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Tungsten carbonyl σ-complexes with charge-compensated *nido*-carboranyl thioether ligands[†‡]

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Abstract

Charge-compensated *nido*-carboranyl thioether ligands [7-MeS-10-Me_2S-7,8-$C_2B_9H_{10}$] and [7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$] were prepared and fully characterized. They readily react with labile tungsten carbonyls to give σ-complexes – mono-substituted $(CO)_5W$[7-MeS-10-Me_2S-7,8-$C_2B_9H_{10}$-κ^1-S(1)] and $(CO)_5W$[7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$-κ^1-S(1)] and chelate $(CO)_4W$[7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$-κ^2-S(1),S(2)]. The synthesized metallocomplexes were characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction. The donor ability of 7-methylsulfide-*nido*-carborane ligand is not sensitive to introduction of the charge-compensating dimethylsulfonium group.

Introduction

ortho-Carborane derivatives with donor substituents at the carbon atoms are of great interest as ligands for transition metals due to a specific combination of steric and electronic properties. The 1,2-dithiolate carborane complexes are received the most attention especially in the construction of multinuclear organometallic clusters and were reviewed on repeated occasions.[1] Another type of complexes that received an increased interest are complexes with 1,2-bis(diphenylphosphino)-*ortho*-carborane ligand and its analogues.[2] In same cases the complexation in nucleophilic solvents, such as alcohols, results in the partial decapitation of the carborane cage giving the complexes with 7,8-bis(diphenylphosphino)-*nido*-carborane ligand.[3] In comparison with these ligands, the complexes with *C*-alkyl sulfide carboranes are much less studied. Since the electron donating properties of the sulfur atom in the *C*-alkyl sulfide

[†] In memory of Professor Kenneth Wade

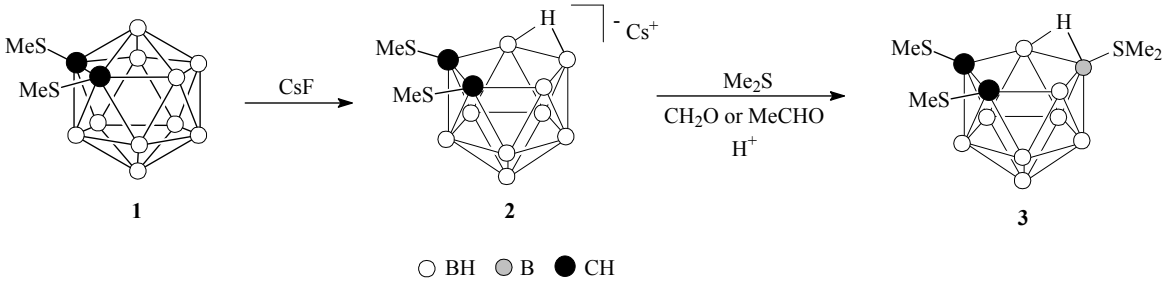
[‡] Electronic supplementary information (ESI) available that contains crystallographic data for monoclinic modification of compound **4**. For ESI and crystallographic data in CIF or other electronic format see DOI:

derivatives are depressed due to strong electron withdrawal effect of the *closo*-carborane cage, a few examples of such complexes are known.[4] However, the partial decapitation of the carborane cage effectively reduces its electron-withdrawal properties and restores the donating properties of the alkyl sulfide groups that results in stabilization of complexes with 7,8-bis(alkylsulfide)-*nido*-carboranes as chelate ligands.[5] It should be mentioned that the carborane decapitation is accompanied by change total ligand charge from neutral to negative that affects physical chemical properties of complexes on its base.

Recently we demonstrated that the δ_{SMe} signals in the ^{1}H and ^{13}C NMR spectra of tungsten carbonyl complexes with *nido*-carboranyl methylsulfide ligands [$(CO)_5W$(MeSCarb)] could serve as indicator of their donor properties.[6] In this contribution we describe synthesis of tungsten carbonyl complexes with neutral charge-compensated *nido*-carboranyl methylsulfide ligands [7-MeS-10-Me_2S-7,8-$C_2B_9H_{10}$] and [7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$].

Results and Discussion

As was mentioned above 1,2-$(MeS)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) is very week ligand and it doesn't give complex under treatment with $W(CO)_4(EtCN)_2$ as well as with $W(CO)_5$(THF). To reduce electron withdrawal effect of the carborane cage it was decapitated by the treatment with cesium fluoride to give Cs[7,8-$(MeS)_2$-7,8-$C_2B_9H_{10}$] (Cs[**2**]) (Scheme 1). Synthesis of (Me_4N)[**2**] by the decapitation of **1** with KOH was described earlier.[5c] The charge compensated derivatives of *nido*-carborane are found extensive use as π-ligands in synthesis of transition metal complexes.[7] The dimethyl sulfonium derivative 9-Me_2S-7,8-$C_2B_9H_{11}$ is the most widely used charge-compensated *nido*-carborane ligand. However, our attempt to prepare 7,8-$(MeS)_2$-9-Me_2S-7,8-$C_2B_9H_9$ by the reaction of **2** with dimethysulfoxide in acidic medium similarly to described by Yan *et al.*[8] was unsuccessful. The charge-compensated ligand 7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$ (**3**) was prepared by the reaction of Cs[**2**] with dimethylsulfide in acidic solution in the presence of acetaldehyde of formaldehyde (Scheme 1) similarly to synthesis of 10-Me_2S-7,8-$C_2B_9H_{11}$ by Plešek *et al.*[9] Thioether **3** is white solid, stable to air and moisture and readily soluble in common organic solvents such as acetone, alcohols and chlorinated hydrocarbons and insoluble in hydrocarbon solvents and water.



