

Syntheses and crystal structures of group 6 metal complexes containing allyl and cyanotrihydroborate groups

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Abstract

Compounds $M(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)$ and $[\text{N}(\text{CH}_3)_4]_2[\text{M}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCBH}_3)_3]$ ($M = \text{Mo}, \text{W}$) were prepared and structurally characterized. In the solid state, the allyl group orients its open face to the two carbonyl groups producing an *endo* form in the above compounds. In solution, an *exo* form coexists with an *endo* form in compound $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)$. The cyanotrihydroborate ligand bonds to the metal through a nitrogen atom. Both of the IR and the ¹¹B NMR spectroscopic data suggest the negative charge of the cyanotrihydroborate ligand on the complex is almost localized on the BH₃ and this negative charge only has small effect on the metal–nitrogen interaction.

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1. Introduction

The organohydroborate anion bonds to a metal through a hydrogen bridge bond, M–H–B, are of three kinds, including monodentate, bidentate, and tridentate [1]. However, cyanotrihydroborate anion behaves differently in that it normally uses a nitrogen atom to bond to the metal, subsequently producing a M–NCBH₃ compound [2]. Occasionally, cyanotrihydroborate anion uses both a nitrogen atom and a BH hydrogen to bond to the metal, to give a M–HBH₂CN–M binuclear compound [3]. Early studies focused on late transition metal complexes [2–5] and rare examples of the early transition metal complexes have been reported [6]. The first structurally characterized early transition metal cyanotrihydroborate complex *trans*-[V(NCBH₃)₂(THF)₄] was reported in 2000 [7]. More recently, we reported our studies of group 6 metal cyanotrihydroborate complexes [8]. Among those previous studies, various metals and ligands along with the cy-

anotrihydroborate anion were used to form complexes. However, no systematic comparison was made of the properties of the cyanotrihydroborate ligand within the complexes. This work explores the features of several neutral and anionic group 6 cyanotrihydroborate compounds through infrared, NMR, and, solid state analyses.

2. Results and discussion

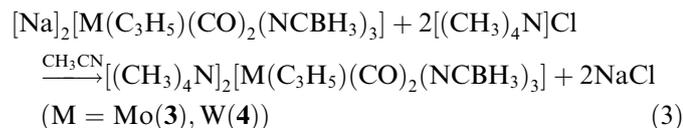
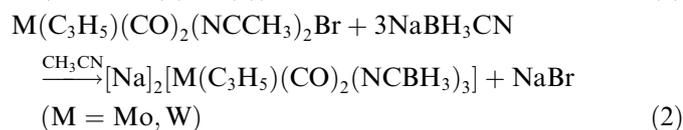
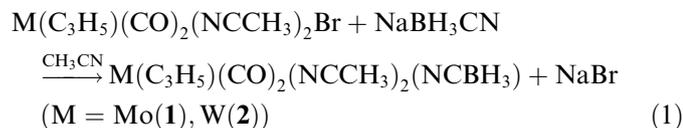
2.1. Preparations and properties of $M(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)$ ($M = \text{Mo}(\mathbf{1}), \text{W}(\mathbf{2})$), and $[\text{N}(\text{CH}_3)_4]_2[\text{M}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCBH}_3)_3] \cdot 1/2\text{DME}$ ($M = \text{Mo}(\mathbf{3}), \text{W}(\mathbf{4})$)

Group 6 cyanotrihydroborate complexes **1–4** were prepared from the reactions of $M(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2\text{Br}$ ($M = \text{Mo}, \text{W}$) with sodium cyanotrihydroborate in a 1:1 ratio, according to Eq. (1), or in a 1:3 ratio, followed by a metathesis of the [Na]⁺ cation by the [N(CH₃)₄]⁺ cation, according to Eqs. (2) and (3). The anion [BH₃CN][−] displaces Br[−] to produce **1** and **2** ($M = \text{Mo}(\mathbf{1}), \text{W}(\mathbf{2})$), or displaces both Br[−] and CH₃CN to yield the dianionic

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compounds **3** and **4** ($M = \text{Mo}(\mathbf{3}), \text{W}(\mathbf{4})$). These reactions were performed in a stoichiometric amount of sodium cyanotrihydroborate in acetonitrile. Thus, the bonding ability of the cyanotrihydroborate anion is stronger than that of the acetonitrile. Compounds **1** and **2** were crystallized from CH_3CN and contain a CH_3CN molecule in the lattice. Compounds **3** and **4** were crystallized from the DME/hexane mixed solvent and contain one half of a DME molecule. The solvent molecule was lost from compounds **1** and **2**. Therefore, fine powders of compounds **1** and **2** were dried in a vacuum before the elemental analysis was performed and the solvent free complex was obtained.



