10.46 (1 B); −14.56 (1 B); −19.20 (1 B); −25.35 (1 B); −27.63 (1 B); −28.88 (1 B)
4b	3.32 (br.s, 1 H); 2.67 (br.s, 1 H)	2.50 (s, 3 H); 2.35 (s, 3 H)	1.87 (s, 15 H, C_5Me_5)	−4.31 (1 B); −6.77 (1 B, $BSMe_2$); −8.38 (1 B); −10.55 (1 B); −15.53 (1 B); −19.60 (1 B); −25.78 (1 B); −27.43 (1 B); −29.68 (1 B)
5a	−0.03 (d, 1 H, C(8)H, J = 4); −0.84 (t, 1 H, C(7)H, J = 4)	2.63 (s, 3 H); 2.12 (s, 3 H)	5.50 (s, 5 H, η-C_5H_5); 1.71(s, 15 H, μ-η:η-C_5Me_5)	96.40 (1 B); 31.52 (1 B); 30.89 (1 B); 18.58 (1 B); 16.81 (1 B); 12.43 (1 B, $BSMe_2$); 12.23 (1 B); −2.75 (1 B); −10.52 (1 B)
5b	−0.72 (d, 1 H, C(8)H, J = 4); −1.41 (t, 1 H, C(7)H, J = 4)	2.63 (s, 3 H); 2.13 (s, 3 H)	1.70 (s, 15 H, μ-η:η-C_5Me_5); 1.64 (s, 15 H, η-C_5Me_5)	97.75 (1 B); 35.06 (1 B); 29.89 (1 B); 18.65 (2 B); 13.05 (1 B); 12.39 (1 B, $BSMe_2$); −2.85 (1 B); −10.94 (1 B)

with zinc dust in tetrahydrofuran and was used in the subsequent reaction without isolation from the reaction mixture. Compounds **4a,b** are colorless (or slightly yellowish) air-stable crystalline substances, which were characterized by the data of elemental analysis and ^1H and $^{11}B\{^1H\}$ NMR spectroscopy (Table 1). The ^1H NMR spectra (in CD_2Cl_2) have a singlet of the protons of the C_5H_5 ring at δ 4.98 (for **4a**) or a singlet of the protons of the methyl groups of the C_5Me_5 ring at δ 1.87 (for **4b**). The signals of the cage CH protons are observed as two broad singlets, while the protons of the methyl groups at the sulfur atom give two narrow singlets. The $^{11}B\{^1H\}$ NMR spectra have nine signals of the boron atoms and only one of them is not split into a doublet on protons. This signal belongs to the boron atom attached to the sulfur atom.

With the aim of preparing 30-electron cationic ruthenacarborane triple-decker complexes, we used ruthenacarborane **4b** in the stacking reaction with the 12-electron cationic fragments $[(\eta\text{-}C_5R_5)Ru]^+$ (R = H or Me) generated from the trisacetonitrile complexes $[(\eta\text{-}C_5R_5)Ru(MeCN)_3]PF_6$. The reactions were performed upon boiling in nitromethane analogously to the synthesis of triple-decker ruthenium complexes **2** (M = M′ = Ru; R = H or Me).[3–5] As a result, we obtained ruthenacarborane triple-decker complexes **5a,b** containing a central pentamethylcyclopentadienyl ligand (Scheme 2).

Compounds **5a,b** are very similar in properties to cyclopentadienyl complexes **2** (M = M′ = Ru; R = H or Me). All these compounds are red-orange crystalline substances, which are stable in air both in the solid state

