

Syntheses, structures, and dynamic properties of $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{NCBH}_3)$ ($M = \text{Mo}, \text{W}$; $\text{L-L} = \text{dppe}, \text{bipy}, \text{en}$)

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Abstract

Compounds $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{NCBH}_3)$ ($\text{L-L} = \text{dppe}$, $M = \text{Mo}(1), \text{W}(2)$; $\text{L-L} = \text{bipy}$, $M = \text{Mo}(3), \text{W}(4)$; $\text{L-L} = \text{en}$, $M = \text{Mo}(5), \text{W}(6)$) were prepared and characterized. The single crystal X-ray analyses of **2–6** revealed that the cyanotrihydroborate anion bonds to the metal through a nitrogen atom, the open face of the allyl group being pointed toward the two carbonyls (*endo*-isomer). In compounds **2**, **5**, and **6**, the two donor atoms of the bidentate ligand occupy equatorial and axial positions, respectively. In the solid state structures of compounds **3** and **4** both nitrogen atoms of the bipy ligand occupy equatorial positions. The NMR spectroscopy reveals a fluxional behavior of compounds **1**, **2**, **5**, and **6** in solution. Although the fluxional behavior of compounds **5** and **6** ceased at about -40°C , that of compound **1** could not be stopped even at -90°C . Their low temperature conformations are consistent with their solid state structures. Both the *endo*- and *exo*-isomers coexist in solution for compounds **3** and **4**.

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Keywords: Allyl complex; Cyanotrihydroborate; Dynamic; Ethylenediamine

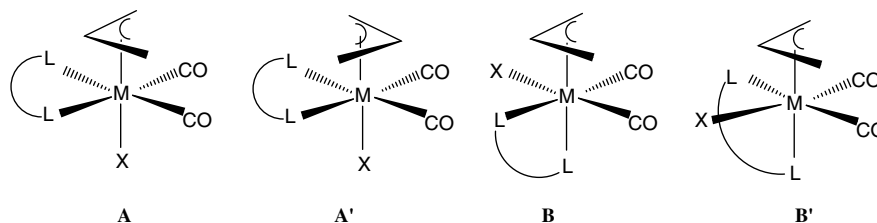
1. Introduction

There is a large number of group 6 bidentate allylic complexes of general formula $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{X})$ ($M = \text{Mo}, \text{W}$; $\text{L-L} = \text{bidentate ligand}$; $\text{X} = \text{anionic monodentate ligand}$) [1]. The interest in this type of complexes encompasses their conformational [2] and dynamic behavior [3–5], as well as allylic alkylation [6] and their possible catalytic properties [5,7]. It was noted that when L-L is a rigid bidentate ligand, the complex possesses conformation **A** (see Scheme 1) in the solid state and exhibits no fluxional behavior in solution [8]. When L-L is a nonrigid bidentate ligand, the complex possesses conformation **B** (**B'**) in the solid state and exhibits a fluxional behavior in solution [1c,9]. However, their conformations are also affected by

the anionic ligand X^- [2b,6], therefore many exceptions to the above observation can be found in the literature [3,5,10].

In our previous work, we have compared the bonding interaction of cyanotrihydroborate and acetonitrile ligands in their group 6 allyl-containing metal complexes [11]. Our results suggested that the cyanotrihydroborate anion is a weak coordinating ligand displaying a similar, albeit a slightly stronger interaction with the metal, than acetonitrile. Although many compounds of the general formula $M(\text{CO})_2(\eta^3\text{-allyl})(\text{L-L})(\text{X})$ have been reported, to the best of our knowledge, the cyanotrihydroborate anion has never been utilized as X in this type of complexes. The cationic complexes $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{NCCH}_3)]^+$ ($\text{L-L} = \text{dppe}, \text{bipy}$), having been reported recently [3], the comparison of properties of the acetonitrile- and cyanotrihydroborate-containing complexes can be extended further. We have examined the cyanotrihydroborate complexes containing three different bidentate ligands, namely,

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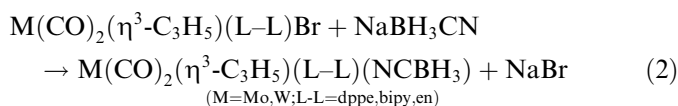
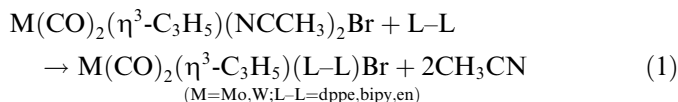
Scheme 1.

