Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2015, **44**, 6449

Received 14th January 2015,
Accepted 13th February 2015

DOI: 10.1039/c5dt00176e

www.rsc.org/dalton

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

Sergey V. Timofeev,* Olga B. Zhidkova, Elena M. Mosolova, Igor B. Sivaev, Ivan A. Godovikov, Kyrill Yu. Suponitsky, Zoya A. Starikova and Vladimir I. Bregadze

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 the 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 have received the most attention especially in the construction of multinuclear organometallic clusters and were reviewed on repeated occasions.[1] Another type of complex that received increased interest is complexes with the 1,2-bis(diphenylphosphino)-*ortho*-carborane ligand and its analogues.[2] In some cases the complexation in nucleophilic solvents, such as alcohols, results in the partial decapitation of the carborane cage giving complexes with the 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 derivatives are depressed due to a strong electron withdrawing 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-withdrawing 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 of the ligand charge that affect strongly physical properties of the complexes.

Recently we demonstrated that the δ_{SMe} signals in the ^1H and ^{13}C NMR spectra of tungsten carbonyl complexes with *nido*-carboranyl methylsulfide ligands [$(CO)_5W$(MeSCarb)] could serve as an indicator of their donor properties.[6] In this contribution we describe the 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

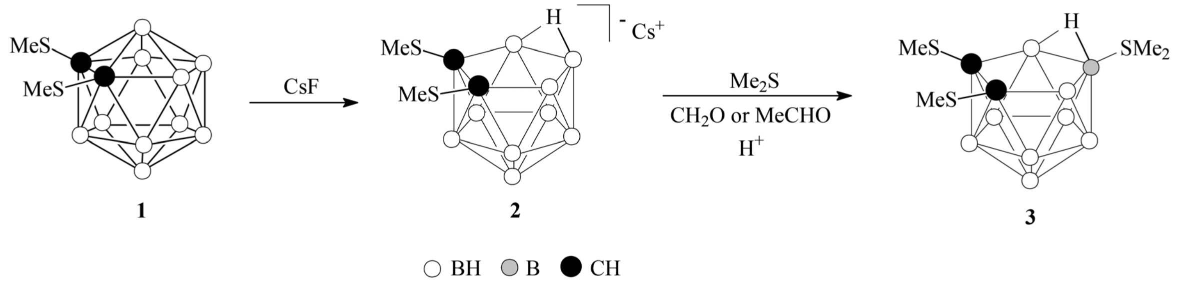
As is mentioned above 1,2-$(MeS)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) is a very weak ligand and it does not give the complex under treatment with $W(CO)_4(EtCN)_2$ as well as with $W(CO)_5$(THF). To reduce the electron withdrawing effect of the carborane cage it was decapitated by the treatment with cesium 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 have found extensive use as π-ligands in the 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 dimethylsulfoxide in acidic medium similarly to that 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 an acidic solution in the presence of acetaldehyde of formaldehyde (Scheme 1) simi-

---

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russian Federation.
E-mail: timofeev@ineos.ac.ru

† In memory of Professor Kenneth Wade.

‡ Electronic supplementary information (ESI) available: Crystallographic data for monoclinic modification of compound **4**. CCDC 1043368–1043371 and 1048359. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00176e



Scheme 1

larly to the synthesis of 10-Me_2S-7,8-$C_2B_9H_{11}$ by Plešek *et al.*[9] Thioether **3** is a white solid, stable in air and moisture and readily soluble in common organic solvents such as acetone, alcohols and chlorinated hydrocarbons and insoluble in hydrocarbon solvents and water.

The ^1H 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 a negligible effect of the methylsulfide groups on the electronic effect of the whole carborane system. The signal of the methyl sulfide group demonstrates a small low-field shift in comparison with the corresponding signal in the spectrum of Cs[**2**], which indicates only a small increase of the electron withdrawing 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**, which indicates a significantly stronger donor ability of **3**.