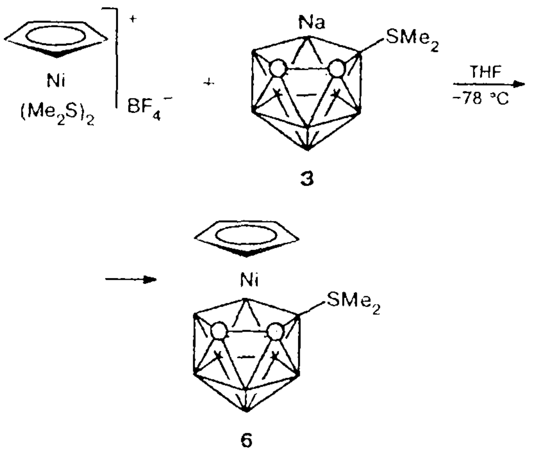
Scheme 2



and in CH_2Cl_2, Me_2CO, and $MeNO_2$ solutions. The structures of ruthenacarborane triple-decker complexes **5a,b** were proposed based on the data of elemental analysis and ^1H and $^{11}B\{^1H\}$ NMR spectroscopy (see Table 1). The ^1H NMR spectra contain signals of the terminal cyclopentadienyl ligands, namely, a singlet of the protons of the C_5H_5 ring at δ 5.50 (for **5a**) or a singlet of the protons of the methyl groups of the C_5Me_5 ring at δ 1.64 (for **5b**). For both compounds, the protons of the methyl groups of the central C_5Me_5 ring give a singlet at δ ~1.70, *i.e.*, at lower field compared to that of the terminal C_5Me_5 ring in compound **5b** (δ 1.64). Analogous downfield shifts of the signals of the protons of the methyl groups of the central ring compared to those of the terminal ring have been observed previously[4] for the related triple-decker compounds **2** (M = M′ = Ru; R = H or Me). Two cage CH protons are observed as a doublet and triplet, while the protons of the methyl groups at the sulfur atom give two singlets. The $^{11}B\{^1H\}$ NMR spectra of triple-decker compounds **5a,b** are similar to those of ruthenacarboranes **4a,b**. However, as a result of an additional coordination of the C_5Me_5 ligand to the cationic fragments $[(\eta\text{-}C_5R_5)Ru]^+$ (R = H or Me), most of signals of the boron atoms are shifted downfield.

We prepared nickelacarborane **6** by the reaction of sodium salt **3** with $[(\eta\text{-}C_5H_5)Ni(Me_2S)_2]BF_4$[14] in tetrahydrofuran at −78 °C (Scheme 3).

Scheme 3



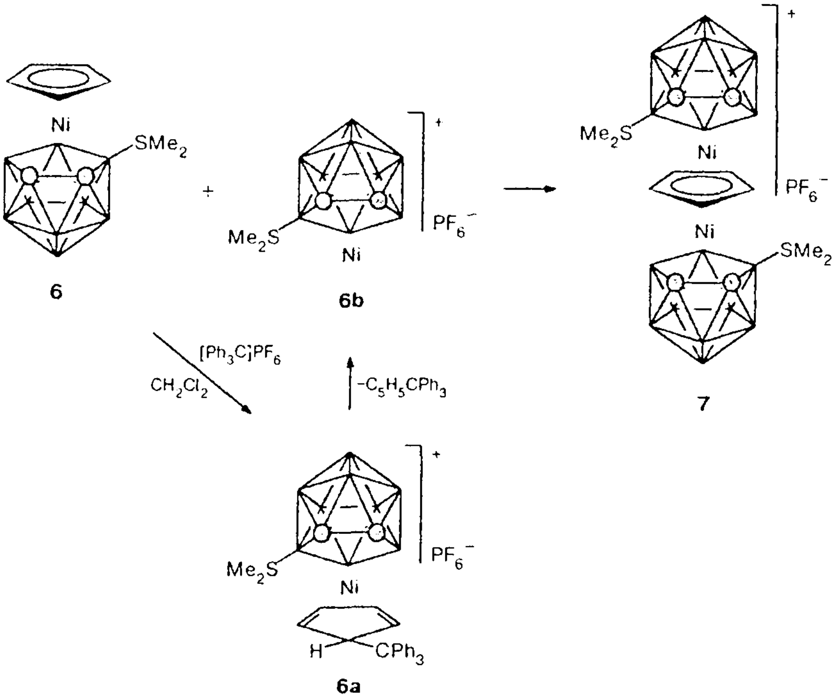
Compound **6** contains 20 valence electrons and is paramagnetic. This compound can be considered as an analog of nickelocene in which one $[C_5H_5]^-$ anion is replaced by the related carborane monoanion $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$. This compound is air-stable in the solid state for several days but it slowly decomposes in CH_2Cl_2 or Me_2CO solutions. Compound **6** was characterized by the data of elemental analysis and ^1H and $^{11}B\{^1H\}$ NMR spectroscopy (Table 2). The chemical shifts of the protons and of the boron atoms vary in substantially wider ranges than those in the case of the analogous diamagnetic compounds of iron $(\eta\text{-}C_5R_5)Fe(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})$ (R = H or Me)[15] and ruthenium **4a,b**. In the ^1H NMR spectrum of compound **6**, the signals of the protons of the C_5H_5 ring are observed as a broad singlet at δ ≈ −259. The protons of the methyl groups at the sulfur atom give two narrow singlets. An interesting feature of the ^1H NMR spectrum of this compound, unlike $(\eta\text{-}C_5R_5)Fe(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})$ (R = H or Me) and **4a,b**, is the fact that all eight BH protons of the carborane cage are distinguishable in addition to the CH protons. Apparently, this is due to the paramagnetism of complex **6**.