1,2-bis(diphenylphosphino)ethane (dppe), 2,2'-bipyridine (bipy) and 1,2-ethylenediamine (en). The bidentate ligands dppe and bipy are routinely found in this type of complexes; however, only rare examples of the en-containing compounds $M(\text{CO})_2(\eta^3\text{-allyl})(\text{en})(\text{X})$ ($M = \text{Mo}, \text{W}$, allyl = C_3H_5 , MeC_3H_4) have been reported [12].

2. Results and discussion

2.1. Preparations and properties of $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{NCBH}_3)$ ($\text{L-L} = \text{dppe}$, $M = \text{Mo}(1)$, $\text{W}(2)$; $\text{L-L} = \text{bipy}$, $M = \text{Mo}(3)$, $\text{W}(4)$; $\text{L-L} = \text{en}$, $M = \text{Mo}(5)$, $\text{W}(6)$)

The cyanotrihydroborate complexes $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{NCBH}_3)$ ($\text{L-L} = \text{dppe}$, $M = \text{Mo}(1)$, $\text{W}(2)$; $\text{L-L} = \text{bipy}$, $M = \text{Mo}(3)$, $\text{W}(4)$; $\text{L-L} = \text{en}$, $M = \text{Mo}(5)$, $\text{W}(6)$) were prepared in a two-step sequence including the reaction of $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{NCCH}_3)_2\text{Br}$ ($M = \text{Mo}, \text{W}$) with a bidentate ligand L-L ($\text{L-L} = 1,2\text{-bis(diphenylphosphino)ethane}$, dppe; 2,2'-bipyridine, bipy; 1,2-ethylenediamine, en) followed by a metathesis of the $[\text{Br}]^-$ ligand with $[\text{NCBH}_3]^-$ as shown in Eqs. (1) and (2). Compounds **1** and **2** decompose on short exposure to air. In contrast, a week-long exposure of compounds **3–6** to air resulted in no noticeable decomposition. However, as observed from their ^{11}B NMR spectra, compounds **3** and **4** decompose in CH_3CN and acetone, while compounds **5** and **6** decompose in CH_3CN , methanol, and acetone.



2.2. X-ray studies

The molecular structures of **2–6** were determined by single crystal X-ray diffraction analyses; crystallographic data and selected bond distances and angles are summarized in Tables 1–4. The molecular structures of **2**, **4**, and **6** are provided in Figs. 1–3. Those for compounds **3** and **5** are included in the supporting information due to their similarity to the structures of compounds **4** and **6**. Each com-

pound possesses a *pseudo*-octahedral structure, with the central atom being surrounded by an allyl group, two carbonyls, a cyanotrihydroborate anion, and a bidentate ligand L-L (L-L : dppe, bipy, en). Both carbonyls are equatorial and *cis*- to each other. The allyl ligand occupies an axial position, with its open face pointing towards the carbonyls (*endo*-isomer). The structures of bipy compounds **3** and **4** are represented by conformation **A**, where the bipy ligand is *trans*- to the carbonyls, while those of compounds **2**, **5**, and **6** are represented by conformation **B** (and its mirror image **B'**), where the bidentate ligand occupies both an axial and an equatorial positions *trans*- to the allyl group and a carbonyl, respectively. It is worth noting that the molecular structures of dppe compound **2** and $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{dppe})(\text{NCCH}_3)]^+$ [3] possess the same conformation **B**, while the bipy compounds **3** and **4**, on the one hand, and $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})(\text{NCCH}_3)]^+$ [3], on the other hand, adopt conformations **A** and **B**, respectively. Our previous study suggested that electronic properties of the acetonitrile ligand are only slightly different from those of its isoelectronic analog, cyanotrihydroborate ligand. Nevertheless, this subtle electronic difference resulted in a change of the preferred structure.