The crystal and molecular structure of **3** was determined by single crystal X-ray diffraction (Fig. 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 the 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]

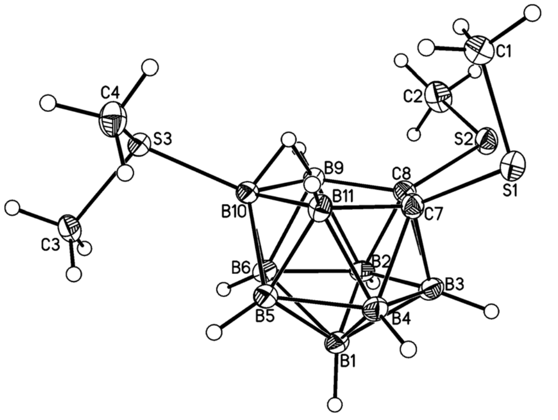


Fig. 1 Molecular structure of ligand **3** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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

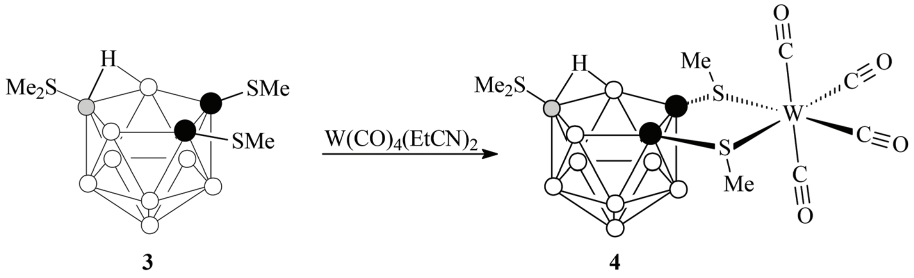
Indeed the reaction of **3** with $W(CO)_4(EtCN)_2$ in dichloromethane at room temperature produces the corresponding complex $(CO)_4W[7,8\text{-}(MeS)_2\text{-}10\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_9\text{-}\kappa^2\text{-}S(1),S(2)]$ (**4**) in a nearly quantitative yield (Scheme 2). In the ^1H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

The crystal structure of **4** was determined by single crystal X-ray diffraction (Fig. 2). The geometry at tungsten is a 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 both the methyls are turned downward relative to the pentagonal face. The C_{carb}–C_{carb} bond in complex **4** is shorter than in ligand **3**, which 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).

The reaction of **3** with 1 equiv. of photochemically generated $W(CO)_5(THF)$ in THF at room temperature gave the 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

Table 1 Lengths (in Å) of the C_{carb}–C_{carb}, C_{carb}–B, C_{carb}–S bonds in the 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)	—	—



4

Scheme 2

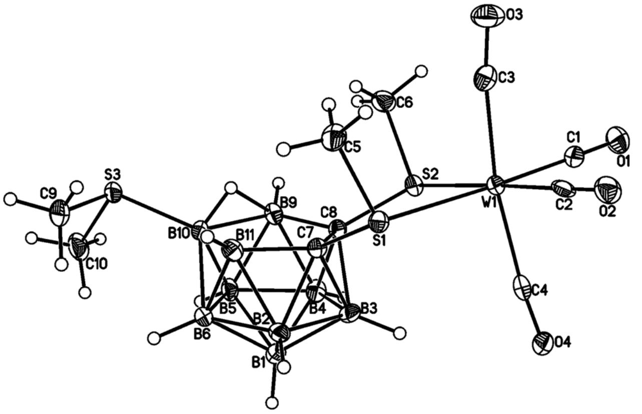
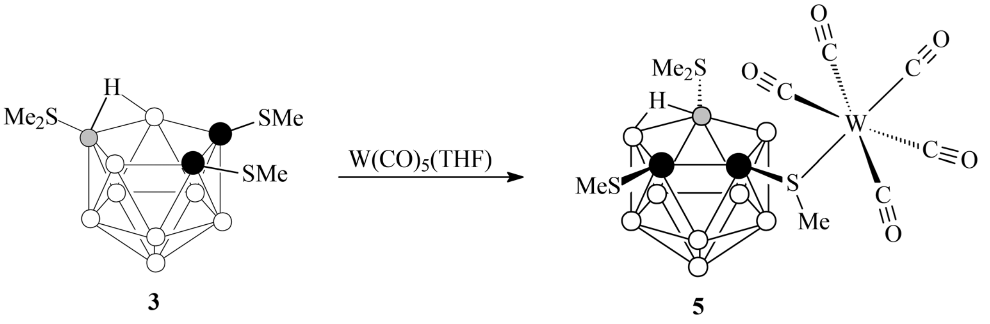


Fig. 2 Molecular structure of complex **4** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): W(1)⋯C(1) 1.966(4), W(1)⋯C(2) 1.971(3), W(1)⋯C(3) 2.034(3), W(1)⋯C(4) 2.028(3), W(1)⋯S(1) 2.5461(8), W(1)⋯S(2) 2.5388(8).