2.2. Infrared studies

Infrared spectroscopy is a useful tool for identifying the bonding mode in the cyanotrihydroborate complexes. In fact, most interactions between the metal and the cyanotrihydroborate ligand have been differentiated using the B–H stretching band [5]. A $\text{M}-\text{NCBH}_3$ -bonded compound displays a ν_{BH} absorption band in the range 2320–2350 cm^{-1} and for a $\text{M}-\text{HBH}_2\text{CN}-\text{M}$, a binuclear compound appears at around 2380 cm^{-1} [3b]. Table 1 presents selected infrared data concerning compounds **1–4** and $[\text{N}(\text{CH}_3)_4][\text{NCBH}_3]$. A band appears at about 2347 cm^{-1} from each compound. It is assigned to the B–H absorption band and suggests a nitrogen-bonded compound in each case. Each compound has an absorption band at 2197 cm^{-1} , which was attributed to the $\text{C}\equiv\text{N}$ stretching band of the cyanotrihydroborate ligand. This value is 25 cm^{-1} higher than that of $[\text{N}(\text{CH}_3)_4][\text{NCBH}_3]$ and is comparable to the value of the ν_{CN} bands found in other cyanotrihydroborate complexes [2,5,7,8]. This shift has been attributed to the strengthening in C–N σ bonding in a weakly

bound $\text{M}-\text{NCBH}_3$ [9]. The ν_{CN} absorption bands of CH_3CN in compounds **1** (2312, 2253 cm^{-1}) and **2** (2314, 2285 cm^{-1}) were assigned by comparing the absorption bands of the starting material $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2\text{Br}$ and that reported for complexed CH_3CN [10]. These two kinds of $\text{C}\equiv\text{N}$ stretching band do not overlap.

Two carbonyl absorption bands are observed in each compound. The lower $\text{C}=\text{O}$ absorption bands of the tungsten complexes reflect the more electron-rich nature of the third-row element [11]. The carbonyl stretching of the anionic species is expected to be weaker than that of the neutral species, if the metal has accumulated more negative charge and facilitates π back bonding. As shown in Table 1, the average frequency of the carbonyl absorption bands in **1** (1945, 1853 cm^{-1}) is 5 cm^{-1} higher than that in **3** (1943, 1846 cm^{-1}), and the value in **2** (1924, 1840 cm^{-1}) is 2 cm^{-1} lower than that in **4** (1935, 1833 cm^{-1}). This near invariance of the $\text{C}=\text{O}$ absorption bands suggests that neutral and anionic compounds have similarly charged environments around the metals, and indicates that both the acetonitrile and the cyanotrihydroborate anion exhibit similar metal–nitrogen interaction. Thus, the negative charge of the anions may be localized mostly around the boron atom, contributing little to the metal–ligand interaction.

2.3. NMR studies

Boron-11 NMR signals of complexes **1–4** were obtained in the range –42.30 to –43.30 ppm as a broad quartet ($J_{\text{B-H}} = 93$ Hz). These chemical shifts are consistent with the negatively charged boron environment and appear in similar positions to those in NaBH_3CN (–43.5 ppm, $J_{\text{B-H}} = 89$ Hz) [12] and other N-bonded cyanotrihydroborate complexes [2a,2b,4d,6a,8]. The boron chemical shift of a hydrogen bridged cyanotrihydroborate complex has not been reported; however, a significant downfield shift of a complexed organohydroborate ligand has commonly been observed [1c]. The boron chemical shifts of complexes **1–4** suggest that the nitrogen-bonded interaction has little effect on the electron density of the boron atom. In the ^1H NMR spectra, the BH hydrogens of complexes **1–4** appear as a very broad hump centered in the range 0.52–0.30 ppm. There are two kinds of cyanotrihydroborate ligand in compounds **3** and **4**, respectively, one is *trans* to the carbonyl and the other is *trans* to the allyl group. An attempt to differentiate their chemical shifts by low-temperature NMR study was

