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Controlled Assembly of Ruthenium Complexes through *ortho*-Carborane Dithiolate and Polysulfide Ligands

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Treatment of *ortho*-carborane, *n*-butyl lithium, sulfur, and $[(p\text{-cymene})RuCl_2]_2$ in varying ratio led to four new compounds $(p\text{-cymene})Ru[S_3(C_2B_{10}H_{10})_2]$ (**3**), $[(p\text{-cymene})Ru_2(\mu_2\text{-}S_2C_2B_{10}H_9)(\mu_3\text{-}S_2C_2B_{10}H_{10})]_2$ (**4**), $[(p\text{-cymene})Ru]_2Ru(\mu_2\text{-}\eta^2{:}\eta^2\text{-}S_2)(\mu_2\text{-}\eta^2{:}\eta^1\text{-}S_2Cl)(\mu_2\text{-}S_2C_2B_{10}H_{10})_2$ (**5**), and $[(p\text{-cymene})Ru]_2Ru(\mu_2\text{-}\eta^1{:}\eta^1\text{-}S_2)(\mu_3\text{-}\eta^2{:}\eta^2\text{-}S_4)(\mu_2\text{-}S_2C_2B_{10}H_{10})_2$ (**6**), respectively. In **3**, the ruthenium atom is coordinated by three S atoms from a in situ generated tridentate $[S_3(C_2B_{10}H_{10})_2]^{2-}$ ligand. **4** consists of two identical dinuclear $(p\text{-cymene})Ru_2(\mu_2\text{-}S_2C_2B_{10}H_9)(\mu_3\text{-}S_2C_2B_{10}H_{10})$ subunits which connect to each other via the Ru−Ru bond and two bridging *o*-carborane-1,2-dithiolate ligands. In **4**, a Ru−B bond is present. **5** contains a $Ru_3(\mu_2\text{-}S)_2(\mu_2\text{-}S_2)(\mu_2\text{-}S_2Cl)$ core, and the central ruthenium atom is coordinated by seven S atoms in a distorted pentagonal bipyramidal geometry. In **5**, a S−Cl bond is generated. **6** has a novel $Ru_3(\mu_2\text{-}S)_2(\mu_2\text{-}S_2)(\mu_3\text{-}S_4)$ core, and the three ruthenium atoms are connected through the two terminal sulfur atoms of the S−S−S−S chain in a μ_3 binding fashion. All the four complexes have been characterized by elemental analysis, mass, NMR, and X-ray crystallography.

Introduction

The design and synthesis of functional complexes, constructed from multicarborane units and transition metals, have attracted much interest because of their high boron content, fundamental properties, and a variety of potential applications in material synthesis, microelectronics, optics, and medicines.[1] During the past decade, considerable attention has been devoted to the synthesis and reactivity of a class of 16-electron mononuclear complexes $Cp^{\#}M(E_2C_2B_{10}H_{10})$ ($Cp^{\#} = Cp, Cp^*$, M = Co, Rh, Ir, E = S, Se) and (*p*-cymene)$M(S_2C_2B_{10}H_{10})$ (M = Ru, Os) containing an *o*-carborane-1,2-dichalcogenolate ligand to take advantage of their unique molecular structures.[2−6] These compounds exhibit rich reaction chemistries to generate, for example, an addition product either at a metal atom[2] or at a M−E bond with a four-membered metal heterocycle;[3] a metal−boron bond[4] or a carbon−boron bond[5] at carborane in the positions of B(3)/B(6); and heteronuclear metal−metal bonding supported by ancillary *o*-carborane-dichalcogenolate ligands.[6]

On the other hand, transition-metal complexes containing sulfide and thiolate ligands are of continuing interest because of their biological and industrial significance.[7−9] Polysulfides