Tables 2–4 list the selected bond distances and bond angles of **2–6**, respectively. The cyanotrihydroborate anion is bonded to the metal through a nitrogen atom. The corresponding M-N bond distances fall into the range of 2.144(3)–2.2107(14) Å. Compared with those found in **3** and **4**, where the cyanotrihydroborate ligand is *trans*- to an allyl group, longer M-N distances were observed in **2**, **5**, and **6**, where it is *trans*- to a carbonyl. These M-NCBH_3 distances of **2–4** are slightly shorter than those found for the isoelectronic compounds $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{NCCH}_3)]^+$ ($\text{L-L} = \text{dppe}$, 2.233(5) Å, $\text{L-L} = \text{bipy}$, 2.197(3) Å) [3]. This is consistent with our previous observation that the cyanotrihydroborate anion displays a slightly stronger interaction with a metal than acetonitrile [11]. The C-C-C allyl angles fall within the range of 114.8(4)–116.4(3)°, which is consistent with other allyl compounds [8,13]. The C-O bond distances of the tungsten compounds **4** and **6** are slightly longer than those of their molybdenum analogs **3** and **5**, reflecting the electron rich nature of the third row transition metal [14]. For the carbonyl ligand *trans*- to a weak π -acceptor ligand (cyanotrihydroborate in **2**), or a good σ -donor ligand (en in **5** and **6**) the C-O bond distance is slightly longer, and M-CO bond distance is slightly shorter than for the

Table 1

Crystallographic data for $W(CO)_2(\eta^3-C_3H_5)(dppe)(NCBH_3)$ (**2**), $Mo(CO)_2(\eta^3-C_3H_5)(bipy)(NCBH_3)$ (**3**), $W(CO)_2(\eta^3-C_3H_5)(bipy)(NCBH_3)$ (**4**), $Mo(CO)_2(\eta^3-C_3H_5)(en)(NCBH_3)$ (**5**), and $W(CO)_2(\eta^3-C_3H_5)(en)(NCBH_3)$ (**6**)