Table 1

Selected infrared data of compounds $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)$ (**1**), $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)$ (**2**), $[\text{N}(\text{CH}_3)_4][\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCBH}_3)_3] \cdot 1/2\text{DME}$ (**3**), $[\text{N}(\text{CH}_3)_4][\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCBH}_3)_3] \cdot 1/2\text{DME}$ (**4**), and $[\text{N}(\text{CH}_3)_4][\text{NCBH}_3]$

Compounds	ν_{CO}	$\nu_{\text{CN}}(\text{BH}_3\text{CN})$	ν_{BH} (cm^{-1})			
1	1945(vs)	1853(vs)	2216(vw)	2196(m)	2347(w)	1121(m)
2	1924(vs)	1840(vs)		2196(s)	2349(m)	1119(m)
3	1943(vs)	1846(vs)		2197(m)	2346(s)	1122(s)
4	1935(vs)	1833(vs)		2197(m)	2347(s)	1121(m)
$[\text{N}(\text{CH}_3)_4][\text{NCBH}_3]$			2230(w)	2172(s)	2339(s)	2301(s, sh)

unsuccessful. Due to the limited solubility of these ionic compounds in most solvent systems, the boron-11 NMR spectrum of compound **3** was examined at $-50\text{ }^{\circ}\text{C}$ in CD_3CN , and no splitting of the boron signal was observed. Even if the spectrum can be measured at a lower temperature, these two kinds of boron signal may appear very close to each other, or even overlap, as the boron atom was not significantly affected upon complexation, and low-temperature NMR spectroscopy may not be able to distinguish these two kinds of boron environments.

^1H NMR analysis revealed two sets of allyl resonances in complex **1** with the ratio 4:1. The allyl group has three possible orientations. As shown below, the allyl group orientates its open face to the two carbonyls, producing an *endo* form (**I**), the open face is between an acetonitrile and a carbonyl group (**II**), or the open face is opposite the two carbonyls, producing an *exo* form (**III**). The preferred orientation of the allyl group on the model compounds $[(\text{HCN})_3(\text{CO})_2\text{Mo}(\eta^3\text{-C}_3\text{H}_5)]^+$ and $[\text{Cl}_3(\text{CO})_2\text{Mo}(\eta^3\text{-C}_3\text{H}_5)]^-$ has been theoretically calculated and the orientation **III** has been found to have the lowest energy [13]. ^1H NMR spectra revealed doublet signals of H_{anti} (δ 1.38 and 1.50 ppm, $J_{\text{H-H}} = 9.8$ Hz) and H_{syn} (δ 3.46 and 3.59 ppm, $J_{\text{H-H}} = 6.4$ Hz) in each isomer in compound **1**. This symmetric nature suggests that the allyl group in the solution is orientated in forms **I** and **III**. ^{13}C NMR analysis provided further evidence of the coexistence of the two isomers: two carbonyl signals (223.14 and 221.82 ppm) and two sets of allyl signals (CH: 74.29 and 74.04 ppm; CH_2 : 60.87 and 59.86 ppm) were observed. Only one allyl group was observed in complexes **2**, **3**, and **4**, and the allyl resonances of the two anionic compounds are slightly up-field than that of the neutral compounds **1** and **2** (see Chart 1).

2.4. X-ray studies

Complexes **1–4** were structurally characterized; results of these studies are summarized in Tables 2 and 3. The molecular structures of **1** and **3** are provided in Figs. 1 and 2. Complexes **2** and **4**, which have similar structures as that of complexes **1** and **3**, are included in the supporting information. Solvent molecule, which stabilizes the lattice structure, was found in each complex. The coordination geometries around the metal in complexes **1–4** are similar, and be described as distorted octahedra. The axial positions are occupied by an allyl group and a cyanotrihydro-

borate ligand. Two carbonyl groups are *trans* to two acetonitriles (**1** and **2**), or *trans* to another two cyanotrihydroborate ligands (**3** and **4**) in the equatorial positions. In compounds **1** and **2**, a crystallographically imposed mirror plane passes through the metal, the central allylic carbon atom, and between the two carbonyls and the two acetonitriles, and the solvent molecule, to generate the rest of the molecule. In each complex, the cyanotrihydroborate ligand bonds to the metal through a nitrogen atom, and the allyl group is oriented with its open face toward the two carbonyls, producing an *endo* form configuration.