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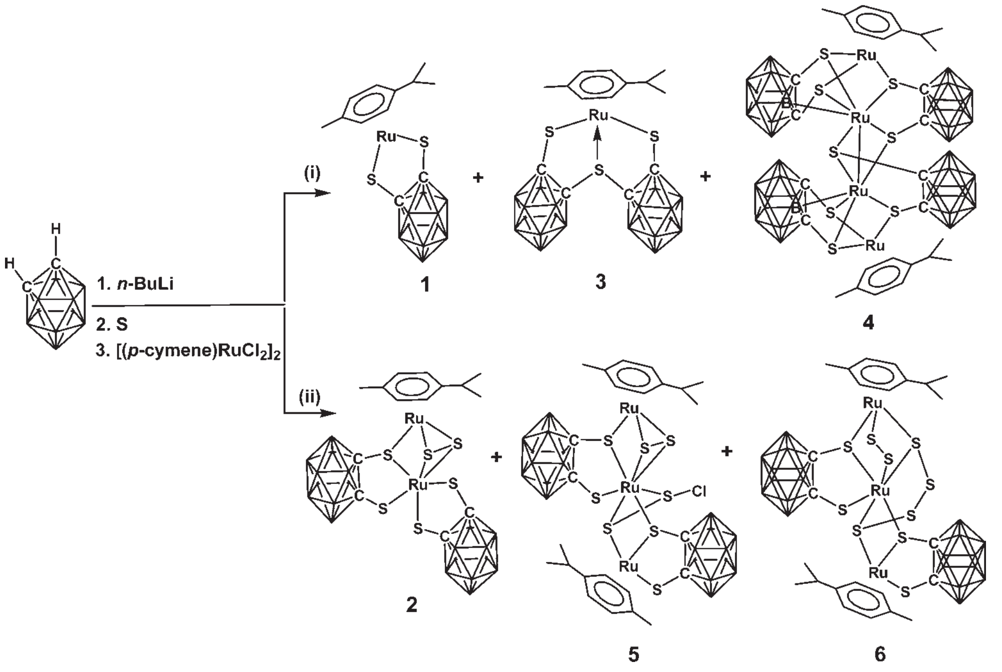
Scheme 1. Synthesis of **1**−**6**[a]



[a] Reaction conditions: (i) THF/Et$_2$O, −10 °C, 2:4.2:4:1; (ii) THF/Et$_2$O, −10 °C, 2:4.2:15:1.

(S_x^{2-}, $x \geqslant 2$) can bridge two or more metal atoms in different modes that leads to diverse structures.[10] Because of the capability of multidentate bonding and self-adjustable chain length plus the compatibility to the preference of the host metals, they can nicely glue metal aggregates.[11] We have synthesized sulfur-rich multinuclear ruthenium compounds that provides a new and clean method to introduce polysulfide ligands into complex frameworks. In our previous studies, the 16-electron complex (*p*-cymene)Ru($S_2C_2B_{10}H_{10}$), dinuclear (*p*-cymene)Ru(μ-S_2)Ru($S_2C_2B_{10}H_{10}$)$_2$ complex with a S−S bond, as well as an unprecedented tetranuclear mixed-valent Ru(IV)Ru(II)$_3$S$_{12}$ cluster (*p*-cymene)$_2$Ru$_4$S$_4$($S_2C_2B_{10}H_{10}$)$_4$ (HC═CFc) were prepared.[12] As a continuation of this interesting chemistry, our research has been focused on the construction of multinuclear transition-metal complexes containing *o*-carborane-dithiolate and polysulfide building blocks. In this paper, we report on the reaction system of *ortho*-carborane, *n*-butyl lithium, sulfur, and [(*p*-cymene)-RuCl$_2$]$_2$ and explore the dependence of the product type on the reactant ratio. Four novel ruthenium compounds, (*p*-cymene)Ru[$S_3(C_2B_{10}H_{10})_2$] (**3**), [(*p*-cymene)Ru$_2$(μ_2-$S_2C_2B_{10}H_9$) (μ_3-$S_2C_2B_{10}H_{10}$)]$_2$ (**4**), [(*p*-cymene)Ru]$_2$Ru(μ_2-η^2:η^2-S_2)(μ_2-η^2:η^1-S_2Cl) (μ_2-$S_2C_2B_{10}H_{10}$)$_2$ (**5**), and [(*p*-cymene)Ru]$_2$-Ru(μ_2-η^1:η^1-S_2)(μ_3-η^2:η^2-S_4) (μ_2-$S_2C_2B_{10}H_{10}$)$_2$ (**6**), were isolated.

Results and Discussion

According to our previous work, complexes **1** and **2** could be synthesized from the reaction of *ortho*-carborane, *n*-butyl lithium, sulfur, and [(*p*-cymene)RuCl$_2$]$_2$ at ambient temperature.[12] In our recent work, four novel ruthenium compounds **3**−**6** have been isolated from this reaction system through controlling of the ratios of the starting materials, as summarized in Scheme 1, Table 1, and Figures 1−4.