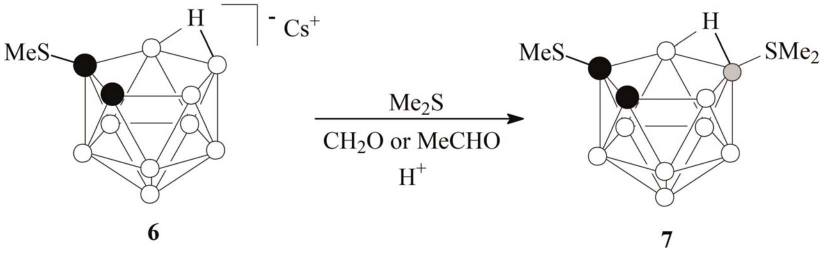
of the dimethyl sulfonium group at 2.61 and 2.60 ppm indicating monodentate coordination of the ligand. The ^{13}C NMR spectrum of **5** contains signals of the coordinated MeS–C_{carb} fragment at 30.7 and 75.1 ppm, signals of the non-coordinated MeS–C_{carb} fragment at 20.7 and 63.7 ppm, signals of 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.

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 a single product identified by single crystal X-ray diffraction (for additional information see ESI‡).

The monodentate methyl sulfide ligand 7-MeS-10-Me_2S-7,8-$C_2B_9H_{10}$ (**7**) was synthesized in a 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



Scheme 3



Scheme 4

to 9-Me_2SCH_2-7,8-$C_2B_9H_{11}$ reported by Plešek *et al.*[9] 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 an acidic solution in the presence of acetaldehyde.[21] The crystal structure of **7** was determined by single crystal X-ray diffraction (Fig. 3) and it demonstrates similar trends in the bond length distribution around C(7) and C(8) atoms observed for ligand **3** (see Table 1).

The reaction of **7** with $W(CO)_5(THF)$ in THF at room temperature gave the complex $(CO)_5W$[7-MeS-10-Me_2S-7,8-$C_2B_9H_{10}$-κ^1-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 the ones found in the complexes $(CO)_5W$[7-MeS-7,8-$C_2B_9H_{11}$-κ^1-S(1)]$^-$ (ref. 6) and $(CO)_5W$[7,8-$(MeS)_2$-10-Me_2S-7,8-$C_2B_9H_9$-κ^1-S(1)] (**5**) which gives strong evidence of the negligible effect of both 8-MeS and 10-Me_2S additional substituents on the donor ability of the 7-methylsulfide-*nido*-carborane ligand.

The crystal structure of **8** was determined by single crystal X-ray diffraction (Fig. 4). The geometry at tungsten is a 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

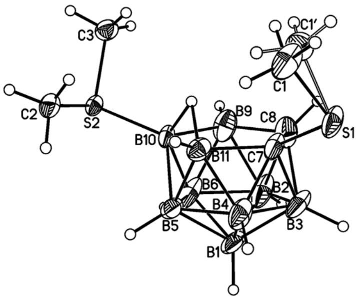


Fig. 3 Molecular structure of ligand **7** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The C1 methyl group is disordered over two positions in the ratio of 0.68(2) : 0.32(2). The minor part is shown by an open line.