Table 3 presents the selected bond distances for **1–4**. The poor crystal quality of **4** makes the corresponding results less accurate. However, the C–O bond distances in **1–3** are falling in a very short range (1.157(3)–1.162(5) Å). This result is consistent with that observed in the infrared study in which the carbonyl absorption bands are almost invariant. The Mo–N and C–N bond distances of the ligands that are *trans* to the CO in **1** and **3** are comparable, so the acetonitrile in **1** and the cyanotrihydroborate ligand in **3** interact similarly with Mo. These M–N and C–N bond distances are also consistent with that observed in compounds $[\text{N}(\text{CH}_3)_4]_3[\text{Mo}(\text{CO})_3(\text{NCBH}_3)_3]$ [8] in which each cyanotrihydroborate ligand is *trans* to a carbonyl. The W–N bond distance of the acetonitrile in **2** (2.214(4) Å) is shorter than the corresponding Mo–N distance in **1** (2.232(2) Å). The electron-rich nature of the tungsten may account for this short W–N distance. A similar result has also been observed in $[\text{N}(\text{CH}_3)_4]_3[\text{M}(\text{CO})_3(\text{NCBH}_3)_3]$ (M = Mo, W) [8].

The cyanotrihydroborate ligand *trans* to the allyl group displays a stronger interaction with the central atom comparing with the ligand *trans* to the carbonyl group. The Mo–N bond distance in the axial position is shorter than that in the equatorial position (0.05 Å in **1** and 0.06 Å in **3**). The allyl group is a weaker π acceptor than the carbonyl group. Thus, the cyanotrihydroborate ligand exhibits greater competition, resulting in a shorter Mo–N distance. A more significant π back bonding effect has been observed in **2**, resulting in a very short W–N and a very long N–C bond. The W–N and N–C bond distances in the axial position in **2** are 2.146(5) and 2.161(7) Å, respectively. The average M–allyl distances of **1–4** are comparable to those of other allyl substituted compounds [14].

The $[\text{BH}_3\text{CN}]^-$ anion is isoelectronic with CH_3CN , explaining why most of the cyanotrihydroborate complexes

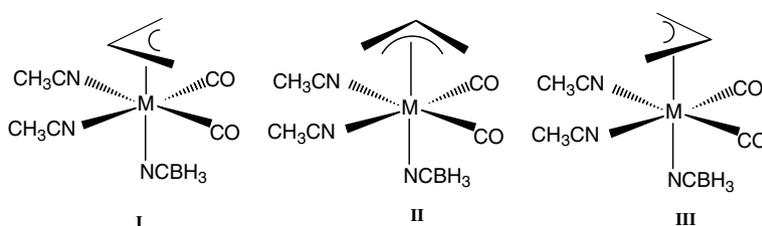


Chart 1.

Table 2

Crystallographic data for Mo(η^3 -C₃H₅)(CO)₂(NCCH₃)₂(NCBH₃) · CH₃CN (**1**), W(η^3 -C₃H₅)(CO)₂(NCCH₃)₂(NCBH₃) · CH₃CN (**2**), [N(CH₃)₄]₂[Mo(η^3 -C₃H₅)(CO)₂(NCBH₃)₃] · 1/2DME (**3**), and [N(CH₃)₄]₂[W(η^3 -C₃H₅)(CO)₂(NCBH₃)₃] · 1/2DME (**4**)