Table 2. ^1H and $^{11}B\{^1H\}$ NMR spectral data for compounds **6**—**8**

Compound	Solvent	^1H, δ, *J*/Hz			$^{11}B\{^1H\}$, δ
		cage CH and BH*	SMe_2	C_5H_5	
6	$(CD_3)_2CO$	3.94 (br.s, 1 H); 1.91 (br.s, 1 H); −9.17 (br.s, 1 H); −9.18 (br.s, 1 H); −12.42 (br.s, 1 H); −133.52 (q, 1 H, J_{BH} ≈ 40); −156.77 (br.s, 1 H); −173.48 (br.s, 1 H); −188.37 (br.s, 1 H); −197.11 (br.s, 1 H)	−3.11 (s, 3 H); −7.55 (s, 3 H)	−258.91 (br.s, 1 H)	221.79 (1 B); 81.71 (1 B); 40.38 (1 B); 39.23 (1 B); −19.36 (2 B); −45.80 (1 B); −90.80 (2 B)
7	CD_3NO_2	3.59 (br.s, 1 H); 3.51 (br.s, 1 H); 3.70 (br.s, 1 H); 3.00 (br.s, 1 H)	2.82 (s, 6 H); 2.58 (s, 6 H)	5.96 (s, 5 H)	−8.10 (1 B); −9.45 (1 B); −12.14 (1 B); −13.56 (1 B); −15.86 (1 B); −18.48 (1 B); −21.72 (1 B)
8	CD_3NO_2	3.45 (br.s, 1 H); 2.94 (br.s, 1 H)	2.76 (s, 3H); 2.53 (s, 3H)	5.65 (s, 5 H, μ-η:η-C_5H_5); 5.38 (s, 1 H, η-C_5H_5)	−0.65 (1 B, BF_4); −8.25 (1 B); −10.64 (1 B); −12.01 (1 B); −14.74 (1 B); −15.88 (1 B); −21.05 (1 B); −21.80 (1 B); −22.73 (1 B); −24.67 (1 B)

* Signals of the cage BH protons are distinguishable only for compound **6**.

Scheme 4



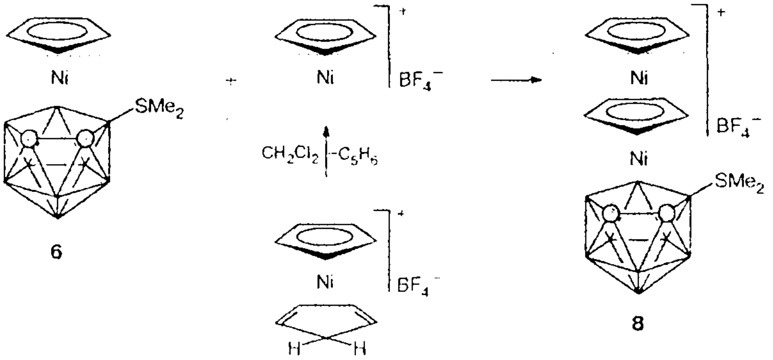
The reaction of compound **6** with $[Ph_3C]PF_6$ taken in a molar ratio of 2 : 1 afforded symmetrical 34-electron triple-decker complex **7**. By analogy with the formation of triple-decker compound **1** in the reaction of nickelocene with $[Ph_3C]X$ ($X = BF_4$ or PF_6),[1] it can be assumed that the reaction proceeds *via* intermediate formation of trityl-substituted cyclopentadiene complex **6a**, which serves as a source of 14-electron fragment **6b**. The stacking reaction of the latter with compound **6** yields triple-decker complex **7** (Scheme 4).