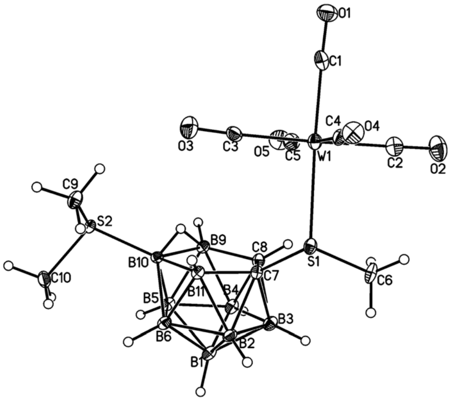
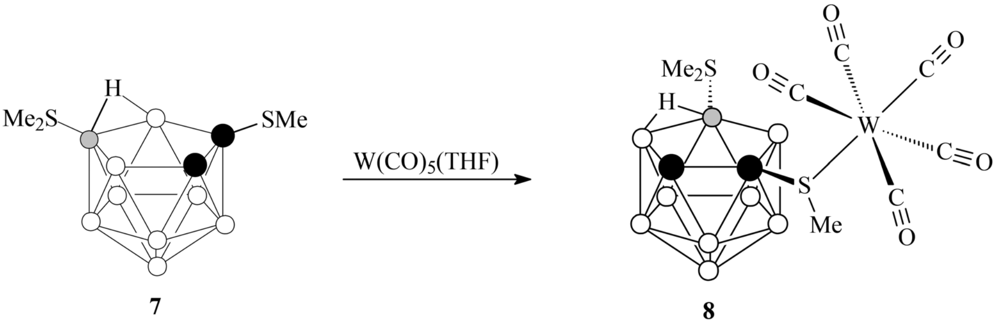


Fig. 4 Molecular structure of complex **8** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): W(1)⋯C(1) 1.984(5), W(1)⋯C(2) 2.053(4), W(1)⋯C(3) 2.049(4), W(1)⋯C(4) 2.054(4), W(1)⋯C(5) 2.064(4), W(1)⋯S(1) 2.562(1).



Scheme 5

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**.

Conclusion

New neutral *nido*-carboranyl methylsulfide ligands $[7\text{-MeS-}10\text{-Me}_2\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$ and $[7,8\text{-(MeS)}_2\text{-}10\text{-Me}_2\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_9]$ 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 $(CO)_5W[7\text{-MeS-}10\text{-Me}_2\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\text{-}\kappa^1\text{-S(1)}]$ and $(CO)_5W[7,8\text{-(MeS)}_2\text{-}10\text{-Me}_2\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_9\text{-}\kappa^1\text{-S(1)}]$ and bidentate $(CO)_4W[7,8\text{-(MeS)}_2\text{-}10\text{-Me}_2\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_9\text{-}\kappa^2\text{-S(1),S(2)}]$ 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 a negligible effect on the donor ability of the 7-methylsulfide-*nido*-carborane ligand.

Experimental

All the reactions with tungsten carbonyl were carried out under dry argon. $1,2\text{-(MeS)}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (**1**), $Cs[7\text{-MeS-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ (Cs[**6**]) and $W(CO)_4(EtCN)_2$ were synthesized according to the literature.[6,12,24] 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 ^{1}H, ^{11}B, ^{11}B{^{1}H}, and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer. ^{1}H 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 a SMART APEX2 CCD (λ(Mo-K$_\alpha$) = 0.71073 Å, graphite monochromator, ω-scans). The collected data were analyzed by the SAINT and SADABS programs incorporated into the APEX2 program package.[25] All structures were solved by 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 1.05 Å. The H(C) positions were calculated. All the hydrogen atoms were refined in isotropic approximation using 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 structure refinement are summarized in Table 2. Crystallographic data (excluding structure factors) for the structures **3**, **4**, **7** and **8** as well as the monoclinic form of **4** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 1043368–1043371 and 1048359, respectively.