Empirical formula	C ₁₂ H ₁₇ BMoN ₄ O ₂	C ₁₂ H ₁₇ BN ₄ O ₂ W	C ₁₈ H ₄₃ B ₃ MoN ₅ O ₃	C ₁₈ H ₄₃ B ₃ N ₅ O ₃ W
Formula weight	356.05	443.96	505.94	593.85
Temperature (K)	150(1)	150(1)	150(1)	150(1)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2(1)/ <i>m</i>	<i>P</i> 2(1)/ <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	6.3891(2)	6.3626(1)	7.6272(4)	7.6535(4)
<i>b</i> (Å)	10.1858(2)	10.1564(2)	11.4367(6)	11.4345(5)
<i>c</i> (Å)	12.4482(2)	12.4637(3)	16.9981(9)	17.0329(8)
α (°)			88.1730(10)	88.539(1)
β (°)	90.5630(13)	90.8559(11)	89.1610(10)	89.455(1)
γ (°)			71.8640(10)	71.367(1)
<i>V</i> (Å ³)	810.07(3)	805.33(3)	1408.35(13)	1412.02(12)
<i>Z</i>	2	2	2	2
ρ_{calc} (g/cm ³)	1.460	1.831	1.193	1.397
Crystal size (mm)	0.35 × 0.08 × 0.04	0.30 × 0.12 × 0.10	0.15 × 0.15 × 0.10	0.28 × 0.20 × 0.05
Radiation (λ , Å)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
2 θ Limits (°)	1.64–27.49	1.63–27.50	1.20–27.50	1.20–27.50
Index ranges	–7 ≤ <i>h</i> ≤ 8, –13 ≤ <i>k</i> ≤ 13, –14 ≤ <i>l</i> ≤ 16	–8 ≤ <i>h</i> ≤ 7, –12 ≤ <i>k</i> ≤ 13, –16 ≤ <i>l</i> ≤ 16	–9 ≤ <i>h</i> ≤ 9, –14 ≤ <i>k</i> ≤ 14, –22 ≤ <i>l</i> ≤ 22	–9 ≤ <i>h</i> ≤ 9, –14 ≤ <i>k</i> ≤ 14, –22 ≤ <i>l</i> ≤ 22
Reflections collected	9801	8570	18,047	18,071
Unique reflections	1973	1955	6441	6455
Unique reflections [<i>I</i> > 2.0 σ (<i>I</i>)]	360	424	534	598
Completeness to θ (%)	100.0	99.9	99.8	99.7
μ (mm ^{–1})	0.814	7.177	0.490	4.115
Data/restraints/parameters	1973/0/111	1955/0/111	6441/0/298	6455/1/267
<i>R</i> ₁ ^a [<i>I</i> > 2.0 σ (<i>I</i>)]	0.0339	0.0278	0.0633	0.0970
<i>wR</i> ₂ ^b (all data)	0.0820	0.0683	0.1562	0.2687
<i>R</i> _{int}	0.0613	0.0606	0.0455	0.0579
Goodness-of-fit on <i>F</i> ²	1.041	1.034	1.261	1.261

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$.

Table 3

Selected bond distances (Å) for Mo(η^3 -C₃H₅)(CO)₂(NCCH₃)₂(NCBH₃) · CH₃CN (**1**), W(η^3 -C₃H₅)(CO)₂(NCCH₃)₂(NCBH₃) · CH₃CN (**2**), [N(CH₃)₄]₂[Mo(η^3 -C₃H₅)(CO)₂(NCBH₃)₃] · 1/2DME (**3**), and [N(CH₃)₄]₂[W(η^3 -C₃H₅)(CO)₂(NCBH₃)₃] · 1/2DME (**4**)

	CO		Allyl	CH ₃ CN (or BH ₃ CN [–]) <i>trans</i> to CO			BH ₃ CN [–] <i>trans</i> to allyl		
	C–O	M–C	Ave. M–allyl	M–N	C–N	C–C (or B–C)	M–N	C–N	B–C
1	1.157(3)	1.957(3)	2.289(4)	2.232(2)	1.131(3)	1.457(4)	2.182(3)	1.120(5)	1.596(6)
2	1.162(5)	1.958(4)	2.289(5)	2.214(4)	1.136(6)	1.444(6)	2.146(5)	1.161(7)	1.578(9)
3	1.158(6)	1.943(5)	2.281(5)	2.225(4)	1.140(6)	1.574(8)	2.171(4)	1.142(6)	1.574(8)
	1.160(6)	1.948(5)		2.233(4)	1.130(6)	1.596(8)			
4	1.16(2)	1.948(16)	2.264(17)	2.206(14)	1.14(2)	1.56(3)	2.166(14)	1.13(2)	1.56(3)
	1.14(2)	1.976(18)		2.212(14)	1.13(2)	1.61(3)			

unsurprisingly exhibited a M–N interaction. Clearly, the nitrogen atom has a stronger bonding ability than the BH hydrogen and the donor ability of the nitrogen atom of the cyanotrihydroborate ligand is enhanced, comparing with the acetonitrile, because of its the negative charge on the ligand. However, most of the negative charge is still localized on the boronhydride. This localized negative charge was confirmed by the infrared and boron-11 NMR spectroscopy and the formation of the M–HBH₂CN–M binuclear compounds [3].