Scheme 1

The ^{1}H NMR spectrum of **3** contains two singlets of dimethyl sulfonium and methyl sulfide groups at 2.58 and 2.30 ppm, respectively. The first one is close to the corresponding signal found in the spectrum of 10-Me_2S-7,8-$C_2B_9H_{11}$ (2.55 [10] and 2.56 [11] ppm) indicating negligible effect of the methylsulfide groups on electronic effect of whole carborane system. The signal of the methyl sulfide group demonstrate small low-field shift in comparison with the corresponding signal in the spectrum of Cs[**2**], that indicates only small increase of electron withdrawal effect of the *nido*-carborane cage on the introduction of the dimethyl sulfonium substituent. It should be noted that its value is markedly less than 2.4 ppm found [12] for the *closo*-carborane **1**, that indicates significantly stronger donor ability of **3**.

Crystal and molecular structure of **3** was determined by single crystal X-ray diffraction (Figure 1). The C_{carb}-C_{carb} bond in **3** is markedly longer than the corresponding bonds in 10-Me_2S-7,8-$C_2B_9H_{11}$ and in 10-$(CH_2)_4S$-7,8-$C_2B_9H_{11}$,[11] and the C(7)-B(11) and C(8)-B(9) bonds are also elongated (Table 1). Such pronounced elongation of those bonds can be explained by the transfer of electron density from the sulfur lone pair to the carborane cage[12] as well as by high lability of the bonds of the carborane cage.[13]

Table 1. Lengths (in Å) of the C_{carb}-C_{carb}, C_{carb}-B, C_{carb}-S bonds in compounds studied in the present work in comparison with 10-R'R"S-7,8-$C_2B_9H_{11}$ charge compensated *nido*-carboranes.

Bond	10-Me_2S-7,8-$C_2B_9H_{11}$	10-$(CH_2)_4S$-7,8-$C_2B_9H_{11}$	Ligand **3**	Complex **4**	Ligand **7**	Complex **8**
C(7)-C(8)	1.547(4)	1.545	1.599(3)	1.579(4)	1.594(8)	1.562(5)
C(7)-B(11)	1.597(4)	1.594(5)	1.611(3)	1.616(5)	1.681(5)	1.608(5)
C(8)-B(9)	1.612(4)	1.597(5)	1.619(3)	1.624(5)	1.672(7)	1.635(5)
C(7)-S(1)	–	–	1.789(2)	1.798(3)	1.785(2)	1.802(3)
C(8)-S(2)	–	–	1.803(2)	1.807(3)	–	–

The C_{carb}-S bonds in **3** are some longer than the similar bonds in the related *closo*-carborane **1** (1.7610(13) and 1.7630(14) Å) [14], that can be considered as additional evidence of weaker electron-withdrawal properties of the *nido*-carborane cage and stronger donor ability of the ligand.

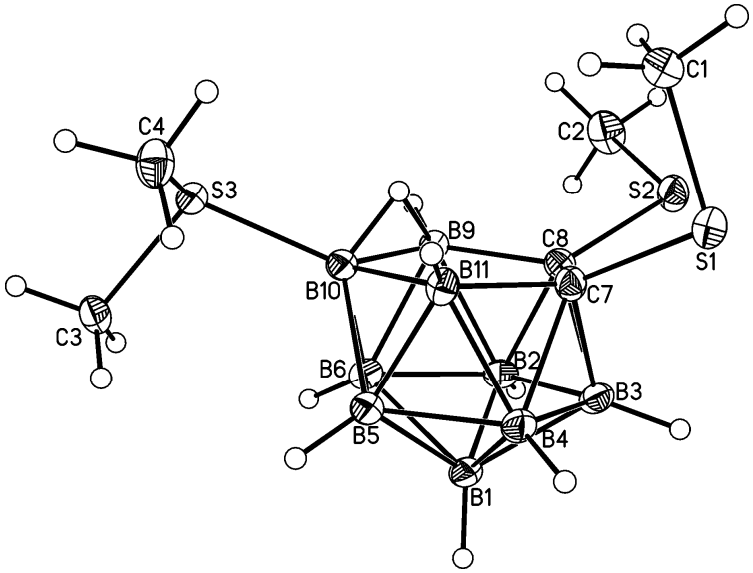
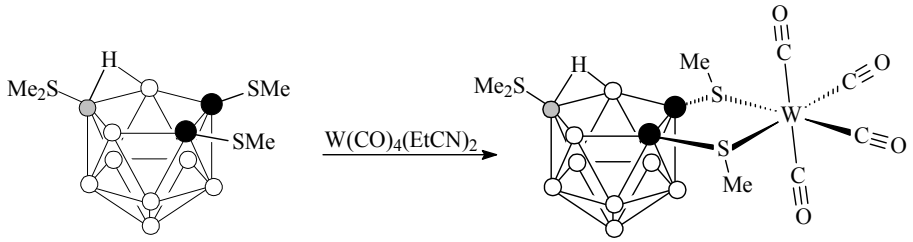