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

A 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

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*	$Pna2_1$	$P2_1$	$P2_1/c$
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/°	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/°	2.78–29.00	2.31–28.00	2.37–28.00	2.64–26.00
Reflections collected	8019	29 588	7699	15 785
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
w$R_2(F^2)$ (all data)[b]	0.0705	0.0367	0.0891	0.0649
Largest diff. peak/hole/e 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] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

10 h. The solvent was removed *in vacuo*, the residue was washed with cold water and dried in air to give 22.50 g (97%) of **2** as a white solid. ^{1}H NMR (CD_3OD, ppm): 2.21 (6H, s, *Me*S), 2.7 to −0.5 (10H, br m, B*H*), −2.3 to −2.8 (1H, br m, B*H*B). ^{11}B NMR (CD_3OD, 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 $C_4H_{16}B_9CsS_2$: 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 a 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 a 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 the eluent. Yield 0.36 g (55%). Method B. A 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 a suspension of **2** (1.50 g, 4.0 mmol) in water (20 ml). Then a 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 the 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 to −1.0 (1H, br. m, B*H*B). ^{1}H NMR (CD_3OD, ppm): 2.59 (6H, s, *Me*$_2$S), 2.25 (6H, s, *Me*S), 2.8 to −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 to −0.4 (9H, br m, B*H*), −0.1 to −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_3OD, 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 $C_6H_{21}B_9S_3$: 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)

The solid $W(CO)_4(EtCN)_2$ (0.32 g, 0.8 mmol) was added to a solution of **3** (0.15 g, 0.5 mmol) in CH_2Cl_2 (5.0 ml). The reaction mixture was stirred overnight at ambient temperature. The solvent was evaporated and the crude product was purified by column chromatography on silica using chloroform as the 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)$_5$W[7,8-(MeS)$_2$-10-Me$_2$S-7,8-C$_2$B$_9$H$_9$-κ^1-S(1)] (5)

Tungsten hexacarbonyl (0.28 g, 0.62 mmol) in THF (5.0 ml) in a quartz reactor cooled by water was irradiated with a UV-lamp for 2 h. When the reaction mixture turned to a yellow solid **3** (0.15 g, 0.52 mmol) was added. After stirring overnight, the solvent was evaporated. The product was purified by column chromatography on silica using chloroform as the 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 to −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$_2$S-7-MeS-7,8-C$_2$B$_9$H$_{10}$] (7)

Method A. To a 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. The precipitate was filtered off, the organic phase was evaporated and the product was finally purified by column chromatography on silica using chloroform as the eluent. Yield 0.10 g (46%). Method B. To a suspension of **6** (2.00 g, 6.38 mmol) in water (6.4 ml), dimethylsulfide (2.3 ml) and benzene (6.4 ml) were added. Hydrochloric acid (3.2 ml) followed by a 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 the 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, CH_{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 to −1.0 (br dd, 1H, $J_{H–B(10)}$ = 133 Hz, $J_{H–H(B10)}$ = 57 Hz, B*H*B). ^{13}C NMR ($CDCl_3$, ppm): 69.7 (d, *J* = 30 Hz, CH_{carb}), 55.1 (d, *J* = 37 Hz, CH_{carb}), 25.8 (S*Me*$_2$), 19.3 (S*Me*).

^{11}B NMR (acetone-d_6, ppm): −10.1 (1B, d, $J_{B–H}$ = 132 Hz, B(9)), −10.9 (1B, d, $J_{B–H}$ = 116 Hz, B(11)), −14.3 (1B, d, $J_{B–H}$ = 166 Hz, B(3)), −16.6 (3B, d, $J_{B–H}$ = 145 Hz, B(4,5,6)), −21.4 (1B, d, $J_{B–H}$ = 156 Hz, B(2)), −25.7 (1B, s, B(10)), −36.4 (1B, d, $J_{B–H}$ = 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 a quartz reactor cooled by water was irradiated with a UV-lamp for 2 h. When the reaction mixture turned to a yellow solid **7** (0.15 g, 0.62 mmol) was added. After stirring overnight, the solvent was evaporated. The product was purified by column chromatography on silica using chloroform as the 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, $\Delta\nu_{\frac{1}{2}}$ 199 Hz). ^{13}C NMR (CDCl$_3$, ppm): 200.0 (t, J_{C-W} = 79 Hz, *cis*-*C*O), 197.5 (t, J_{C-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-H} = 137 Hz), −12.0 (2B, d, J_{B-H} = 146 Hz), −13.1 (1B, d, J_{B-H} = 144 Hz), −19.0 (3B, d), −25.3 (1B, s), −35.0 (2B, d, J_{B-H} = 146 Hz).