3. Experimental

3.1. General procedures

All manipulations were carried out on a standard high vacuum line or in a drybox under an atmosphere of nitrogen. Unless otherwise noted, reagents were used as obtained from the commercial suppliers. 1,2-Dimethoxyethane (DME), and hexane were dried over sodium/benzophenone and freshly distilled prior to use. Acetonitrile was dried over

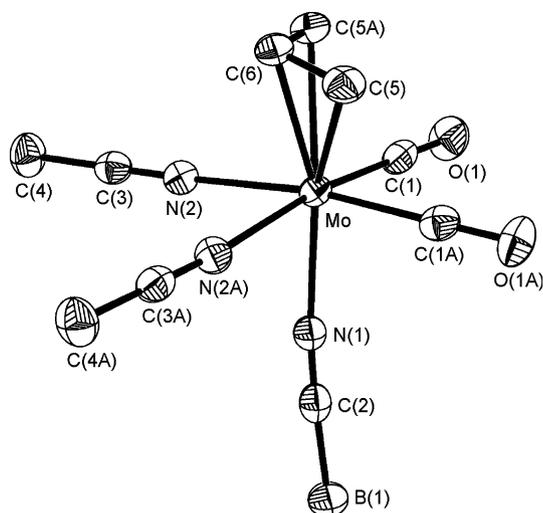


Fig. 1. Molecular structure of $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)\cdot\text{CH}_3\text{CN}$, (**1**), showing 50% probability thermal ellipsoids. The solvent molecule is omitted.

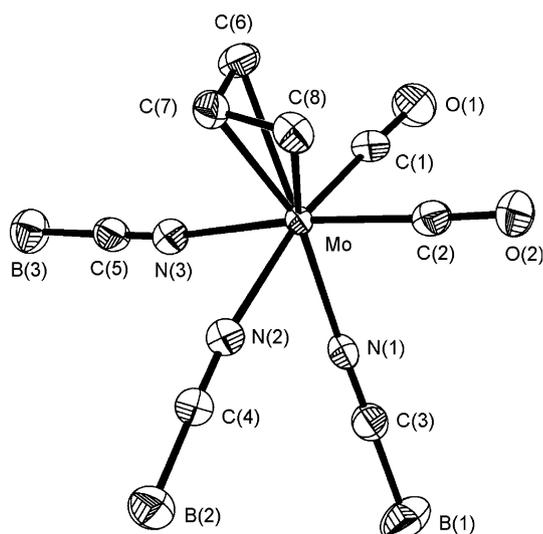


Fig. 2. Molecular structure of the anion in $[\text{N}(\text{CH}_3)_4]_2[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCBH}_3)_3]\cdot\frac{1}{2}\text{DME}$, (**3**), showing 50% probability thermal ellipsoids.

P_2O_5 and freshly distilled prior to use. $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Br}$ and $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Br}$ were prepared by the literature procedures.[15] Elemental analyses were recorded on a Hitachi 270-30 spectrometer. Proton spectra ($\delta(\text{TMS})$ 0.00 ppm) were recorded on a Varian Mercury 200 spectrometer operating at 199.975 MHz or recorded on a Varian Unity Inova 600 spectrometer operating at 599.948 MHz. ^{11}B spectra (externally referenced to $\text{BF}_3\cdot\text{OEt}_2$ (δ 0.00 ppm)) were recorded on a Bruker Avance DPX300 operating at 96.293 MHz or on a Varian Unity Inova 600 operating at 192.481 MHz. Infrared spectra were recorded on a Jasco FT/IR-460 Plus spectrometer with 2 cm^{-1} resolution.

3.2. X-ray structure determination

Suitable crystals of **1**, **2**, **3** and **4** were mounted and sealed inside glass capillaries under nitrogen. Crystallographic data collections were carried out on a Nonius KappaCCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 150(1) K. Cell parameters were retrieved and refined using DENZO-SMN [16] software on all reflections. Data reduction was performed with the DENZO-SMN [16] software. An empirical absorption was based on the symmetry-equivalent reflections and was applied to the data using SORTAV [17] program. The structure was solved using the SHELXS-97 [18] program and refined using SHELXL-97 [19] program by full-matrix least-squares on F^2 values. All nonhydrogen atoms in each structure were located and refined anisotropically. The hydrogen atoms on the boron atoms in **1**, **2**, and **3** were located and refined isotropically and other hydrogen atoms were fixed at calculated positions and refined using a riding mode. Crystallographic data of **1**, **2**, **3**, and **4** are summarized in Tables 2 and 3.