Figure 1. Molecular structure of ligand **3** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Indeed the reaction of **3** with $W(CO)_4(EtCN)_2$ in dichloromethane at room temperature produces the corresponding complex $(CO)_4W[7,8\text{-}(MeS)_2\text{-}10\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_9\text{-}\kappa^2\text{-}S(1),S(2)]$ (**4**) in nearly quantitative yield (Scheme 2). In the ^1H NMR spectrum of **4** the signal of the coordinated methyl sulfide groups undergo strong low-field shift to 2.72 ppm clearly indicating bidentate coordination of the ligand. In the ^{13}C NMR spectrum the coordination results in strong low-field shift of both the methyl and the carborane carbons from 19.5 to 30.9 ppm and from 67.5 to 72.5 ppm, respectively.



3 **4**

Scheme 2.

Crystal structure of **4** was determined by single crystal X-ray diffraction (Figure 2). The geometry at tungsten is slightly distorted octahedron with angles in the ranges of 81.44(2) – 95.50(9) and 171.0(1) – 176.76(9)°. The two equatorial W-C bonds (1.966(4) and 1.971(3) Å) are somewhat shorter than their axial counterparts (2.028(3) and 2.034(3) Å). The W-S bonds in the complex **4** (2.5388(8) and 2.5460(8) Å) are close to those found in $(CO)_4W(1,2\text{-}(MeS)_2C_6H_4\text{-}\kappa^2\text{-}S(1),S(2))$[15], $(CO)_4W[(MeSC_5H_3)_2Fe)\text{-}\kappa^2\text{-}S(1),S(2)]$[16], $(CO)_4W[(1,2\text{-}(MeS)_2C_5H_3)Fe\text{-}(C_5H_4SMe)\text{-}\kappa^2\text{-}S(1),S(2)]$[17], $(CO)_4W[(MeSC_5H_3)_2Ru)\text{-}\kappa^2\text{-}S(1),S(2)]$[18], $[(CO)_4W]_2\text{-}[(C_5(SMe)_5)Mn(CO)_3\text{-}\kappa^4\text{-}S(1),S(2),S(1'),S(2')]$[19], *rac*- and *meso*-$(CO)_4W\text{-}((MeSCH_2)_2C\text{-}(CH_2SMe)_2\text{-}\kappa^2\text{-}S(1),S(2))$[20]. The two methyls are in a *syn* relationship and are turned upward relative to the pentagonal face of the carborane ligand in contrast to the structure of $(Ph_3P)_2Ir(O_2)[7,8\text{-}(MeS)_2\text{-}7,8\text{-}C_2B_9H_{10}\text{-}\kappa^2\text{-}S(1),S(2)]$ [5d] where the both methyls are turned downward relative to the pentagonal face. The C_{carb}-C_{carb} bond in complex **4** is shorter than in ligand **3**, that reflects reduced electron donation from the sulfur atoms to the carborane cage while C(7)-B(11) and C(8)-B(9) are only slightly elongated (Table 1).

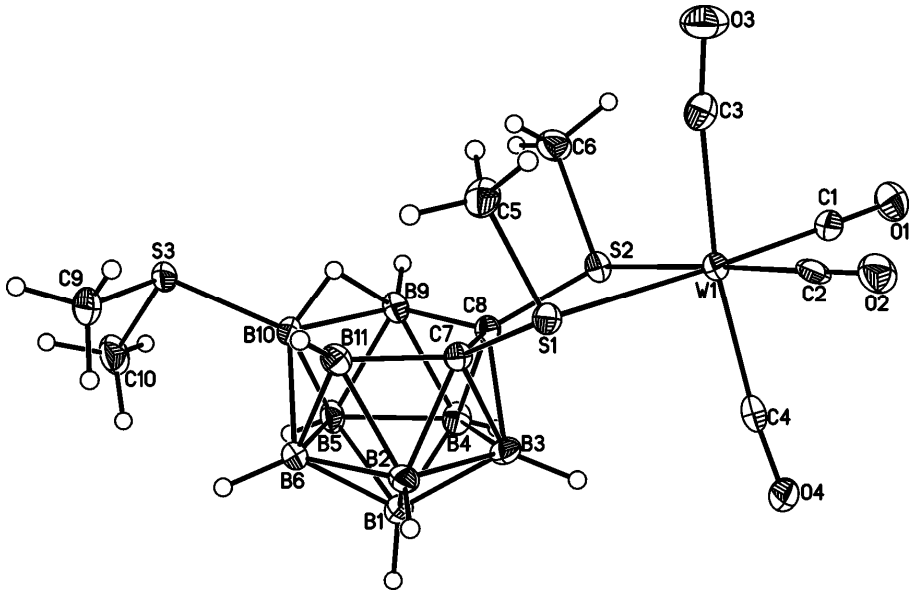
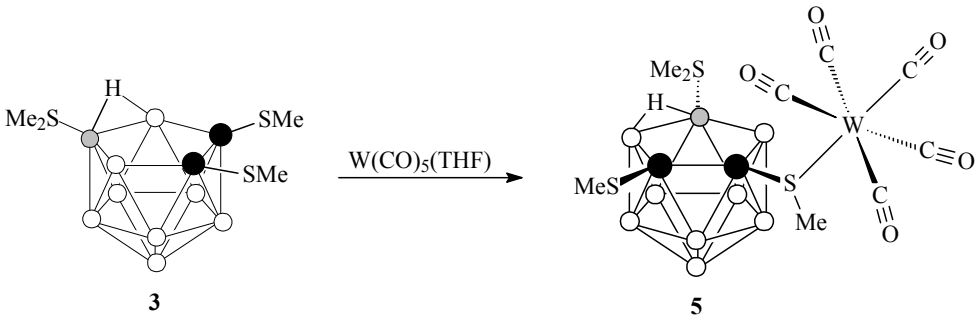