Empirical formula	$C_{32}H_{32}BN_2O_2P_2W$	$C_{18}H_{16}BMoN_3O_2$	$C_{16}H_{16}BN_3O_2W$	$C_8H_{16}BMoN_3O_2$	$C_8H_{16}BN_3O_2W$
Formula weight	719.19	413.09	476.98	292.99	380.90
<i>T</i> (K)	150(1) K	150(1)	150(1)	150(1)	150(1)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$	$C2/c$	$C2/c$
<i>a</i> (Å)	8.2886(6)	8.4094(5)	8.3305(1)	22.9600(8)	22.9047(3)
<i>b</i> (Å)	12.1431(8)	10.1503(6)	10.2364(1)	6.4545(2)	6.4328(1)
<i>c</i> (Å)	15.1970(10)	19.6128(13)	19.5605(3)	16.2120(5)	16.1151(2)
α (°)	91.998(1)				
β (°)	92.177(1)	90.438(1)	90.8600(8)	96.024(1)	96.4307(9)
γ (°)	106.967(1)				
<i>V</i> (Å ³)	1460.24(17)	1674.06(18)	1667.82(4)	2389.28(13)	2359.48(6)
<i>Z</i>	2	4	4	8	8
ρ_{calc} (g/cm ³)	1.636	1.639	1.900	1.629	2.145
Crystal size (mm)	0.28 × 0.25 × 0.25	0.45 × 0.30 × 0.20	0.23 × 0.15 × 0.15	0.30 × 0.25 × 0.10	0.45 × 0.30 × 0.30
Radiation (λ , Å)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
2 θ Limits (°)	1.34–27.50	2.08–27.50	2.08–27.50	1.78–27.50	2.08–27.50
Index ranges	–10 ≤ <i>h</i> ≤ 10 –15 ≤ <i>k</i> ≤ 15 –19 ≤ <i>l</i> ≤ 19	–10 ≤ <i>h</i> ≤ 10 –12 ≤ <i>k</i> ≤ 13 –25 ≤ <i>l</i> ≤ 25	–10 ≤ <i>h</i> ≤ 10 –13 ≤ <i>k</i> ≤ 13 –25 ≤ <i>l</i> ≤ 25	–29 ≤ <i>h</i> ≤ 29 –8 ≤ <i>k</i> ≤ 8 –21 ≤ <i>l</i> ≤ 21	–29 ≤ <i>h</i> ≤ 29 –8 ≤ <i>k</i> ≤ 8 –20 ≤ <i>l</i> ≤ 20
Reflections collected	19,312	16,156	19,714	15,068	12,613
Unique reflections	6678	3834	3834	2759	2721
Unique reflections [<i>I</i> > 2.0 σ (<i>I</i>)]	712	832	912	1184	1440
Completeness to θ (%)	99.6	99.8	99.9	100.0	99.9
μ (mm ^{–1})	4.095	0.800	6.937	1.082	1.041
Maximum/minimum transmission	0.4275, 0.3935	0.8564, 0.7148	0.377, 0.218	0.8995, 0.7372	0.167, 0.095
Data/restraints/parameters	6678/0/361	3834/0/217	3834/0/210	2759/0/165	32721/0/138
R_1^a [<i>I</i> > 2.0 σ (<i>I</i>)]	0.0225	0.0285	0.0250	0.0188	0.0260
wR_2^b (all data)	0.0633	0.0705	0.0533	0.0483	0.0711
R_{int}	0.0314	0.0288	0.0513	0.0233	0.0668
Goodness-of-fit on F^2	1.104	1.073	1.009	1.096	1.041

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

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

Table 2

Selected bond distances (Å) and bond angles (°) for $W(CO)_2(\eta^3-C_3H_5)(dppe)(NCBH_3)$ (**2**)

<i>Bond lengths</i>			
W–C(1)	1.949(3)	O(1)–C(1)	1.173(4)
W–C(2)	1.975(3)	O(2)–C(2)	1.155(4)
W–N(1)	2.187(3)	N(1)–C(6)	1.155(4)
W–P(1)	2.5287(8)	B(1)–C(6)	1.580(5)
W–P(2)	2.5780(8)		
<i>Angles</i>			
C(1)–W–C(2)	79.75(13)	C(15)–P(1)–W	121.18(11)
C(1)–W–N(1)	174.74(12)	C(7)–P(1)–W	109.36(10)
C(2)–W–N(1)	97.26(12)	C(27)–P(2)–W	111.72(11)
C(1)–W–P(1)	94.43(10)	C(21)–P(2)–W	122.54(11)
C(2)–W–P(1)	85.81(10)	C(8)–P(2)–W	107.56(11)
N(1)–W–P(1)	80.99(7)	C(6)–N(1)–W	178.2(3)
C(1)–W–P(2)	99.43(10)	O(1)–C(1)–W	176.1(3)
C(2)–W–P(2)	163.41(10)	O(2)–C(2)–W	175.2(3)
N(1)–W–P(2)	82.19(7)	C(3)–C(4)–C(5)	116.4(3)
P(1)–W–P(2)	77.71(3)	N(1)–C(6)–B(1)	176.4(4)
C(9)–P(1)–W	113.79(11)		

other carbonyl. The bidentate biting angles L–M–L are ligand-dependent. The rigid ligand displays a smaller biting angle. Thus the L–M–L biting angles in **3** (72.84(6)°) and **4** (72.98(10)°) are smaller than those in **2**

(77.71(3)°), **5** (75.29(5)°), and **6** (75.17(12)°). All these values fall into the range reported in the literature [3,15].