Compounds 3 and 4. The reaction of *ortho*-carborane, *n*-butyl lithium, sulfur, and [(*p*-cymene)RuCl$_2$]$_2$ in a ratio of 2:4.2:4:1 at −10 °C leads to products **1** (30%), **3** (8%) and **4** (5%) (Scheme 1). At ambient temperature, **3** and **4** are formed in much lower quantities, and **1** is predominant. The molecular structure of **3** was solved by single crystal X-ray analysis as given in Figure 1. **3** has a three-legged piano-stool arrangement with the ruthenium atom bonded to a *p*-cymene ring in an η^6 mode and three S atoms stemmed from the novel tridentate [$S_3(C_2B_{10}H_{10})_2$]$^{2-}$ ligand. This arrangement makes Ru satisfy the 18-electron rule, thus the complex is stable. Such a coordination mode is not known in the *ortho*-carborane chalcogenolate ligand system since the specific *ortho*-carborane trithiolate ligand is in situ generated and hard

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Table 1. Crystallographic Data and Structural Refinement Details of Compounds **3**−**6**

	3	**4**	**5**	**6**
chemical formula	$C_{14}H_{34}B_{20}RuS_3$	$C_{28}H_{66}B_{40}Ru_4S_8 \cdot 4H_2O$	$C_{24}H_{48}B_{20}ClRu_3S_8 \cdot C_2H_5OH$	$C_{24}H_{48}B_{20}Ru_3S_{10}$
crystal size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.26 × 0.22	0.24 × 0.20 × 0.18	0.28 × 0.24× 0.22
formula weight	615.86	1568.03	1194.03	1176.63
temperature (K)	291(2)	291(2)	291(2)	291(2)
crystal system	triclinic	monoclinic	orthorhombic	tetragonal
space group	$P\bar{1}$	$C2/c$	$Pna2_1$	$I\bar{4}$
a (Å)	6.9477(6)	29.373(4)	25.435(2)	26.7945(18)
b (Å)	10.3469(9)	16.587(2)	11.2199(1)	26.7945(18)
c (Å)	20.8896(2)	18.476(5)	16.7870(2)	14.3185(13)
α (deg)	83.045(2)	90	90	90
β (deg)	84.6830(1)	128.0250(1)	90	90
γ (deg)	78.3970(1)	90	90	90
V (Å^3)	1456.6(2)	7091(2)	4790.6(8)	10279.9(14)
Z	2	4	4	8
ρ_{calcd} (g·cm^{-3})	1.404	1.469	1.656	1.521
abs coeff (mm^{-1})	0.762	1.104	1.365	1.298
F(000)	620	3112	2380	4672
θ range (deg)	1.97−25.00	1.65−25.00	1.98−26.00	1.61−26.00
reflns collected	7294(R_{int} = 0.0791)	17508(R_{int} = 0.0739)	25262(R_{int} = 0.0701)	28405(R_{int} = 0.0508)
indep. reflns	5038	6236	8841	10048
refns obs. [$I > 2\sigma(I)$]	4543	3958	6667	8493
data/restr./params	5038/0/346	6236/9/376	8841/1/527	10048/0/508
GOF	1.068	1.009	0.992	1.061
R_1/R_2 [$I > 2\sigma(I)$]	0.0367/0.1046	0.0611/0.1614	0.0584/0.1181	0.0437/0.0928
R_1/R_2 (all data)	0.0403/0.1097	0.1021/0.1765	0.0733/0.1213	0.0523/0.0946
largest peak/hole (e·Å^{-3})	0.620/−0.849	1.696/−0.889	0.861/−0.535	0.327/−0.427

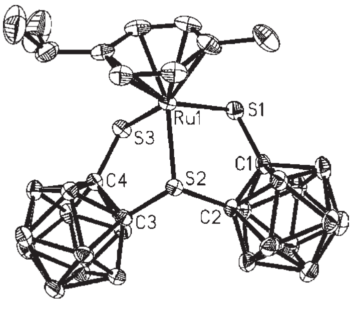

Figure 1. Molecular structure of **3** with 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−S1 2.361(1), Ru1−S2 2.352(8), Ru1−S3 2.378(8), C1−C2 1.675(4), C3−C4 1.660(4), S1−Ru1−S3 90.24(3), S2−Ru1−S3 85.81(3), S2−Ru1−S1 89.33(3).

to control its formation. However, the analogous coordination chemistry with a thiolate-thioether ligand has appeared in the complexes [(η^6-C_6Me_6)Ru(η^3-$SCH_2CH_2SCH_2CH_2S$)][13] and [ReOX(η^3-$SCH_2CH_2SCH_2CH_2S$)] (X = Cl, SR).[14] The dihedral angle between the planes Ru1/S1/S2 and Ru1/S2/S3 is 90.3°. The planar pseudoaromatic system of the metalladithiolene heterocycle in **1** is no longer present in **3**, each RuS_2C_2 ring is slightly folded, for example, the dihedral angles at the S···S vector in the RuS_2C_2 rings are 167.5° (Ru1−S1−C1−C2−S2) and 152.9° (Ru1−S2−C3−C4−S3), respectively.