Figure 2. Molecular structure of complex **4** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond length (Å): W(1)…C(1) 1.966(4), W(1)…C(2) 1.971(3), W(1)…C(3) 2.034(3), W(1)…C(4) 2.028(3), W(1)…S(1) 2.5461(8), W(1)…S(2) 2.5388(8).

The reaction of **3** with 1 equiv. of photochemically generated $W(CO)_5(THF)$ in THF at room temperature gave complex $(CO)_5W[7,8\text{-}(MeS)_2\text{-}10\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_9\text{-}\kappa^1\text{-}S(1)]$ (**5**) in moderate yield (Scheme 3). The ^1H NMR spectrum of **5** contains signals of coordinated and non-coordinated methyl sulfide groups at 2.73 and 2.24 ppm, respectively, and signals of dimethyl sulfonium group at 2.61 and 2.60 ppm indicating monodentate coordination of the ligand. The ^{13}C NMR spectrum of **5** contains signals of coordinated MeS-C_{carb} fragment at 30.7 and 75.1 ppm, signals of non-coordinated MeS-C_{carb} fragment at 20.7 and 63.7 ppm, signals of the dimethyl sulfonium group at 25.5 and 25.4 ppm, as well as signals of *cis*- and *trans*-carbonyls at 200.6 and 198.1 ppm, respectively.

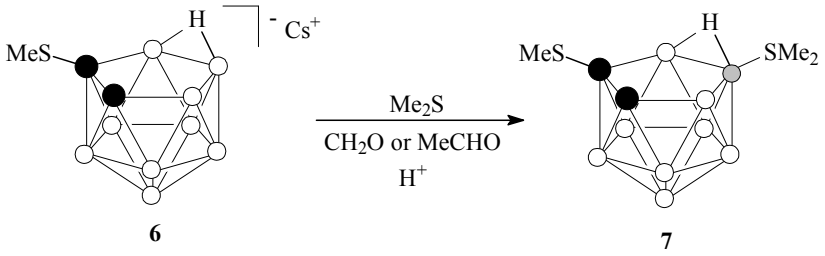


3 **5**

Scheme 3.

An attempt to prepare $[(CO)_5W]_2[7,8\text{-}(MeS)_2\text{-}10\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_9\text{-}\kappa^1\text{-}S(1), \kappa^1\text{-}S(2)]$ by reaction of **3** with an excess of $W(CO)_5(THF)$ resulted in a complex mixture of complexes which after work-up gave complex **4** as single product identified by single crystal X-ray diffraction (for additional information see ESI).

The monodentate methyl sulfide ligand $7\text{-}MeS\text{-}10\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}$ (**7**) was synthesized in the similar way from 7-methylsulfido-*nido*-carborane $Cs[7\text{-}MeS\text{-}7,8\text{-}C_2B_9H_{11}]$ (Cs[**6**]) (Scheme 4). It is interesting to note that no *C*-substituted products similar to $9\text{-}Me_2SCH_2\text{-}7,8\text{-}C_2B_9H_{11}$ reported by Plešek *et al.*[7] for the parent *nido*-carborane were detected in the reactions of both **3** and **6** with formaldehyde. Earlier compound **7** was prepared by the reaction of K[**6**] with dimethylsulfide in acidic solution in the presence of acetaldehyde.[21] Crystal structure of **7** was determined by single crystal X-ray diffraction (Figure 3) and it demonstrates similar trends in the bond lenghts distribution around C(7) and C(8) atoms observed for ligand **3** (see Table 1).



6 7

Scheme 4.

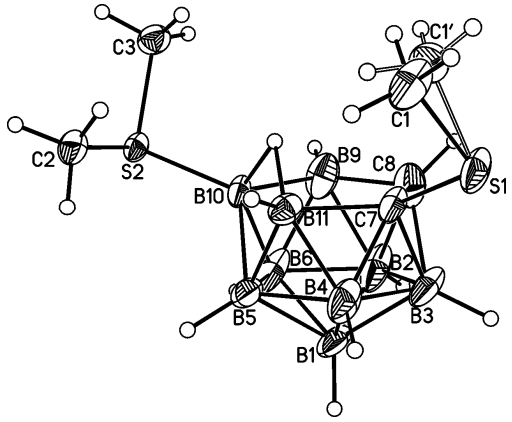
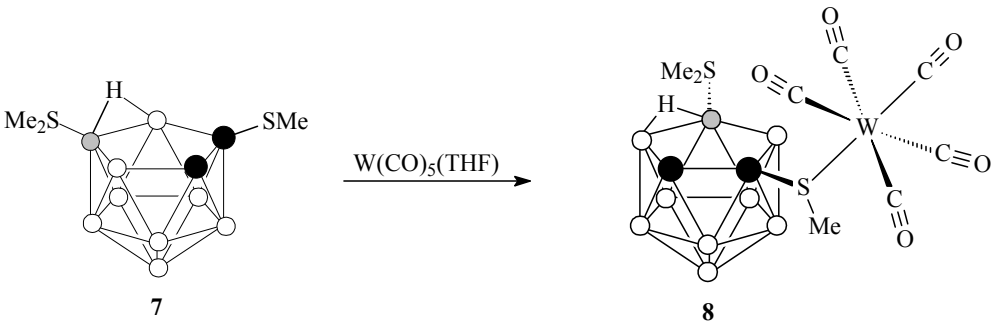


Figure 3. Molecular structure of ligand **7** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The C1 methyl group is disordered over two positions in the ratio of 0.68(2):0.32(2). Minor part is shown by open line.