This symmetrical triple-decker complex can be considered as a carborane analog of the classical triple-decker nickel compound **1**, which contains two carborane $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anions instead of two terminal $[C_5H_5]^-$ anions.

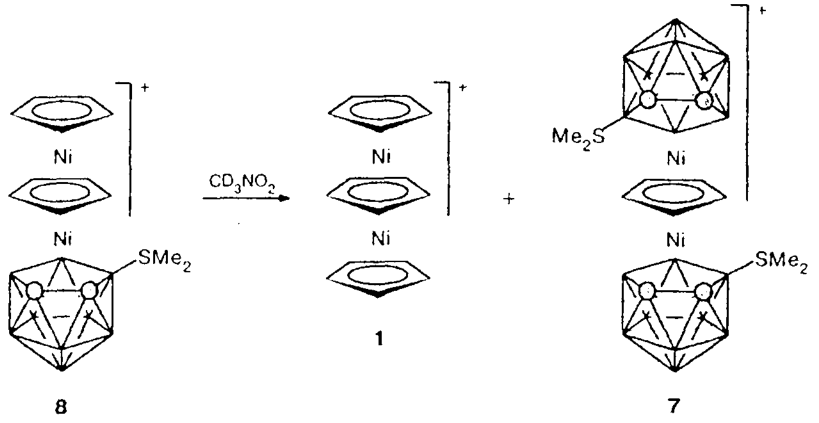
We also studied the stacking reaction of compound **6** with the 14-electron $[(\eta\text{-}C_5H_5)Ni]^+$ fragment generated *in situ* from the corresponding cyclopentadiene complex $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_6)]BF_4$.[16] This reaction yielded unsymmetrical 34-electron triple-decker compound **8** (Scheme 5).

This compound occupies an intermediate position between the classical triple-decker complex **1** [1,2] and symmetrical bis-carborane complex **7**. Compound **8** contains the $[C_5H_5]^-$ anion along with the $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion as terminal ligands. Triple-decker compounds **7** and **8**, like compound **1** described previously, are air-stable in the solid state over a short period, compound **8** being somewhat less stable. It should be noted that all the above-mentioned compounds are substantially less stable than

Scheme 5



Scheme 6



ruthenium-containing analogs **5a,b**. Complexes **7** and **8** are readily soluble in nitromethane, forming solutions stable at low temperature. Complex **8** is poorly soluble in dichloromethane, giving a solution stable at room temperature, while compound **7** is virtually insoluble in CH_2Cl_2. The use of coordinating solvents (acetone, methanol, acetonitrile, *etc.*) leads to rapid decomposition of compounds **7** and **8**. The structures of triple-decker complexes **7** and **8** were proposed based on the data of elemental analysis and ^1H and $^{11}B\{^1H\}$ NMR spectroscopy (see Table 2). The spectral data indicate that compounds **7** and **8** are diamagnetic, like the related complex **1**. The ^1H NMR spectrum of unsymmetrical compound **8** has a signal of the protons of the terminal cyclopentadienyl ring at δ 5.38, which agrees well with the data for triple-decker complex **1** (δ 5.4).[1,2] The signal of the protons of the central ring in compound **8** (δ 5.65) is substantially shifted downfield compared to the signal of compound **1** (δ 4.7).[1,2] Apparently, this is due to the substantial effect exerted by the carborane ligand. The ^1H NMR spectrum of symmetrical triple-decker complex **7** has signals of the protons of the central C_5H_5 ligand at even lower field (δ 5.95) due to the fact that this compound contains simultaneously two carborane ligands. In addition to the signals of the protons of the cyclopentadienyl rings, the ^1H NMR spectra of compounds **7** and **8** have signals of the cage CH protons and of the methyl groups at the sulfur atom. It should be emphasized that the spectrum of compound **7** contains two sets of signals of the cage CH protons. This is associated with the fact that the $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion is a racemic mixture of two enantiomers and, consequently, compound **7** exists as three stereoisomers (DD, LL, and *meso*). An analogous situation has been observed previously[13] for the $Fe(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})_2$ compound, which possesses a symmetry similar to that of compound **7**. The ^1H and $^{11}B\{^1H\}$ NMR spectral data confirm that unsymmetrical triple-decker compound **8** is less stable than its symmetrical analogs **1** and **7**. The symmetrization reaction proceeds at room temperature upon storage of a solution of complex **8** in CD_3NO_2 (Scheme 6).

