

Tungsten Carbonyl σ -Complexes with C-thioethers based on 7,8-C₂B₉H₁₁-9-Me₃N

Sergey V. Timofeev,^{a,*} Elena A. Prikaznova,^a Olga B. Zhidkova,^a Anna A. Druzina,^a Zoya A. Starikova, Kyrill Yu. Suponitsky,^{a,b} Ivan A. Godovikov,^a Igor B. Sivaev,^a Vladimir I. Bregadze^a

^a*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences
28 Vavilov Str., 119991, Moscow, Russia*

^b*N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninskii Prosp., 119991, Moscow, Russia*

E-mail: timofeev@ineos.ac.ru

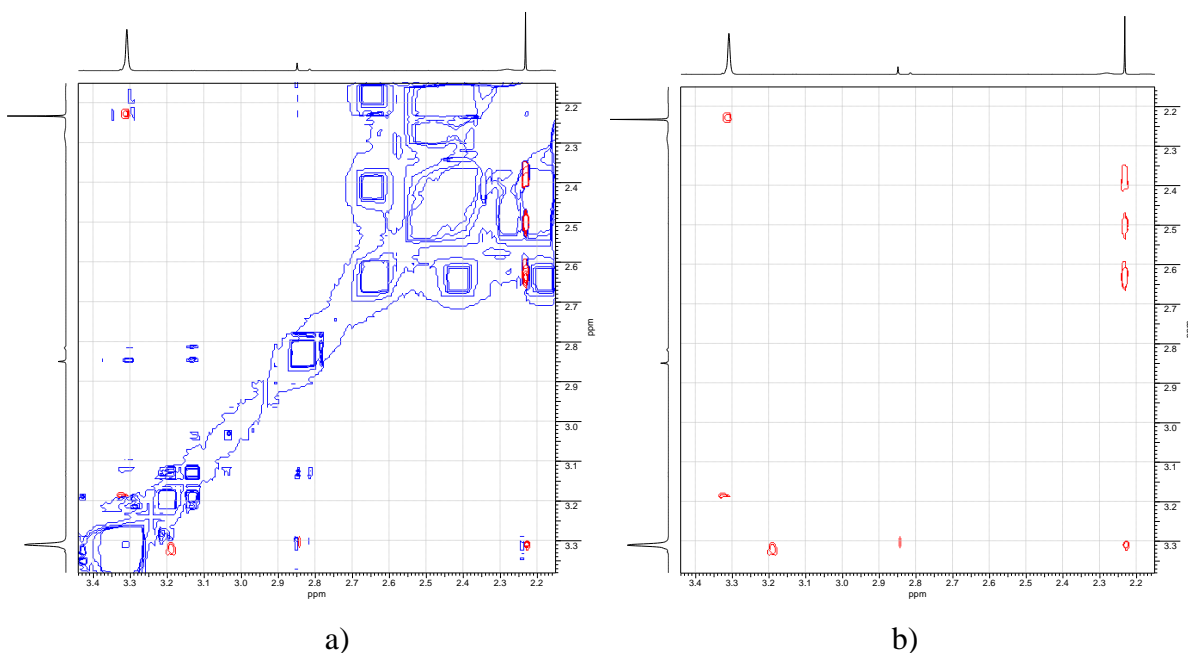


Fig. S1 2D ¹H-¹H NMR ROESY of **3**. a) common spectrum; b) negative area.

Experimental

All manipulations with tungsten complexes were performed under an atmosphere of dry argon with the rigid exclusion of air and moisture. Carboranes **1** [1] and **4** [2] were synthesized according to literature. NMR spectra were recorded on a Bruker Avance 400 spectrometer (¹H-

400.13 MHz, ^{11}B 128.39 MHz, ^{13}C 101.61 MHz). All chemical shifts were reported in δ units with reference to the residual protons and carbons of the deuterated solvents for proton and carbon chemical shifts, and to external $\text{BF}_3\cdot\text{OEt}_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were carried out at Laboratory of Microanalysis of A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences.