The reaction of **7** with $W(CO)_5(THF)$ in THF at room temperature gave complex $(CO)_5W[7\text{-MeS-10-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_{10}\text{-}\kappa^1\text{-S(1)}]$ (**8**) in high yield (Scheme 5). In the ^1H and ^{13}C NMR spectra of **8** signals of the coordinated methyl sulfide group are at 2.65 and 29.5 ppm, respectively. The signals of *cis*- and *trans*-carbonyls in the ^{13}C NMR spectrum are at 200.0 and 197.5 ppm, respectively. These values are very close to ones found in the complexes $(CO)_5W[7\text{-MeS-7,8-C}_2\text{B}_9\text{H}_{11}\text{-}\kappa^1\text{-S(1)}]^-$ [6] and $(CO)_5W[7,8\text{-(MeS)}_2\text{-10-Me}_2\text{S-7,8-C}_2\text{B}_9\text{H}_9\text{-}\kappa^1\text{-S(1)}]$ (**5**) that gives strong evidence of negligible effect of both 8-MeS and 10-Me_2S additional substituents on donor ability of 7-methylsulfide-*nido*-carborane ligand.



Scheme 5.

Crystal structure of **8** was determined by single crystal X-ray diffraction (Figure 4). The geometry at tungsten is slightly distorted octahedron with angles in the ranges of 87.3(1) – 95.2(1) and 174.9(1) – 177.3(2)°. The trans W-C bond (1.984(5) Å) is shorter than other W-C bonds (2.049(4)-2.054(4) Å). The W-S bond in complex **8** (2.562(1) Å) is somewhat longer than the corresponding bonds in chelate complex **4** and is of the same order as in known complexes $(CO)_5W(SMeR)$.[22,23] As in the case of **3** and **4**, the C_{carb}-C_{carb} bond in **8** is shorter than that in **7** while C(7)-B(11) and C(8)-B(9) bonds are also shortened in comparison with **7**.

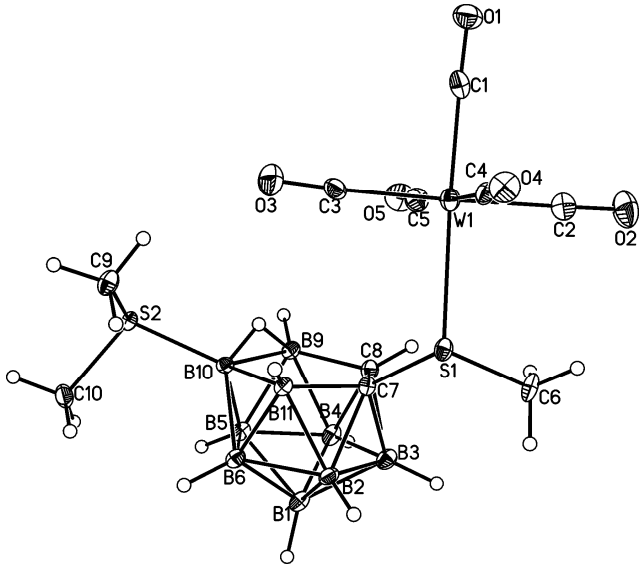


Figure 4. Molecular structure of complex **8** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond length (Å): W(1)…C(1) 1.984(5), W(1)…C(2) 2.053(4), W(1)…C(3) 2.049(4), W(1)…C(4) 2.054(4), W(1)…C(5) 2.064(4), W(1)…S(1) 2.562(1).

Conclusion

New neutral *nido*-carboranyl methylsulfide ligands [7-MeS-10-Me_2S-7,8-$C_2B_9H_{10}$] and [7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$] were prepared and their reactions with tungsten carbonyl complexes were studied. The carborane cage decapitation increases the donor properties of the ligands and introduction of the charge-compensated substituent restores the total charge of the ligand. The monodentate $(CO)_5W$[7-MeS-10-Me_2S-7,8-$C_2B_9H_{10}$-κ^1-S(1)] and $(CO)_5W$[7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$-κ^1-S(1)] and bidentate $(CO)_4W$[7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$-κ^2-S(1),S(2)] complexes were prepared and characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction. It was found that an introduction of 10-Me_2S and 8-MeS substituents has negligible effect of on donor ability of 7-methylsulfide-*nido*-carborane ligand.