Even after several minutes, two additional sets of signals appear in the ^1H NMR spectrum. These signals correspond to symmetrical triple-decker cations **1** and **7**, their ratio being approximately 1 : 1. The observed symmetrization reaction provides additional supporting evidence for the structure of **8** as an unsymmetrical triple-decker complex. Interestingly, unsymmetrical carborane triple-decker ruthenium complexes **5a,b** are substantially more stable. Thus, the symmetrization reaction of the latter compounds does not proceed even in boiling $MeNO_2$ (these conditions were used for preparing compounds **5a,b**).

In summary, using ruthenium and nickel as examples, we prepared the first representatives of metallacarborane triple-decker complexes with a central cyclopentadienyl ligand.

Experimental

All reactions were carried out under an argon atmosphere with the use of anhydrous solvents. Nickel-containing complexes **7** and **8** were isolated under an inert atmosphere. In the other cases, the reaction products were isolated in air.

The initial compounds $Na[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]$,[13] $[(\eta\text{-}C_5H_5)Ru(MeCN)_3]PF_6$,[17] $[(\eta\text{-}C_5Me_5)Ru(MeCN)_3]PF_6$,[18] $[(\eta\text{-}C_5Me_5)RuCl_2]_2$,[19] $[(\eta\text{-}C_5H_5)Ni(Me_2S)_2]BF_4$,[14] and $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_6)]BF_4$ [16] were prepared according to known procedures. The ^1H and $^{11}B\{^1H\}$ NMR spectra were recorded on a Bruker AMX-400 instrument. The $^{11}B\{^1H\}$ NMR spectra were measured relative to $BF_3 \cdot Et_2O$ as the external standard.

(η-Cyclopentadienyl)- (4a) and (η-pentamethylcyclopentadienyl)(η-9-dimethylsulfonio-7,8-dicarbollide)ruthenium (4b), $(\eta\text{-}C_5R_5)Ru(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})$ (4a, R = H; 4b, R = Me). *A.* Tetrahydrofuran (10 mL) and a 0.5 *M* $Na[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]$ solution in THF (2 mL, 1 mmol) were added to $[(\eta\text{-}C_5H_5)Ru(MeCN)_3]PF_6$ (434 mg, 1 mmol) or $[(\eta\text{-}C_5Me_5)Ru(MeCN)_3]PF_6$ (504 mg, 1 mmol). The reaction mixture was stirred for 24 h. Then the solvent was distilled off *in vacuo* and methanol (5 mL) was added to the residue. The solid compound was filtered off and washed several times with methanol (2—3-mL portions). The crude product was dissolved in CH_2Cl_2. Then ethanol (15—20 mL) was added and the solution was concentrated to ~10—15 mL *in vacuo* with the use of a water-jet pump. The precipitate was filtered off and washed with ether. Complexes **4a** and **4b** were isolated as virtually colorless (or very pale-yellow) finely crystalline solids. The yields were ~80%. Complex **4a**. Found (%): C, 30.24; H, 6.01. $C_9H_{21}B_9RuS$. Calculated (%): C, 30.05; H, 5.89. Complex **4b**. Found (%): C, 39.36; H, 7.42. $C_{14}H_{31}B_9RuS$. Calculated (%): C, 39.12; H, 7.27.