The compound **4** crystallizes in the monoclinic $C2/c$ space group with a crystallographically imposed inversion center (Figures 2a and b). The tetranuclear core consists of two identical dinuclear (p-cymene)Ru_2(μ_2-$S_2C_2B_{10}H_9$)(μ_3-$S_2C_2B_{10}H_{10}$) subunits which connect to each other via two bridging sulfur atoms from the two $[S_2C_2B_{10}H_{10}]^{2-}$ ligands and the metal−metal bond. The terminal Ru1 is bonded to a p-cymene ring and three S atoms from both $[S_2C_2B_{10}H_9]^{3-}$ and $[S_2C_2B_{10}H_{10}]^{2-}$ ligands, whereas Ru2 is seven-coordinate surrounded by three S atoms from two $[S_2C_2B_{10}H_{10}]^{2-}$ ligands, two S atoms, and one B atom from one $[S_2C_2B_{10}H_9]^{3-}$ unit, and one Ru atom from the M−M bond. The geometry of the central Ru2 can be viewed as a distorted pentagonal bipyramid with S3 and B3 occupying the pyramidal apexes and the four S atoms (S1, S2, S4A, and S4) and Ru2A taking the equatorial sites. Here the o-carborane-1,2-dithiolate ligand plays a key role in determining the type of product. A similar finding was also observed in the formation of the heterotetranuclear complexes [Cp*Re($S_2C_2B_{10}H_{10}$)$_2$Mo(CO)]$_2$ and [Cp*Re($S_2C_2B_{10}H_{10}$)$_2$Ni]$_2$ (Cp* = η^5-C_5Me_5).[15] In **4**, the Ru2−Ru2A bond (2.750 Å) is present in the typical range of 2.71−3.02 Å,[16] which is supported by two bridging $[S_2C_2B_{10}H_{10}]^{2-}$ ligands, and the generated four-membered ring Ru2S4Ru2AS4A is nearly planar with a deviation of 0.0401 Å. Note that one o-carboranyl unit is drawn sufficiently close to the metal center to initiate B−H activation at B(3,6) sites, leading to the corresponding cyclometalated ligand species. Metal-induced B−H activation has been extensively observed in the reaction systems with alkynes,[4] but scarcely reported in such a similar system.[17] Because of the formation of the Ru2−B3 bond (2.335Å), the dihedral

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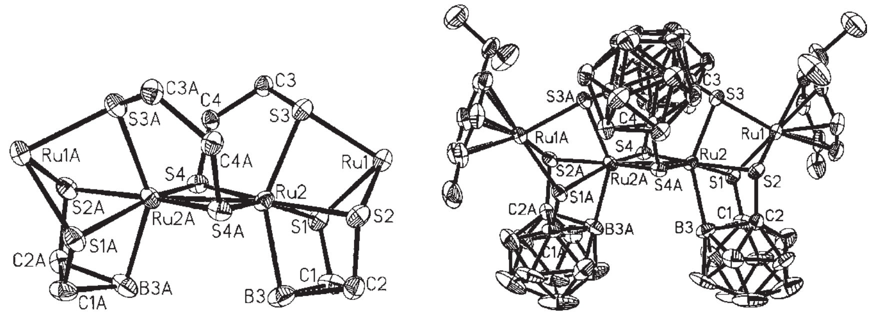

(a) **(b)**

Figure 2. (a) $Ru_4S_8C_8B_2$ skeleton in **4**. (b) Molecular structure of **4** (30% probability displacement ellipsoids); hydrogen atoms and H_2O molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−S1 2.370(2), Ru1−S2 2.394(2), Ru1−S3 2.414(2), Ru2−S1 2.457(2), Ru2−S2 2.389(2), Ru2−S3 2.423(2), Ru2−S4 2.298(2), Ru2−S4A 2.290(2), Ru2−B3 2.335(1), Ru1···Ru2 3.242(1), Ru2−Ru2A 2.750(3), C1−C2 1.603(1), C3−C4 1.693(1), S1−Ru1−S2 77.07(8), S4A−Ru2−S4 106.19(7), B3−Ru2−S2 73.0(3), S4−Ru2−S3 91.74(7), B3−Ru2−S1 70.9(3), S1−Ru2−S2 75.52(7).