Synthesis of [11-Me₃N-7-MeS-7,8-C₂B₉H₁₀] (2) and [9-Me₃N-7-MeS-7,8-C₂B₉H₁₀] (3)

Solution of trimethylamine hydrochloride (1.53 g, 16.0 mmol) in 3.2 ml of water was added to suspension of **1** (1.00 g, 3.2 mmol) in water (4.5 ml) followed by 16 ml of dichloromethane. Aqueous ammonia (25%, 3.2 ml) was added to vigorously stirred two-layer system and when solution of 6.90 g (27.6 mmol) of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ in 16 ml of water was added dropwise. The reaction mixture was stirred for 7 days at ambient temperature, filtered, organic layer was separated, and aqueous layer was extracted with dichloromethane (2 x 50 ml). Combined organic phases was dried over Na_2SO_4 , solvent was removed *in vacuo*. Products were separated by column chromatography on silica using chloroform as eluent. Yield 0.08 g (10%) of **3** (first fraction) and 0.42 g (55%) of **2** (second fraction). **2**: ^1H NMR (acetone-*d*₆, ppm, δ): 3.22 (3H, s, NMe_3), 2.99 (1H, s, CH_{carb}), 2.32 (3H, s, SMe), 2.9 \div 0.0 (8H m, , BH), -2.5 \div -3.3 (1H, br s, BHB). ^{11}B NMR (acetone-*d*₆, ppm, δ): 5.9 (1B, s, B^9), -7.0 (1B, d, $J_{\text{B-H}} = 137$ Hz, B^5), -12.6 (1B, d, $J_{\text{B-H}} = 154$ Hz, B^2), -15.0 (2B, d, $J_{\text{B-H}} = 161$ Hz, $\text{B}^{3,11}$), -24.2 (1B, d, $J_{\text{B-H}} = 142$ Hz, B^4), -27.5 (1B, d, $J_{\text{B-H}} = 137$ Hz, B^6), -32.6 (1B, d, $J_{\text{B-H}} = 121$ Hz, B^{10}), -37.9 (1B, d, $J_{\text{B-H}} = 150$ Hz, B^1). ^{13}C NMR (acetone-*d*₆, ppm, δ): 55.1 (NMe_3), 46.3 (C_{carb}), 17.4 (SMe). **3**: ^1H NMR (acetone-*d*₆, ppm, δ): 3.31 (3H, s, NMe_3), 2.28 (1H, s, CH_{carb}), 2.24 (3H, s, SMe), 3.0 \div 0.2 (8H, br m, BH), -2.6 \div -3.3 (1H, br s, BHB). ^{11}B NMR (acetone-*d*₆, ppm, δ): 5.6 (1B, s), -7.1 (1B, d, $J_{\text{B-H}} = 135$ Hz), -15.2 (1B, d, $J_{\text{B-H}} = 170$ Hz), -17.6 (2B, d, $J_{\text{B-H}} = 152$ Hz), -23.1 (1B, d, $J_{\text{B-H}} = 158$ Hz), -26.7 (1B, d, $J_{\text{B-H}} = 145$ Hz), -32.5 (1B, d, $J_{\text{B-H}} = 128$ Hz), -37.7 (1B, d, $J_{\text{B-H}} = 147$ Hz). ^{13}C NMR (acetone-*d*₆, ppm, δ): 55.3 (NMe_3), 55.0 (C_{carb}), 50.1 (C_{carb}), 18.7 (SMe). Elem. Anal. Found (%): C 30.32; H 9.33; B 40.76. Calc. for $\text{C}_6\text{H}_{22}\text{B}_9\text{NS}$ (%): C 30.33; H 9.33; B 40.95.

Synthesis of [9-Me₃N-7,8-(MeS)₂-7,8-C₂B₉H₉] (5)

Solution of $\text{Me}_3\text{N}\cdot\text{HCl}$ (3.92 g, 20.0 mmol) in 10 ml of water was added to the suspension of **4** (3.58 g, 10 mmol) in 15 ml of water then 50 ml of CH_2Cl_2 was added. $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (12.00 g, 48.0 mmol) was dissolved in 50 ml of water. Resulting solution was added dropwise to vigorously stirred two-