Experimental

All the reactions with tungsten carbonyl were carried out under dry argon. 1,2-$(MeS)_2$-1,2-$C_2B_{10}H_{10}$ (**1**), Cs[7-MeS-7,8-$C_2B_9H_{11}$] (Cs[**6**]) and $W(CO)_4(EtCN)_2$ were synthesized according to the literature.[12,6,24] The reaction progress was monitored by TLC (Merck F254 silica gel on aluminum plates). Acros Organics silica gel (0.060-0.200 mm) was used for column chromatography. The ^1H, ^{11}B, $^{11}B\{^1H\}$, and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer. ^1H chemical shifts were referenced to residual protons in the lock solvents. ^{11}B chemical shifts were referenced externally to $BF_3 \cdot OEt_2$. Elemental analyses were performed at the Laboratory of Microanalysis of A. N. Nesmeyanov Institute of Organoelement Compounds. X-ray experiments were carried out using SMART APEX2 CCD (λ(Mo-K_α) = 0.71073 Å, graphite monochromator, ω-scans). Collected data were analized by the SAINT and SADABS programs incorporated into the APEX2 program package.[25] All structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The positions of hydrogen atoms attached to the boron atoms were located in the difference Fourier maps and then normalized to 1.05Å. The H(C) positions were calculated. All the hydrogen atoms were refined in isotropic approximation by the riding model. The bridged H10 atom was refined without any constraints. The refinement was carried out with the SHELXTL program.[26] The details of data collection and crystal structures refinement are summarized in Table 2. Crystallographic data (excluding structure factors) for the structures **3**, **4**, **7** and **8** as well as monoclinic form of **4** have been deposited at the Cambridge Crystallographic

Data Centre (CCDC) as supplementary publications no. CCDC 1043368-1043371 and 1048359, respectively.

Synthesis of Cs[7,8-(MeS)$_2$-7,8-C$_2$B$_9$H$_{10}$] (2).

Solution of **1** (15.30 g, 64.7 mmol) and CsF (19.75 g, 130 mmol) in ethanol (500 ml) was heated under reflux for 10 h. Solvent was removed *in vacuo*, residue was washed with cold water and dried in air to give 22.50 g (97%) of **2** as white solid. ^{1}H NMR (CD$_3$OD, ppm): 2.21 (6H, s, *Me*S), 2.7 ÷ -0.5 (10H, br m, B*H*), -2.3 ÷ -2.8 (1H, br m, B*H*B). ^{11}B NMR (CD$_3$OD, ppm): -8.1 (2B, d, J_{B-H} = 135 Hz), -13.3 (1B, d, J_{B-H} = 164 Hz), -17.4 (2B, d, J_{B-H} = 139 Hz), -18.8 (2B, d, J_{B-H} = 146 Hz), -34.8 (1B, d, J_{B-H} = 141 Hz), -36.3 (1B, d, J_{B-H} = 141 Hz). Anal. Calcd for C$_4$H$_{16}$B$_9$CsS$_2$: C, 13.40; H, 4.56; B, 27.14. Found: C, 13.41; H, 4.60; B, 26.73.

Synthesis of [7,8-(MeS)$_2$-10-Me$_2$S-7,8-C$_2$B$_9$H$_9$] (3).

Method A. Dimethylsulfide (0.69 g, 0.8 ml, 11.1 mmol) was added dropwise to stirred suspension of **2** (1.00 g, 2.3 mmol) in toluene (2.6 ml). To the reaction mixture 10 % aq. HCl (4.0 ml) followed by solution of acetaldehyde (0.3 ml) in water (1.6 ml) were added. The reaction mixture was vigorously stirred at ambient temperature for 1 week. The formed precipitate was filtered and purified by column chromatography on silica using CHCl$_3$ as eluent. Yield 0.36 g (55%). *Method B.* Solution of dimethylsulfide (1.30 g, 1.5 ml, 20.0 mmol) in benzene (4.0 ml) followed by 85% phosphorous acid (2 ml) were added at 20 °C to suspension of **2** (1.50 g, 4.0 mmol) in water (20 ml). Then 37% aq. solution of formaldehyde (0.9 ml) was added. The reaction mixture was vigorously stirred at ambient temperature for 1 week. The formed precipitate was filtered and purified by column chromatography on silica using CHCl$_3$ as eluent. Yield 0.53 g (46%). ^{1}H NMR (CDCl$_3$, ppm): 2.58 (6H, s, *Me*$_2$S), 2.30 (6H, s, *Me*S), 3 - 0.5 (9H, br m, B*H*), -0.6 ÷ -1.0 (1H, br. m, B*H*B). ^{1}H NMR (CD$_3$OD, ppm): 2.59 (6H, s, *Me*$_2$S), 2.25 (6H, s, *Me*S), 2.8 ÷ -0.4 (9H, br m, B*H*). ^{1}H NMR (acetone-*d*$_6$, ppm): 2.73 (6H, s, *Me*$_2$S), 2.23 (6H, s, *Me*S), 2.8 ÷ -0.4 (9H, br m, B*H*), -0.1 ÷ -1.0 (1H, br m, B*H*B). ^{13}C NMR (acetone-*d*$_6$, ppm) δ 67.5 (*C*$_{carb}$), 24.5 (S*Me*$_2$), 19.5 (S*Me*). ^{11}B NMR (CD$_3$OD, ppm): -8.6 (2B, d, J_{B-H} = 151 Hz), -12.6 (1B, d, J_{B-H} = 148 Hz), -16.0 (2B, d, J_{B-H} = 149 Hz), -17.3 (2B, d, J_{B-H} = 167 Hz), -26.6 (1B, s), -35.4 (1B, d, J_{B-H} = 151 Hz). ^{11}B NMR (acetone-*d*$_6$, ppm): -8.6 (2B, d, J_{B-H} = 147 Hz), -13.2 (1B, d, J_{B-H} = 164 Hz), -16.6 (2B, d, J_{B-H} = 159 Hz), -18.0 (2B, d, J_{B-H} = 181 Hz), -27.3 (1B, s), -35.9 (1B, d, J_{B-H} = 147 Hz). Anal. Calcd for C$_6$H$_{21}$B$_9$S$_3$: C, 25.14; H, 7.38; B, 33.93. Found: C, 24.92; H, 7.13; B, 33.75.