B. Tetrahydrofuran (10 mL) was added to $[(\eta\text{-}C_5Me_5)RuCl_2]_2$ (307 mg, 1 mg-equiv.) and zinc dust (0.5 g, an excess). The reaction mixture was stirred at room temperature for ~1—2 h. The color of the solution changed from red-brown to dark-green and then again to red-brown. A 0.5 *M* $Na[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]$ solution in THF (2 mL, 1 mmol) was added to the reaction mixture containing $[(\eta\text{-}C_5Me_5)RuCl]_4$. The mixture was stirred for 24 h and the solvent was distilled off *in vacuo*. Then the residue was washed several times with methanol (2—3-mL portions) and extracted with dichloromethane. Ethanol (15—20 mL) was added to the reaction mixture and the solution was concentrated to ~10—15 mL *in vacuo* with the use of a water-jet pump. The finely crystalline virtually colorless precipitate was filtered off and washed with ether. The yield of complex **4b** was 343 mg (80 %).

(μ-η:η-Pentamethylcyclopentadienyl)(η-cyclopentadienyl)-(5a) and (μ-η:η-pentamethylcyclopentadienyl)(η-pentamethylcyclopentadienyl)(η-9-dimethylsulfonio-7,8-dicarbollide)diruthenium hexafluorophosphate (5b), $[(\eta\text{-}C_5R_5)Ru(\mu\text{-}\eta{:}\eta\text{-}C_5Me_5)Ru(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})]PF_6$ (5a: R = H; 5b: R = Me). To a mixture of compound **4b** (43 mg, 0.1 mmol) and $[(\eta\text{-}C_5R_5)Ru(MeCN)_3]PF_6$ (R = H or Me) (0.1 mmol) $MeNO_2$ (0.5 mL) was added and the reaction mixture was heated on an oil bath (120 °C) for 0.5 h (R = H) or 4 h (R = Me). Then the solvent was distilled off *in vacuo* and the residue was dissolved in Me_2CO and chromatographed on an alumina column (1×15 cm) using acetone as the eluent. The yellow band was collected and the solvent was distilled off *in vacuo*. The residue was dissolved in CH_2Cl_2 (2—3 mL) and a tenfold excess of ether was added. Compound **5a** was isolated as a yellow-orange precipitate and compound **5b** was isolated as small dark-red crystals. The yields were ~60%. Complex 5a. Found (%): C, 31.23; H, 5.08. $C_{19}H_{36}B_9F_6PRu_2S$. Calculated (%): C, 30.80; H, 4.90. Complex **5b**. Found (%): C, 35.89; H, 5.96. $C_{24}H_{46}B_9F_6PRu_2S$. Calculated (%): C, 35.34; H, 5.72.

(η-Cyclopentadienyl)(η-9-dimethylsulfonio-7,8-dicarbollide)nickel, $(\eta\text{-}C_5H_5)Ni(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})$ (6). A 0.35 *M* $Na[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]$ solution in THF (12 mL, 4.2 mmol) was added to a solution of $[(\eta\text{-}C_5H_5)Ni(Me_2S)_2]BF_4$ (1.40 g, 4.2 mmol) in THF (10 mL) at −78 °C. The reaction mixture was slowly warmed with stirring to room temperature. The solvent was evaporated and the residue was washed several times with small portions of methanol until the methanol ceased to turn brown. To prepare the analytically pure product, the solid compound was dissolved in CH_2Cl_2, an equal volume of alcohol was added, and a large portion of dichloromethane was distilled off *in vacuo* with the use of a water-jet pump. The precipitate that formed was filtered off and dried *in vacuo*. Compound **6** was obtained in a yield of 700 mg (50%) as a finely crystalline dark-green substance. Found (%): C, 34.11; H, 6.51. $C_9H_{21}B_9NiS$. Calculated (%): C, 34.06; H, 6.67.

(μ-η:η-Cyclopentadienyl)bis[(η-9-dimethylsulfonio-7,8-dicarbollide)nickel] hexafluorophosphate, $[(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})Ni(\mu\text{-}\eta{:}\eta\text{-}C_5H_5)Ni(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})]PF_6$ (7). Dichloromethane (10 mL) was added to a mixture of compound **6** (150 mg, 0.47 mmol) and $[Ph_3C]PF_6$ (91 mg, 0.23 mmol) and the reaction mixture was stirred at ~20 °C for 48 h. The brown precipitate that formed was filtered off and washed 3—4 times with small portions of CH_2Cl_2. The solid residue was dissolved in $MeNO_2$ (2—3 mL) on a filter and the solution was filtered into a flask containing Et_2O (~50 mL). The precipitate that formed was filtered off, washed several times with Et_2O, and dried *in vacuo*. Complex **7** was obtained in a yield of 130 mg (~50%) as a brown solid. Found (%): C, 21.84; H, 5.22. $C_{13}H_{37}B_{18}F_6Ni_2PS_2$. Calculated (%): C, 21.85; H, 5.22.