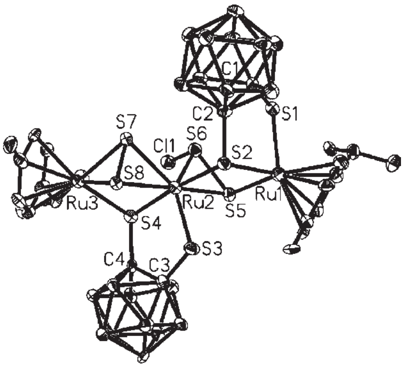

Figure 3. Molecular structure of **5** with 30% probability ellipsoids. Hydrogen atoms and C_2H_5OH molecules were omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−S1 2.382(2), Ru1−S2 2.398(2), Ru1−S5 2.365(2), Ru2−S2 2.437(2), Ru2−S3 2.349(2), Ru2−S4 2.376(2), Ru2−S5 2.386(5), Ru2−S6 2.382(2), Ru2−S7 2.373(2), Ru2−S8 2.451(2), Ru3−S4 2.418(2), Ru3−S7 2.343(2), Ru3−S8 2.391(2), Cl1−S6 2.064(3), S1−Ru1−S2 86.59(8), S2−Ru1−S5 81.81(8), S3−Ru2−S4 91.91(8), S7−Ru2−S8 49.67(8), S7−Ru3−S8 50.70(8), S4−Ru3−S8 82.11(8).

angle at the S1···S2 vector in the Ru(2)S_2C_2 ring is 73.9°, in contrast to the angle of 135.8° at the S1···S2 vector in the Ru(1)S_2C_2 ring.

Compounds 5 and 6. In contrast to the generation of **3** and **4**, if excess sulfur is used, for example, the reaction of *ortho*-carborane, *n*-butyl lithium, sulfur, and $[(p\text{-cymene})RuCl_2]_2$ in a ratio of 2:4.2:15:1 can lead to products **2** (27%), **5** (6%), and **6** (6%) (Scheme 1). At ambient temperature, **5** and **6** are generated in much lower yields, and **2** is the major product. The molecular structure of **5** was solved by single crystal X-ray analysis as given in Figure 3. Its solid-state structure shows that the bridging disulfide and dithiolate are present instead of the bridging Cl atoms in the starting material $[(p\text{-cymene})RuCl_2]_2$, but one Cl atom still remains in a terminal S−Cl bond. The outer ruthenium atoms (Ru1 and Ru3) hold their *p*-cymene rings; however, the *p*-cymene fragment at Ru2 is replaced by S atoms. The geometry of the central Ru2 can be considered as a distorted pentagonal bipyramid with the two bridging S atoms of the two *o*-carborane-1,2-dithiolate ligands at the pyramidal apexes. And the four S atoms from μ_2-S_2 and μ_2-S_2Cl units, and one S atom from *o*-carborane-1,2-dithiolate ligand occupy the equatorial sites. To our best knowledge, such a RuS_7 core is not known even though seven-coordinate complexes with a RuS_6X (X = Cl or I)[18] core have been previously reported. Similar to **2**, the disulfide ligand (S_2^{2-}) bridges the two ruthenium atoms (Ru2 and Ru3) in a $\mu,\eta^2{:}\eta^2$ mode, whereas the S_2Cl unit shows a little bit different binding owing to the presence of the S−Cl bond, i.e. the S atom can not be coordinated to the metal (Ru1). Note that a S−S bond, especially in disulfanes,[19] has been extensively studied, but a S−Cl bond has received little structural attention. Here the S−Cl bond (2.064 Å) and the S−S−Cl angle (108.92°) are nearly identical to the reported those in Ph_3CS_2Cl (2.073 Å, 108.45°).[20] Moreover, the MALDI-TOF MS spectrum displays the most intense peak at *m*/*z* 1149.04, corresponding to $[M + H]^+$. And the measured isotope pattern fits well the calculated one, further demonstrating the presence of Cl. Thus the spectral data support the solid-state structure. Owing to the binding characteristic of the μ_2-S_2 and μ_2-S_2Cl ligands, the dihedral angle at the S1···S2 vector in the Ru(1)S_2C_2 ring is 152.6°, in contrast to the angle of 179.6° at the S3···S4 vector in the Ru(2)S_2C_2 ring. The S−S distances (S5−S6 2.079 Å, S7−S8 2.027 Å) are close to the corresponding bond length of 2.0358 Å in **2**.[12] The Ru···Ru distances (Ru1···Ru2 3.634 Å, Ru2···Ru3 3.430 Å) preclude any metal−metal interactions since a typical Ru−Ru single bond is in the range of 2.71−3.02 Å.[16]

The solid-state structure of **6** is shown in Figures 4a and b. It contains a novel $Ru_3(\mu_2\text{-}S)_2(\mu_2\text{-}S_2)(\mu_3\text{-}S_4)$ core, consisting of two both bridging and chelating $[S_2C_2B_{10}H_{10}]^{2-}$ ligands, one μ_2-S_2^{2-} and one μ_3-S_4^{2-} units. The two outer ruthenium atoms bonded to a *p*-cymene ring adopt a three-legged piano-stool configuration as appeared in **3**, **4**, and **5**. The central Ru2 is coordinated by six S atoms in a distorted octahedral geometry with S4 and S10 occupying the axial positions at an angle of S4−Ru2−S10 163.01° and the four S2, S3, S6,

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[18] (a) Given, K. W.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 3152–3156. (b) Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1977**, *16*, 488–491.