Synthesis of (CO)$_4$W[7,8-(MeS)$_2$-10-Me$_2$S-7,8-C$_2$B$_9$H$_9$-κ^2-S(1),S(2)] (4).

Solid $W(CO)_4(EtCN)_2$ (0.32 g, 0.8 mmol) was added to solution of **3** (0.15 g, 0.5 mmol) in of CH_2Cl_2 (5.0 ml). The reaction mixture was stirred overnight at ambient temperature. Solvent was evaporated and crude product was purified by column chromatography on silica using chloroform as eluent. Yield 0.29 g (96%). ^{1}H NMR ($CDCl_3$, ppm) 2.72 (6H, s, S*Me*), 2.63 (6H, s, S*Me*$_2$), -0.78 (1H, br d, J = 75 Hz). ^{13}C NMR ($CDCl_3$, ppm) 208.5 (*C*O), 201.3 (*C*O), 72.5 (C_{carb}), 30.9 (S*Me*), 25.7 (S*Me*$_2$) , 25.6(S*Me*$_2$). ^{11}B NMR ($CDCl_3$, ppm) -8.8 (2B, d, J_{B-H} = 139 Hz), -11.9 (1B, d) , -16.6 (2B, d, J_{B-H} = 126 Hz), -21.5 (2B, d), -25.7 (1B, s), -31.7 (1B, d, J_{B-H} = 135 Hz).

Synthesis of $(CO)_5W[7,8-(MeS)_2-10-Me_2S-7,8-C_2B_9H_9-\kappa^1-S(1)]$ (5).

Tungsten hexacarbonyl (0.28 g, 0.62 mmol) in THF (5.0 ml) in quartz reactor cooled by water was irradiated with UV-lamp for 2 h. When the reaction mixture was turned yellow solid **3** (0.15 g, 0.52 mmol) was added. After stirring overnight, solvent was evaporated. Product was purified by column chromatography on silica using chloroform as eluent. Yield 0.21 g (66%).

^{1}H NMR ($CDCl_3$, ppm): 2.73 (3H, s, *Me*S-coord.), 2.61 (3H, s, *Me*$_2$S), 2.60 (3H, s, *Me*$_2$S), 2.24 (3H, s, *Me*S-uncoord.), 3.5 - 0.5 (9H, br m, B*H*), -0.3 ÷ -1.2 (1H, br m, B*H*B). ^{13}C NMR ($CDCl_3$, ppm) 200.6 (t, J_{C-W} = 79 Hz, *cis*-*C*O), 198.1 (t, J_{C-W} = 65 Hz, *trans*-*C*O), 75.1 (C_{carb}), 63.7 (C_{carb}), 30.7 (*Me*S-coord.), 25.5 (S*Me*$_2$), 25.4 (S*Me*$_2$), 20.7 (*Me*S-uncoord.). ^{11}B NMR ($CDCl_3$, ppm): -8.9 (2B, d), -11.8 (1B, d), -14.0 (1B, d), -15.9 (1B, d), -18.3 (1B, d), -19.4 (1B, d), -25.8 (1B, s), -43.3 (1B, d, J_{B-H} = 137 Hz).

Synthesis of $[10-Me_2S-7-MeS-7,8-C_2B_9H_{10}]$ (7)

Method A. To suspension of **6** (0.91 g, 2.9 mmol) in toluene (2.4 ml) dimethylsulfide (0.69 g, 0.8 ml, 11.1 mmol) was added. Then 15 % aq. HCl (0.5 ml) followed by acetaldehyde (0.24 ml) in water (1.26 ml) were added dropwise. The reaction mixture was vigorously stirred for 24 h at ambient temperature. Precipitate was filtered off, organic phase was evaporated and product was finally purified by column chromatography on silica using chloroform as eluent. Yield 0.10 g (46%). *Method B.* To the suspension of **6** (2.00 g, 6.38 mmol) in water (6.4 ml) of dimethylsulfide (2.3 ml) and of benzene (6.4 ml) were added. Hydrochloric acid (3.2 ml) followed by 37% aq. solution of formaldehyde (3.2 ml) were added dropwise. The reaction mixture was vigorously stirred for one week, extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica using hexane-chloroform 1:1 as eluent. Yield 0.22 g (45%). ^{1}H NMR ($CDCl_3$, ppm): 2.59 (3H, s, *Me*$_2$S), 2.58 (3H, s, *Me*$_2$S), 2.46 (1H, s, C*H*$_{carb}$), 2.28 (3H, s, *Me*S), -0.92 (1H, br d, J = 82 Hz). ^{1}H NMR (acetone-d_6, ppm): 2.74 (3H, s, *Me*$_2$S), 2.73 (3H, s, *Me*$_2$S), 2.39 (1H, s), 2.27 (3H, s, *Me*S), 3.3 -