Acknowledgements

The authors (SVT, OBZ, IBS and VIB) are grateful to the Russian Foundation for Basic Research (13-03-00581) for financial support and KYS is thankful to the Russian Scientific Foundation (14-13-00884) for financial support for structural investigations.

References

1 (*a*) I. B. Sivaev, K. A. Solntsev and N. T. Kuznetsov, *Russ. J. Coord. Chem.*, 1993, **19**, 179–188; (*b*) F. Teixidor, R. Núñez and C. Viñas, *Contrib. Sci.*, 2000, **1**, 435–449; (*c*) G.-X. Jin, *Coord. Chem. Rev.*, 2004, **248**, 587–602; (*d*) S. Liu, Y.-F. Han and G.-X. Jin, *Chem. Soc. Rev.*, 2007, **36**, 1543–1560; (*e*) X. Meng, F. Wang and G.-X. Jin, *Coord. Chem. Rev.*, 2010, **254**, 1260–1272; (*f*) L. Jain, V. K. Jain, N. Kushwah, M. K. Pal, A. P. Wadawale, V. I. Bregadze and S. A. Glazun, *Coord. Chem. Rev.*, 2014, **258–259**, 72–118.

2 (*a*) H. D. Smith, *J. Am. Chem. Soc.*, 1965, **87**, 1817–1818; (*b*) M. Kumada, K. Sumitani, Y. Kiso and K. Tamao, *J. Organomet. Chem.*, 1973, **50**, 319–326; (*c*) W. E. Hill, B. G. Rackley and L. M. Silva-Trivino, *Inorg. Chim. Acta*, 1983, **75**, 51–56; (*d*) J. G. Contreras, L. M. Silva-Triviño and M. E. Solis, *Inorg. Chim. Acta*, 1986, **114**, 51–54; (*e*) O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1601–1605; (*f*) O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *J. Chem. Soc., Chem. Commun.*, 1993, 1696–1697; (*g*) E. Bembenek, O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Chem. Ber.*, 1994, **127**, 835–840; (*h*) S. Paavola, R. Kivekäs, F. Teixidor and C. Viñas, *J. Organomet. Chem.*, 2000, **606**, 183–187; (*i*) S. Paavola, F. Teixidor, C. Viñas and R. Kivekäs, *J. Organomet. Chem.*, 2002, **645**, 39–46; (*j*) J. J. Adams, A. S. Del Negro, N. Arulsamy and B. P. Sullivan, *Inorg. Chem.*, 2008, **47**, 1871–1873; (*k*) J. Dou, F. Su, Y. Ni, D. Li and D. Wang, *Dalton Trans.*, 2008, 4152–4156; (*l*) L. Yang, C. Zhu, D.-P. Zhang, D. Li, D. Wang and J. Dou, *Polyhedron*, 2011, **30**, 1469–1477; (*m*) L. Kong, D. Zhang, F. Su, J. Lu, D. Li and J. Dou, *Inorg. Chim. Acta*, 2011, **370**, 1–6; (*n*) M. Joost, A. Zeineddine, L. Estevez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune and D. Bourissou, *J. Am. Chem. Soc.*, 2014, **136**, 14654–14657; (*o*) S. Bayer and E. Hey-Hawkins, in *Boron Science: New Technologies and Applications*, ed. N. S. Hosmane, Taylor & Francis Books/CRC Press, Boca Raton, 2012, p. 529.

3 (*a*) F. Teixidor, C. Viñas, M. M. Abad, M. Lopez and J. Casabo, *Organometallics*, 1993, **12**, 3766–3768; (*b*) F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs and J. Casabo, *Inorg. Chem.*, 1994, **33**, 2645–2650; (*c*) F. Teixidor, C. Viñas, M. M. Abad, R. Kivekäs and R. Sillanpää, *J. Organomet. Chem.*, 1996, **509**, 139–150; (*d*) O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Inorg. Chem.*, 1996, **35**, 1361–1366; (*e*) D. Zhang, J. Dou, D. Li and D. Wang, *Inorg. Chim. Acta*, 2006, **359**, 1361–1366; (*f*) J. Dou, D. Zhang, D. Li and D. Wang, *Polyhedron*, 2007, **26**, 719–724.