layer reaction mixture followed by 20 ml of concentrated aqueous ammonia. The color was changed from white to dirty-dark. The reaction mixture was vigorously stirred at room temperature for 170 h and extracted with CH₂Cl₂ (2 x 50 ml). Organic phases were combined, dried over Na₂SO₄. Crude product was purified on silica column using chloroform as eluent. Yield 1.13 g (40%). ¹H NMR (acetone-*d*₆, ppm, δ): 3.31 (9H, s, NMe₃), 2.27 (3H, s, SMe), 2.15 (3H, s, SMe), 3.2-0.2 (8H, br. m, BH), -2.3 ÷ -3.3 (1H, br. s, BHB). ¹¹B NMR (acetone-*d*₆, ppm, δ): 7.1 (1B, s, B⁹), -7.4 (1B, d, J_{B-H} = 136 Hz, B⁵), -13.2 (1B, d, B¹¹), -14.8 (2B, d, B^{2,3}), -23.1 (1B, d, J_{B-H} = 147 Hz, B⁴), -25.9 (1B, d, J_{B-H} = 148 Hz, B⁶), -34.0 (1B, d, J_{B-H} = 140 Hz, B¹⁰), -37.3 (1B, d, J_{B-H} = 146 Hz, B¹). ¹³C NMR (acetone-*d*₆, ppm, δ): 65.8 (C_{carb}), 61.7 (C_{carb}), 55.1 (NMe), 19.7 (SMe), 19.4 (SMe). Elem. Anal: Found (%): C 29.74; H 8.68; B 34.19. Calc. for C₇H₂₄B₉NS₂: C 29.64; H 8.53; B 34.30.

Synthesis of (CO)₅W[11-Me₃N-7-MeS-7,8-C₂B₉H₁₀-κ¹-S(1)] (6)

Tungsten hexacarbonyl (0.11 g, 0.3 mmol) in 5 ml of THF in quartz reactor cooled by water was irradiated with UV-lamp for 2 h. Reaction mixture was turned yellow and 0.07 g (0.3 mmol) of **2** was added. After stirring overnight, solvent was evaporated. Product was purified by column chromatography on silica using chloroform as eluent. Yield 0.14 g (87%). ¹H NMR (CDCl₃, ppm, δ): 3.23 (9H, s, NMe₃), 2.71 (3H, s, SMe), 2.41 (1H, s, CH_{carb}), 3.0 ÷ 0.0 (8H, m, BH), -2.5 ÷ -3.5 (1H, br.s., BHB). ¹¹B NMR (CDCl₃, ppm, δ): 5.8 (1B, s), -5.9 (1B, d, J_{B-H} = 119 Hz), -16.0 (1B, d, J_{B-H} = 105 Hz), -16.6 (2B, d), -23.0 (1B, d, J_{B-H} = 146 Hz), -26.0 (1B, d, J_{B-H} = 145 Hz), -32.2 (1B, d, J_{B-H} = 116 Hz), -36.3 (1B, d, J_{B-H} = 158 Hz). ¹³C NMR (CDCl₃, ppm, δ): 199.0 (t, J_{C-W} = 79 Hz, *cis*-CO), 196.6 (t, J_{C-W} = 65 Hz, *trans*-CO), 56.8 (NMe₃), 47.6 (C_{carb}), 30.1 (SMe).

Synthesis of (CO)₅W[9-Me₃N-7-MeS-7,8-C₂B₉H₁₀-κ¹-S(1)] (7)

Tungsten hexacarbonyl (0.32 g, 0.9 mmol) in 5 ml of THF in quartz reactor cooled by water was irradiated with UV-lamp for 2 h. Reaction mixture was turned yellow and 0.20 g (0.9 mmol) of **3** was added. After stirring overnight, solvent was removed *in vacuo*. Product was purified by column chromatography on silica using chloroform as eluent. Yield 0.40 g (86%). ¹H NMR (acetone-*d*₆, ppm, δ): 3.26 (9H, s, NMe₃), 3.01 (3H, s, SMe), 3.0 ÷ 0.0 (8H, m, BH), -2.5 ÷ -3.3 (1H, br. s, BHB). ¹¹B NMR (acetone-*d*₆, ppm, δ): 6.2 (1B, s), -5.8 (1B, d, J_{B-H} = 131 Hz), -12.6 (1B, d, J_{B-H} = 158 Hz), -15.6 (2B, d, J_{B-H} = 158 Hz), -24.1 (1B, d, J_{B-H} = 148 Hz), -27.5 (1B, d, J_{B-H} = 148 Hz), -32.1 (1B, d), -37.4 (1B, d, J_{B-H} = 150 Hz). ¹³C NMR (acetone-*d*₆, ppm, δ): 201.3 (t, J_{C-W} = 78 Hz, *cis*-CO), 197.2 (t, J_{C-W} = 65 Hz, *trans*-CO), 54.4 (NMe₃), 51.8 (C_{carb}), 31.1 (SMe).