3.3. Preparations of complexes

3.3.1. $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)$ (**1**)

$\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2\text{Br}$ (880.5 mg, 2.48 mmol) and NaBH_3CN (156.0 mg, 2.48 mmol) were placed in a 50-mL flask. After degassing, about 20 mL of CH_3CN was transferred into the flask at $-78\text{ }^\circ\text{C}$. The system was warmed to room temperature and continued to stir for 6 h. After removal of NaBr through filtration, the CH_3CN solvent was removed. The resulting yellow solid was redissolved in a minimum amount of CH_3CN for crystallization. A 566.9 mg (64.2%) of yellow crystals were isolated. ^{11}B NMR (CH_3CN): δ -43.06 ppm (q, $J_{\text{B-H}} = 92$ Hz). ^1H NMR (CD_3CN): δ 3.98 (m, 1.24 H, CH), 3.59 (d, $J_{\text{H-H}} = 6.4$ Hz, H_{syn} , minor), 3.46 (d, $J_{\text{H-H}} = 6.4$ Hz, 2H, H_{syn} , major), 1.98 (s, CH_3CN), 1.50 (d, $J_{\text{H-H}} = 9.8$ Hz, H_{anti} , minor), 1.38 (d, $J_{\text{H-H}} = 9.8$ Hz, 2H, H_{anti} , major), and 0.51 ppm (q, br, 3H, BH_3). ^{13}C NMR (CD_3CN): δ 223.14 (CO, major), 221.82 (CO, minor), 118.28 (CN), 74.29 (CH, minor), 74.04 (CH, major), 60.87 (CH_2 , minor), 59.86 (CH_2 , major), and 1.44 ppm (CH_3). IR (KBr): 2997(vw), 2964(vw), 2936(vw), 2347(m), 2312(w), 2285(w), 2253(vw), 2216(vw), 2196(m), 1945(vs, br), 1853(vs), 1262(w), 1121(m), 1030(m), 962(vw), 931(vw), 860(vw), 802(w), 635(vw), 577(vw), 562(vw), 512(w), 486(vw), and 468(vw) cm^{-1} . Anal. Calc. for $\text{C}_{10}\text{H}_{14}\text{BMoN}_3\text{O}_2$: N, 13.34; C, 38.13; H, 4.48. Found: N, 13.41; C, 38.33; H, 4.52%.

3.3.2. $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2(\text{NCBH}_3)$ (**2**)

Similar procedure has been used to prepare compound **2** through the reaction of $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCCH}_3)_2\text{Br}$ (443.0 mg, 1.0 mmol) with NaBH_3CN (63.0 mg, 1.0 mmol). A 310.0 mg (69.8% yield) of orange crystals were isolated through acetonitrile solution. ^{11}B NMR (CH_3CN): δ -43.17 ppm (q, $J_{\text{B-H}} = 93$ Hz). ^1H NMR (CD_3CN): δ 3.25 (s, br, 2H, H_{syn}), 3.20 (m, 1H, CH), 1.98 (s, CH_3CN), 1.54

(d, br, 2H, H_{anti}), and 0.52 ppm (q, br, 3H, BH_3). IR(KBr): 3064(vw), 2998(vw), 2935(vw), 2349(m), 2314(w), 2286(w), 2253(vw), 2196(s), 1924(vs), 1840(vs), 1469(w), 1412(vw), 1370(vw), 1356(vw), 1225(vw), 1119(m), 1031(w), 967(vw), 930(vw), 910(vw), 858(vw), 822(vw), 636(vw), 576(w), 527(w), 490(vw), and 477(w) cm^{-1} . Anal. Calc. for $C_{10}H_{14}BN_3O_2W$: N, 10.43; C, 29.81; H, 3.50. Found: N, 10.39; C, 30.46; H, 3.56%.