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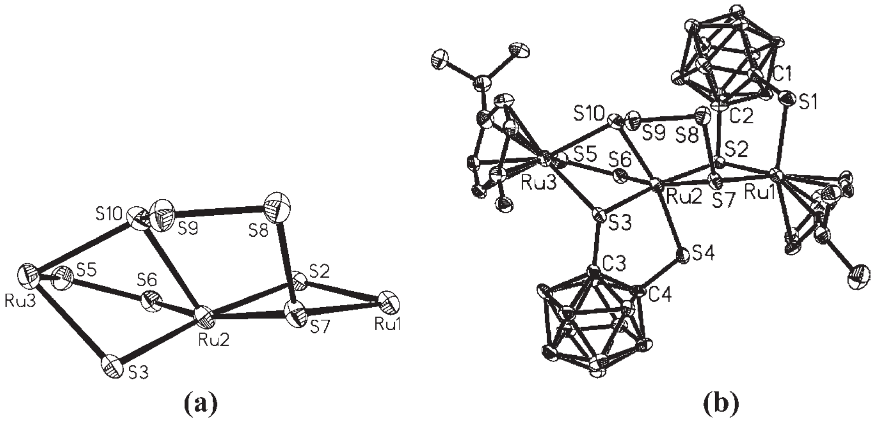

(a) (b)

Figure 4. (a) View of the $Ru_3(\mu_2\text{-}S)_2(\mu_2\text{-}S_2)(\mu_3\text{-}S_4)$ core in **6**. (b) Molecular structure of **6** (30% probability displacement ellipsoids); hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Ru1−S1 2.3729(2), Ru1−S2 2.3839(2), Ru1−S7 2.3853(1), Ru2−S2 2.4317(1), Ru2−S3 2.3393(1), Ru2−S4 2.3656(2), Ru3−S5 2.2624(2), Ru3−S3 2.4217(2), Ru3−S10 2.3981(2), S5−S6 1.991(2), S7−S8 2.142(2), S8−S9 2.002(2), S9−S10 2.114(2), S1−Ru1−S2 89.41(5), S2−Ru1−S7 81.32(5), S2−Ru2−S7 78.71(5), S3−Ru2−S4 89.38(5), S3−Ru2−S6 97.74(5), S5−Ru3−S10 84.13(5), S3−Ru3−S5 95.39(6).

S7 atoms positioning in the equatorial plane. Interestingly, in **6** there are two types of polysulfide groups. One is the S_4^{2-} unit which links the Ru1···Ru2···Ru3 array through the two terminal S atoms in a μ_3-η^2:η^2 fashion. Its central S−S distance is 2.002(2) Å, and the other two S−S distances are 2.142(2) Å and 2.114(2) Å, respectively. A similar example was reported for the complex $[(Re(\mu\text{-}S)(S_2CN(C_4H_9)_2)_4)_2(\mu\text{-}S_4)](PF_6)_2\cdot OC_3H_6$.[21] The other is the S_2^{2-} ligand which bridges the two ruthenium atoms in a μ_2-η^1:η^1 binding mode, rather than the μ_2-η^2:η^2 mode in **5**. The Ru−S distances related to the μ_2-η^1:η^1-S_2 unit (Ru2−S6 2.1662 Å, Ru3−S5 2.2624 Å) are shorter than those related to the μ_3-η^2:η^2-S_4^{2-} binding (2.3853−2.4688 Å). The three Ru1···Ru2···Ru3 atoms are in a nonlinear arrangement with the angle of 152.94° at Ru2, and the Ru···Ru distances (Ru1···Ru2 3.659 Å, Ru2···Ru3 3.560 Å) are longer than a typical Ru−Ru bond in the range of 2.71−3.02 Å.[16]

Thus in this specific reaction system usage of excess sulfur leads to polysulfide ligands, such as S_2^{2-} (μ_2-η^2:η^2 and μ_2-η^1:η^1), S_2Cl^{2-} (μ_2-η^2:η^1), and S_4^{2-} (μ_3-η^2:η^2) which demonstrate various binding modes to metal.