Synthesis of $(\text{CO})_5\text{W}[\text{nido-7,8-(MeS)}_2\text{-9-Me}_3\text{N-7,8-C}_2\text{B}_9\text{H}_9\text{-}\kappa^1\text{-S(1)}]$ (**8**)

Tungsten hexacarbonyl (0.35 g, 1.0 mmol) in 5 ml of THF in quartz reactor cooled by water was irradiated with UV-lamp for 3 h. Reaction mixture was turned yellow and solid **5** (0.25 g, 0.9 mmol) was added. After stirring overnight, solvent was evaporated. Product was purified by column chromatography on silica using hexane/toluene (1:3, v/v) as eluent. Yield 0.37 g (60%). ^1H NMR (acetone- d_6 , ppm, δ): 3.39 (9H, s, NMe_3), 3.35 (3H, s, SMe), 2.25 (3H, s, SMe), 3.3-0.3 (8H, br. m, BH), -2.4 \div -3.2 (1H, br. s, BHB). ^{11}B NMR (acetone- d_6 , ppm, δ) δ 7.1 (1B, s), -6.4 (1B, d), -13.4 (1B, d), -14.9 (2B, d), -23.0 (1B, d, $J = 157$ Hz), -25.9 (1B, d, $J = 146$ Hz), -33.1 (1B, d), -36.5 (1B, d). ^{11}B NMR (CDCl_3 , ppm, δ): 6.3 (1B, s, B^9), -6.2 (1B, d, $J_{\text{B-H}} = 116$ Hz, B^5), -14.5 (3B, $\text{B}^{11,2,3}$), -22.3 (1B, d, $J_{\text{B-H}} = 139$ Hz, B^4), -25.8 (1B, d, $J_{\text{B-H}} = 148$ Hz, B^6), -32.0 (1B, d, B^{10}), -35.9 (1B, d, $J_{\text{B-H}} = 139$ Hz, B^1). ^{13}C NMR (acetone- d_6 , ppm, δ): 198.6 (*cis*-CO), 191.5 (*trans*-CO), 55.5 (NMe_3), 19.9 (SMe). IR (MeOH, cm^{-1}): 2075 (CO), 1993 (CO), 1889 (CO). Elem. Anal.: Found (%): C 23.93; H 3.77; N 2.25; B 16.11. Calc. for $\text{C}_{12}\text{H}_{25}\text{B}_9\text{NO}_5\text{S}_2\text{W}$: C 23.68; H 4.14; N 2.30; B 15.99.

Synthesis of $(\text{CO})_4\text{W}[\text{nido-7,8-(MeS)}_2\text{-9-Me}_3\text{N-7,8-C}_2\text{B}_9\text{H}_9\text{-}\kappa^2\text{-S(1), S(2)}]$ (**9**)

Carborane **5** (0.25 g, 0.9 mmol) was added at room temperature to solution of $\text{W}(\text{CO})_3(\text{MeCN})_3$ (0.50 g, 1.3 mmol) in 10 ml of CH_2Cl_2 . Reaction mixture was stirred at room temperature overnight. Solvent was removed *in vacuo*. Crude product was purified on silica column using toluene as eluent. Complex **9** was isolated as yellow powder. Yield 0.36 g (71%). ^1H NMR (CDCl_3 , ppm, δ) δ 3.27 (9H, s, NMe_3), 2.33 (3H, s, SMe), 2.20 (3H, s, SMe), 3.0-0.0 (8H, br. m, BH) -2.6 \div -3.4 (1H, br. s, BHB). ^1H NMR (acetone- d_6 , ppm, δ) δ 3.34 (9H, s, NMe_3), 2.30 (3H, s, SMe), 2.18 (3H, s, SMe), -3.0 \div -0.1 (8H, br. m, BH), -2.4 \div -3.3 (1H, br. s, BHB). ^{11}B NMR (CDCl_3 , ppm, δ) δ 6.7 (1B, s), -7.1 (1B, d, $J = 142$ Hz), -12.8 (1B, d), -15.1 (2B, d), -22.9 (1B, d, $J = 156$ Hz), -25.9 (1B, d, $J = 144$ Hz), -33.8 (1B, d), -37.2 (1B, d, $J = 148$ Hz). ^{11}B NMR (acetone- d_6 , ppm, δ) 7.1 (1B, s), -7.5 (1B, d, $J = 142$ Hz), -13.3 (1B, d, $J = 178$ Hz), -14.9 (2B, d, $J = 178$ Hz), -23.1 (1B, d, $J = 156$ Hz), -25.9 (1B, d, $J = 147$ Hz), -34.0 (1B, d, $J = 136$ Hz), -37.3 (1B, d, $J = 147$ Hz). ^{13}C NMR (CDCl_3 , ppm, δ) 207.8 (CO), 201.8 (CO), 55.9 (NMe_3), 20.5 (SMe), 20.3 (SMe). ^{13}C NMR (acetone- d_6 , ppm, δ) 207.6 (CO), 201.1 (CO), 66.0 (C_{carb}), 61.7 (C_{carb}) 55.2 (NMe_3), 30.8 (SMe), 30.5 (SMe).