4 P. Hu, J.-Q. Wang, F. Wang and G.-X. Jin, *Chem. – Eur. J.*, 2011, **17**, 8576–8583.

5 (*a*) F. Teixidor, J. Casabo, C. Viñas, E. Sanchez, L. Escriche and R. Kivekäs, *Inorg. Chem.*, 1991, **30**, 3053–3058; (*b*) F. Teixidor, J. A. Ayllon, C. Viñas, R. Kivekäs, R. Sillanpää and J. Casabo, *J. Chem. Soc., Chem. Commun.*, 1992, 1281–1282; (*c*) F. Teixidor, J. A. Ayllon, C. Viñas, R. Kivekäs, R. Sillanpää and J. Casabo, *Organometallics*, 1994, **13**, 2751–2760; (*d*) F. Teixidor, J. A. Ayllon, C. Viñas, R. Sillanpää, R. Kivekäs and J. Casabo, *Inorg. Chem.*, 1994, **33**, 4815–4818.

6 S. V. Timofeev, M. V. Zakharova, E. M. Mosolova, I. A. Godovikov, I. V. Ananyev, I. B. Sivaev and V. I. Bregadze, *J. Organomet. Chem.*, 2012, **721–722**, 92–96.

7 (*a*) S. V. Timofeev, I. B. Sivaev, E. A. Prikaznova and V. I. Bregadze, *J. Organomet. Chem.*, 2014, **751**, 221–250 and references therein; (*b*) R. N. Grimes, *Carboranes*, Academic Press, London, 2011, p. 773 and references therein.

8 Y.-K. Yan, D. M. P. Mingos, T. E. Muller, D. J. Williams and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1994, 1735–1741.

9 J. Plešek, T. Jelínek, F. Mareš and S. Heřmánek, *Collect. Czech. Chem. Commun.*, 1993, **58**, 1534–1547.

10 J. Plešek, Z. Janoušek and S. Heřmanek, *Collect. Czech. Chem. Commun.*, 1978, **43**, 2862–2868.

11 O. Tutusaus, F. Teixidor, R. Nuñez, C. Viñas, R. Sillanpää and R. Kivekäs, *J. Organomet. Chem.*, 2002, **657**, 247–255.

12 J. Llop, C. Viñas, F. Teixidor, L. Victori, R. Kivekäs and R. Sillanpää, *Organometallics*, 2001, **20**, 4024–4030.

13 T. V. Timofeeva, K. Y. Suponitsky, A. I. Yanovsky and N. L. Allinger, *J. Organomet. Chem.*, 1997, **536–537**, 481–488.

14 A. Laromaine, C. Viñas, R. Sillanpää and R. Kivekäs, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, **60**, o532–o526.

15 R. Ros, M. Vidali and R. Graziani, *Gazz. Chim. Ital.*, 1970, **100**, 407–413.

16 M. B. Hursthouse, E. W. Abel, M. A. Mazid and N. J. Long, private communication, 2003 (MEKBOU).

17 N. J. Long, J. Martin, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 3083–3085.

18 E. W. Abel, N. J. Long, K. G. Orrell, A. G. Osborne, V. Šik, P. A. Bates and M. B. Hursthouse, *J. Organomet. Chem.*, 1990, **394**, 455–468.

19 K. Sünkel, A. Blum, K. Polborn and E. Lippmann, *Chem. Ber.*, 1990, **123**, 1227–1231.

20 W. Levason, L. P. Ollivere, G. Reid, N. Tsoureas and M. Webster, *J. Organomet. Chem.*, 2009, **694**, 2299–2308.

21 O. Tutusaus, C. Vinas, R. Kivekäs, R. Sillanpää and F. Teixidor, *Chem. Commun.*, 2003, 2458–2459.

22 R. A. Pickering, R. A. Jacobson and R. J. Angelici, *J. Am. Chem. Soc.*, 1981, **103**, 817–821.

23 K. Kowalski and A. J. P. White, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m392–m393.

24 C.-A. Dickson, A. W. McFarlane and N. J. Coville, *Inorg. Chim. Acta*, 1989, **158**, 205–209.

25 *APEX2*, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.

26 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.