Summary

Compounds **1**−**6** were isolated from the reaction system of *ortho*-carborane, *n*-butyl lithium, sulfur and $[(p\text{-cymene})RuCl_2]_2$. The product type is dependent on the ratio of the reactants used. In the presence of sulfur polysulfide ligands, S_2^{2-} (μ_2-η^2:η^2 and μ_2-η^1:η^1), S_2Cl^{2-} (μ_2-η^2:η^1), and S_4^{2-} (μ_3-η^2:η^2) are observed showing different binding modes to metal. In this reaction system the structures of the multicarborane ruthenium compounds strongly depend upon the coordinative situation at metal. The bridging and chelating feature of *o*-carborane-1,2-dithiolate, the flexidentate and self-adjusting chain length of polysulfides (S_x^{2-}, $x \geq 2$) according to the preference of the host metal, and the catenating and reducible nature of the sulfur atom are combined together to construct these novel multisulfur-containing ruthenium structures. The ruthenium−sulfur chemistry described here demonstrates both metal and sulfur undergo redox reactions that may involve induced internal electron transfer.

In addition, the tridentate $[S(C_2B_{10}H_{10})S(C_2B_{10}H_{10})S]^{2-}$ ligand is in situ generated for the first time. And without assistance of a second ligand metal-induced B−H activation of carborane can occur as well if steric and electronic requirements are met. These findings enrich binding chemistry of sulfides and thiolates and the structures of transition-metal complexes that might help design of useful sulfur-containing compounds.

Experimental Section

General Procedures. The preparative work was carried out under an argon atmosphere using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from either sodium or calcium hydride prior to use. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *ortho*-carborane ($1,2\text{-}C_2B_{10}H_{12}$), and other chemicals were used as commercial products without further purification. $[(p\text{-cymene})RuCl_2]_2$ was prepared according to literature.[22] Elemental analysis was performed in an elementar vario EL III elemental analyzer. NMR data were obtained on a Bruker DRX-500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ $^1H = 7.24$) and external $Et_2O\text{-}BF_3$ (δ $^{11}B = 0$). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000−400 cm^{-1} region. Matrix-assisted laser desorption/ionization (MALDI) in a linear time-of-flight mass spectrometry (MS) was recorded in a Bruker autoflex TOF/TOF equipped with an acquisition operation mode of reflector and signal averaging of 30 laser shots. Finnigan MAT TSQ7000 was used for ESI-MS.

Synthesis of 3 and 4. To a solution of *ortho*-carborane (58 mg, 0.4 mmol) in dry diethylether (20 mL) at −10 °C a 2.0 M solution of *n*-BuLi (0.42 mL, 0.84 mmol) was added. After 30 min sulfur (25.6 mg, 0.8 mmol) was added, followed by addition of $[(p\text{-cymene})RuCl_2]_2$ (123 mg, 0.2 mmol) in dry THF (30 mL) at −10 °C. The resulting mixture was stirred for 2 h accompanied by the temperature gradually rising to ambient temperature. Then the solvents were evaporated under reduced pressure. The components of the residue were separated by column chromatography on silica gel. Elution with CH_2Cl_2/ petroleum ether 1:2 v/v gave **1** (53.1 mg, 30%), **3** (9.8 mg, 8%) and **4** (7.5 mg, 5%) based on *ortho*-carborane. Crystals suitable for X-ray crystallography were obtained by slow diffusion of petroleum ether

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into a dichloromethane solution of the corresponding compound. **3**: purple solid, mp (dec.) 208 °C. Anal. Calcd for $C_{14}H_{34}B_{20}RuS_3$: C, 27.28; H, 5.52. Found: C, 27.37; H, 5.61. ESI-MS (*m*/*z*): calcd for $C_{14}H_{34}B_{20}RuS_3$, 615.88; found, 616.80 ($[M+H]^+$, 100%). ^1H NMR ($CDCl_3$): δ 1.29, 1.58 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$ for each), 2.52 (s, 3H, CH_3), 2.81 (sept, 1H, $CH(CH_3)_2$), 5.84, 5.86, 5.91, 6.31 (d, J = 6.0 Hz, 1H, C_6H_4 for each). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −0.3, −2.9, −5.7, −6.6, −8.8 (1:3:1:2:3). IR (KBr, cm^{-1}): 2581 (ν_{B-H}). **4**: yellow solid, mp (dec.) 225 °C. Anal. Calcd for $C_{28}H_{66}B_{40}Ru_4S_8\cdot 4H_2O$: C, 21.43; H, 4.72. Found: C, 21.31; H, 4.63. MALDI-TOF MS (*m*/*z*): calcd for $C_{28}H_{66}B_{40}Ru_4S_8$, 1496.02; found, 1497.12 ($[M+H]^+$, 75%). ^1H NMR ($CDCl_3$): δ 1.19, 1.26, 1.29, 1.54 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$ for each), 2.25, 2.48 (s, 3H, CH_3 for each), 2.89, 3.45 (sept. J = 7.0 Hz, 1H, $CH(CH_3)_2$ for each), 4.95, 5.02, 5.10, 5.34, 5.47, 5.48, 5.52, 5.61 (d, J = 6.0 Hz, 1H, C_6H_4 for each). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −3.1, −5.1, −6.8, −12.9 (3:2:2:3). IR (KBr, cm^{-1}): 2576 (ν_{B-H}).