X-ray diffraction study

Suitable for X-ray diffraction crystals of **3** and **9** were grown from chloroform solution. Crystals of **8** was grown by crystallization from chloroform solution layered with carbon tetrachloride. Single crystal X-ray study of compounds **3**, **8** and **9** were carried out with SMART APEX II CCD diffractometer ($\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, graphite monochromator, ω -scans) at 100 K. Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 1988624 for **3**, 1988625 for **8** and 1988626 for **9**.

Compound **3**: crystals $\text{C}_6\text{H}_{22}\text{B}_9\text{NS}$ are orthorhombic, space group $P2_12_12_1$: $a = 8.9801(11) \text{ \AA}$, $b = 10.0922(12) \text{ \AA}$, $c = 14.8274(19) \text{ \AA}$, $V = 1343.8(3) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.174 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.207 \text{ mm}^{-1}$, $wR2 = 0.1321$ calculated on F^2_{hkl} for all 3918 independent reflections with $2\theta < 30.0^\circ$, ($GOF = 0.991$, $R = 0.0547$ calculated on F_{hkl} for 2829 reflections with $I > 2\sigma(I)$).

Compound **8**: crystals ($\text{C}_{12}\text{H}_{24}\text{B}_9\text{NO}_5\text{S}_2\text{W}\cdot\text{CHCl}_3$) are monoclinic, space group $P2_1/c$: $a = 8.7839(6) \text{ \AA}$, $b = 24.7066(16) \text{ \AA}$, $c = 12.4515(8) \text{ \AA}$, $\beta = 98.5310(10)$, $V = 2672.3(3) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.807 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 4.805 \text{ mm}^{-1}$, $wR2 = 0.1021$ calculated on F^2_{hkl} for all 5223 independent reflections with $2\theta < 52.0^\circ$, ($GOF = 1.178$, $R = 0.0420$ calculated on F_{hkl} for 4371 reflections with $I > 2\sigma(I)$).

Compound **9**: crystals ($\text{C}_{11}\text{H}_{24}\text{B}_9\text{NO}_4\text{S}_2\text{W}$) are monoclinic, space group $P2_1/c$: $a = 9.2287(9) \text{ \AA}$, $b = 12.8890(12) \text{ \AA}$, $c = 17.9254(17) \text{ \AA}$, $\beta = 99.325(2)$, $V = 2104.0(3) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.830 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 5.706 \text{ mm}^{-1}$, $wR2 = 0.0496$ calculated on F^2_{hkl} for all 5718 independent reflections with $2\theta < 58.5^\circ$, ($GOF = 1.073$, $R = 0.0191$ calculated on F_{hkl} for 5411 reflections with $I > 2\sigma(I)$).

References

1. S.V. Timofeev, M.V. Zakharova, E.M. Mosolova, I.A. Godovikov, I.V. Ananyev, I.B. Sivaev, V.I. Bregadze, J. Organomet. Chem. 721-722 (2012) 92-96.
2. S.V. Timofeev, O.B. Zhidkova, E.M. Mosolova, I.B. Sivaev, I.A. Godovikov, K.Yu. Suponitsky, Z.A. Starikova, V.I. Bregadze, Dalton Trans. 44 (2015) 6449–6456.