0.1 (10H, br m, B*H*), -0.2 ÷ -1.0 (br dd, 1H, $J_{H\text{-}B(10)}$ = 133 Hz, $J_{H\text{-}H(B10)}$ = 57 Hz, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): 69.7 (d, *J* = 30 Hz, *C*H$_{carb}$), 55.1 (d, *J* = 37 Hz, *C*H$_{carb}$), 25.8 (S*Me*$_2$), 19.3 (S*Me*). ^{11}B NMR (acetone-d_6, ppm): -10.1 (1B, d, $J_{B\text{-}H}$ = 132 Hz, B(9)), -10.9 (1B, d, $J_{B\text{-}H}$ = 116 Hz, B(11)), -14.3 (1B, d, $J_{B\text{-}H}$ = 166 Hz, B(3)), -16.6 (3B, d, $J_{B\text{-}H}$ = 145 Hz, B(4,5,6)), -21.4 (1B, d, $J_{B\text{-}H}$ = 156 Hz, B(2)), -25.7 (1B, s, B(10)), -36.4 (1B, d, $J_{B\text{-}H}$ = 133 Hz, B(1)).

Synthesis of (CO)$_5$W[7-MeS-10-Me$_2$S-7,8-C$_2$B$_9$H$_{10}$-κ^1-S(1)] (8)

Tungsten hexacarbonyl (0.28 g, 0.62 mmol) in THF (5 ml) in quartz reactor cooled by water was irradiated with UV-lamp for 2 h. when the reaction mixture was turned yellow solid **7** (0.15 g, 0.62 mmol) was added. After stirring overnight, solvent was evaporated. Product was purified by column chromatography on silica using chloroform as eluent. Yield 0.32 g (91%). ^{1}H NMR ($CDCl_3$ ppm): 2.65 (3H, s, S*Me*), 2.61 (3H, s, S*Me*$_2$), 2.60 (3H, s, S*Me*$_2$), 2.38 (1H, s, C*H*$_{carb}$), 2.9 - 0.4 (10H, br m, B*H*), -0.94 (1H, br d, *J* = 81 Hz, $\Delta\nu_{½}$ 199 Hz). ^{13}C NMR ($CDCl_3$, ppm): 200.0 (t, $J_{C\text{-}W}$ = 79 Hz, *cis*-*C*O), 197.5 (t, $J_{C\text{-}W}$ = 65 Hz, *trans*-*C*O), 46.6 (*C*H$_{carb}$), 29.5 (S*Me*), 25.6 (S*Me*$_2$), 25.5 (S*Me*$_2$). ^{11}B NMR ($CDCl_3$ ppm): -9.3 (1B, d, $J_{B\text{-}H}$ = 137 Hz), -12.0 (2B, d, $J_{B\text{-}H}$ = 146 Hz), -13.1 (1B, d, $J_{B\text{-}H}$ = 144 Hz), -19.0 (3B, d), -25.3 (1B, s), -35.0 (2B, d, $J_{B\text{-}H}$ = 146 Hz).

Table 2. Crystallographic data for compounds **3**, **4**, **7**, **8**.

Parameter	**3**	**4**	**7**	**8**
Empirical formula	$C_6H_{21}B_9S_3$	$C_{10}H_{21}B_9O_4S_3W$	$C_5H_{19}B_9S_2$	$C_{10}H_{19}B_9O_5S_2W$
Fw	286.70	582.59	240.61	564.51
Temperature, K	100	120	100	100
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	*Cc*	*Pna*2$_1$	*P*2$_1$	*P*2$_1$/*c*
a, Å	9.5559(7)	27.9281(12)	7.7780(6)	16.4654(9)
b, Å	12.9988(10)	9.3091(4)	10.1928(7)	9.0388(5)
c, Å	12.8588(9)	8.0289(3)	9.3394(7)	14.9863(8)
β, deg	111.6100(10)	90.00	112.9470(10)	116.5010(10)
V, Å^3	1484.99(19)	2087.4(2)	681.83(9)	1996.02(19)
Z	4	4	2	4
d_{calc}, g·cm^{-3}	1.282	1.854	1.172	1.879
μ, mm^{-1}	0.468	5.847	0.350	6.015
F(000)	600	1120	252	1080

θ range, deg.	2.78 – 29.00	2.31 – 28.00	2.37 – 28.00	2.64 – 26.00
reflections collected	8019	29588	7699	15785
independent reflections	3857	5063	3278	3911
R_{int}	0.0315	0.0365	0.0230	0.0416
refined parameters	171	252	157	251
Completeness to theta θ, %	99.8	100	99.7	99.7
GOF (F^2)	0.952	0.984	1.062	1.016
reflections with $I>2\sigma(I)$	3390	4695	2805	3440
$R_1(F)$ ($I>2\sigma(I)$)[a]	0.0325	0.0178	0.0343	0.0234
$wR_2(F^2)$ (all data)[b]	0.0705	0.0367	0.0891	0.0649
Largest diff. peak/hole, $e\cdot$Å^{-3}	0.451 / -0.310	0.553 / -0.903	0.433 / -0.252	1.310 / -1.896

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

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