(μ-η:η-Cyclopentadienyl)(η-cyclopentadienyl)(η-9-dimethylsulfonio-7,8-dicarbollide)dinickel tetrafluoroborate, $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}\eta{:}\eta\text{-}C_5H_5)Ni(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})]BF_4$ (8). Dichloromethane (5 mL) was added to compound **6** (400 mg, 1.26 mmol) and $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_6)]BF_4$ (350 mg, 1.26 mmol). The reaction mixture was stirred at ~20 °C for 4 h. The dark-brown precipitate that formed was filtered off and washed with a small amount of CH_2Cl_2. The solid residue was dissolved in $MeNO_2$ (2—3 mL) at 0 °C and the resulting solution was rapidly filtered into a flask containing Et_2O (~50 mL). The product was obtained as a black oil, which was crystallized out upon washing with ether. Complex **8** was obtained in a yield of 357 mg (50%) as a black finely crystalline compound. Found (%): C, 31.88; H, 5.24. $C_{14}H_{26}B_{10}F_4Ni_2S$. Calculated (%): C, 31.85; H, 4.96.

References

1. H. Werner and A. Salzer, *Synth. Inorg. Met.-Org. Chem.*, 1972, **2**, 239.
2. A. Salzer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 930.
3. A. R. Kudinov and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, 1987, **293**, 1137 [*Dokl. Chem.*, 1987 (Engl. Transl.)].
4. A. R. Kudinov, M. I. Rybinskaya, Yu. T. Struchkov, A. I. Yanovsky, and P. V. Petrovskii, *J. Organomet. Chem.*, 1987, **336**, 187.
5. P. O. Lumme, U. Turpeinen, A. R. Kudinov, and M. I. Rybinskaya, *Acta Cryst.*, 1990, **C46**, 1410.
6. J. M. Forward, D. M. P. Mingos, W. Siebert, J. Hauss, and H. R. Powell, *J. Chem. Soc., Dalton Trans.*, 1993, 1783.
7. W. Weinmann, A. Wolf, H. Pritzkow, W. Siebert, B. A. Barnum, P. J. Carroll, and L. G. Sneddon, *Organometallics*, 1995, **14**, 1911.
8. W. Weinmann, F. Metzner, H. Pritzkow, W. Siebert, and L. Sneddon, *Chem. Ber.*, 1996, **129**, 213.
9. W. Weinmann, H. Pritzkow, W. Siebert, and L. G. Sneddon, *Chem. Ber./Recueil*, 1997, **130**, 329.
10. J. Plešek, Z. Janoušek, and S. Heřmánek, *Coll. Czech. Chem. Comm.*, 1978, **43**, 2862.
11. J. Cowie, E. J. M. Hamilton, J. C. V. Laurie, and A. J. Welch, *J. Organomet. Chem.*, 1990, **394**, 1.
12. N. L. Douek and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1993, 1917.
13. Y.-K. Yan, D. M. P. Mingos, T. E. Müller, D. J. Williams, and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1994, 1735.
14. N. Kuhn and M. Winter, *Chem.-Ztg.*, 1983, **107**, 73.
15. A. R. Kudinov, V. I. Meshcheryakov, P. V. Petrovskii, and M. I. Rybinskaya, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 177 [*Russ. Chem. Bull.*, 1999, **48**, 176 (Engl. Transl.)].
16. N. Kuhn and M. Winter, *Chem.-Ztg.*, 1983, **107**, 14.
17. T. P. Gill and K. R. Mann, *Organometallics*, 1982, **1**, 485.
18. J. L. Schrenk, A. M. McNair, F. B. McCormick, and K. R. Mann, *Inorg. Chem.*, 1986, **25**, 3501.
19. T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, *Organometallics*, 1984, **3**, 274.
20. G. M. Rosair, A. J. Welch, and A. S. Weller, *Organometallics*, 1998, **17**, 3227.

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