Synthesis of 5 and 6. To a solution of *ortho*-carborane (58 mg, 0.4 mmol) in dry diethylether (20 mL) at −10 °C a 2.0 M solution of *n*-BuLi (0.42 mL, 0.84 mmol) was added. After 30 min sulfur (96 mg, 3 mmol) was added, followed by addition of $[(p\text{-cymene})RuCl_2]_2$ (123 mg, 0.2 mmol) in dry THF (30 mL) at −10 °C. The resulting mixture was stirred for 2 h accompanied by the temperature gradually rising to ambient temperature. Then the solvents were evaporated under reduced pressure. The components of the residue were separated by column chromatography on silica gel. Elution with CH_2Cl_2/ petroleum ether 1:1 v/v gave **2** (43.9 mg, 27%), **5** (13.8 mg, 6%) and **6** (14.12 mg, 6%) based on *ortho*-carborane. Crystals suitable for X-ray crystallography were obtained by slow diffusion of hexane into a dichloromethane -ethanol solution of the corresponding compound. **5**: yellow solid, mp (dec.) 231 °C. Anal. Calcd for $C_{24}H_{48}B_{20}ClRu_3S_8\cdot C_2H_5OH$: C, 26.13; H, 4.52. Found: C, 26.22; H, 4.41. MALDI-TOF MS (*m*/*z*): calcd for $C_{24}H_{48}B_{20}ClRu_3S_8$, 1148.02; found, 1149.04 ($[M+H]^+$, 80%). ^1H NMR ($CDCl_3$): δ 0.88, 1.22, 1.31, 1.57 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$ for each), 2.04, 2.38 (s, 3H, CH_3 for each), 2.74, 2.85 (sept. J = 7.0 Hz, 1H, $CH(CH_3)_2$ for each), 4.78, 4.95, 5.27, 5.39, 5.61, 5.95, 6.06, 6.08 (d, J = 6.0 Hz, 1H, C_6H_4 for each). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −2.4, −7.2, −11.3 (2:1:2). IR (KBr, cm^{-1}): 2581 (ν_{B-H}). **6**: red solid, mp (dec.) 225 °C. Anal. Calcd for $C_{24}H_{48}B_{20}Ru_3S_{10}$: C, 21.43; H, 4.72. Found: C, 21.24; H, 4.83. MALDI-TOF MS (*m*/*z*): calcd for $C_{24}H_{48}B_{20}Ru_3S_{10}$, 1176.69; found, 1177.71 ($[M+H]^+$, 75%). ^1H NMR ($CDCl_3$): δ 1.24, 1.33, 1.52, 1.56 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$ for each), 2.33, 2.53 (s, 3H, CH_3 for each), 2.91, 3.37 (sept. J = 7.0 Hz, 1H, $CH(CH_3)_2$ for each, 5.19, 5.62, 5.67, 5.70, 5.83, 6.01, 6.09, 6.34 (d, J = 6.0 Hz, 1H, C_6H_4 for each). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −2.9, −5.2, −10.2 (2:1:2). IR (KBr, cm^{-1}): 2583 (ν_{B-H}).

X-ray Structure Determinations.[23]**.** Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo−Kα (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with the SADABS program. The structures were solved by direct methods using the SHELXL-97 program. All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. The crystal of **6** contains solvent-accessible voids (572 $Å^3$/unit cell) filled with severely disordered solvent molecules, and discrete atoms could not model them reliably (despite repeated recrystallization and data collection). Correspondingly, in the crystallographic evaluation the contribution of the disordered solvents was subtracted from the diffraction data by the SQUEEZE procedure with the aid of the PLATON software.[24] Crystallographic data and details of data collection and structure refinements of **3**−**6** are provided in Table 1 and CIF files (CCDC No. 723528−723531).

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Supporting Information Available: CIF and checkcif files giving X-ray crystallographic data for the structure determinations of compounds **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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