3.3.3. $[N(CH_3)_4]_2[Mo(\eta^3-C_3H_5)(CO)_2(NCBH_3)_3] \cdot 1/2DME$ (**3**)

In a dry box, 355.0 mg (1.0 mmol) of $Mo(\eta^3-C_3H_5)(CO)_2(NCCH_3)_2Br$ and 189.1 mg (3.0 mmol) of $NaBH_3CN$ were added into a 50-mL flask. The flask was evacuated and about 20 mL of CH_3CN was transferred into the flask. After stirring for 8 h, a 220.1 mg (2.0 mmol) of $N(CH_3)_4Cl$ was added to the system and the solution was continued to stir for additional 6 h. The salts were removed by filtration and the solvent was removed under vacuum. The resulting yellow solids were washed with 20 mL of DME several times until the yellow color disappeared. The DME solution was collected and the solvent was removed. The resulting yellow solids were crystallized through a hexane/DME mixed solution. A 344.0 mg (68% yield) of yellow crystals were isolated. ^{11}B NMR (DME): δ -42.30 ppm (q, $J_{B-H} = 93$ Hz). 1H NMR (CD_3CN): δ 3.69 (m, 1H, CH), 3.44 (s, 2H, DME), 3.27 (s, 3H, DME), 3.21 (d, $J_{H-H} = 6.6$ Hz, 2H, H_{syn}), 3.07 (s, 24H, CH_3), 1.11 (d, $J_{H-H} = 8.4$ Hz, 2H, H_{anti}), and 0.30 ppm (q, br, 3H, BH_3). IR(KBr): 3077(vw), 3035(vw), 2979(vw), 2962(vw), 2932(vw), 2904(vw), 2820(vw), 2346(br, s), 2197(m), 1943(vs), 1846(vs), 1484(m), 1466(w), 1459(w), 1261(vw), 1233(vw), 1190(w), 1122(m), 1086(w), 1028(w), 950(m), 934(w), 859(vw), 798(w), 638(vw), 610(vw), 580(vw), 566(vw), 518(vw), 494(vw), and 470(vw) cm^{-1} . Anal. Calc. for $C_{18}H_{43}B_3MoN_5O_3$: N, 13.85; C, 42.73; H, 8.57. Found: N, 13.77; C, 42.81; H, 8.52%.

3.3.4. $[N(CH_3)_4]_2[W(\eta^3-C_3H_5)(CO)_2(NCBH_3)_3] \cdot 1/2DME$ (**4**)

Similar procedure has been used to prepare compound **4** through the reaction of $W(\eta^3-C_3H_5)(CO)_2(NCCH_3)_2Br$ (443.0 mg, 1.0 mmol) with $NaBH_3CN$ (190.7 mg, 3.0 mmol) for 19 h, and followed by a metathesis of the $[Na]^+$ cation by adding $N(CH_3)_4Cl$ (218 mg, 2.0 mmol). A 398.0 mg (67% yield) of yellow crystals was isolated through a hexane/DME mixed solution. ^{11}B NMR (DME): δ -43.30 ppm (q, $J_{B-H} = 93$ Hz). 1H NMR (CD_3CN): δ 3.39 (s, 2H, DME), 3.25 (s, 3H, DME), 3.08 (s, 24H, CH_3), 3.00 (d, $J_{H-H} = 6.6$ Hz, 2H, H_{syn}), 2.88 (m, 1H, CH), 1.26 (d, $J_{H-H} = 8.4$ Hz, 2H, H_{anti}), and 0.33 ppm (q, br, 3H, BH_3). IR(KBr): 3067(vw), 3035(vw), 2981(vw), 2932(vw), 2903(vw), 2820(vw), 2347(s), 2197(m), 1935(vs, br), 1833(vs), 1484(s), 1468(w), 1460(w), 1450(vw), 1420(vw), 1288(vw), 1262(vw), 1227(vw), 1189(vw), 1121(m), 1028(w), 950(m), 934(w), 857(vw), 806(vw), 637(vw), 577(vw), 530(w), 494(vw), and 481(w)

cm^{-1} . Anal. Calc. for $C_{18}H_{43}B_3N_5O_3W$: N, 11.80; C, 36.04; H, 7.29. Found: N, 11.72; C, 36.17; H, 7.34%.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 290266 (compound **1**), 290267 (compound **2**), 290268 (compound **3**), 290269 (compound **4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.031.

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