2.3. Infrared studies

Table 5 presents selected infrared data of compounds **1–6** and $[N(CH_3)_4][NCBH_3]$. Appearance of the ν_{BH} absorption band for each compound between 2329 and 2348 cm^{-1} and that of the ν_{CN} absorption band between 2184 and 2196 cm^{-1} are consistent with a M–NCBH₃-bonded complex [16]. Two carbonyl absorption bands are observed for each compound. Since tungsten is an electron-rich third row transition metal [14], the C≡O absorption bands of its complexes are found at lower frequencies than those of related Mo complexes. This is consistent with their solid state structures, where longer C≡O bond distances are observed for the tungsten complexes. The infrared spectroscopy is a useful tool to differentiate the bonding modes of the carbonyl ligand. In general, the terminal M–CO carbonyl absorption occurs in the range of 1850–2120 cm^{-1} , whereas the bridging carbonyl absorption falls into the range of 1700–1860 cm^{-1} [17]. This general rule could not be applied to compounds **5** and **6**. As observed in Table 5, one of the C≡O absorptions

Table 3

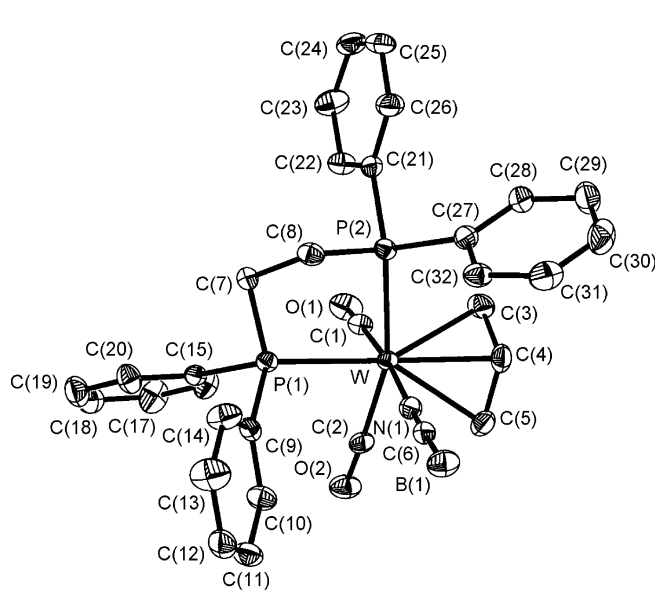
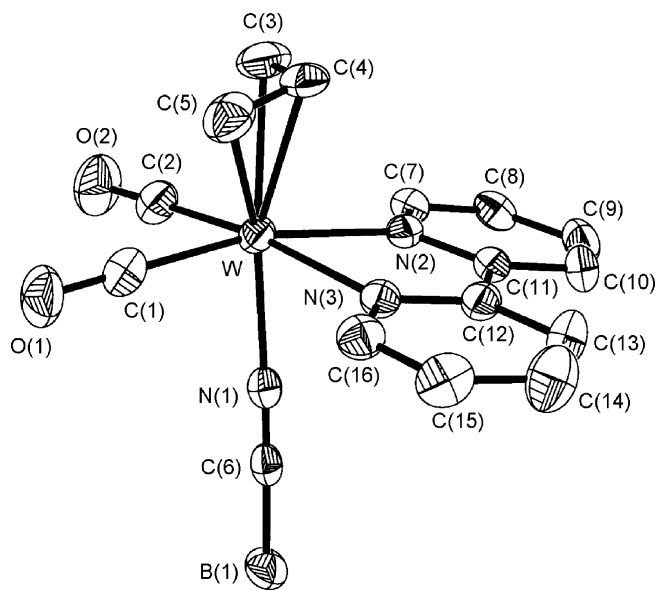
Selected bond distances (Å) and bond angles (°) for Mo(CO)₂(η³-C₃H₅)(bipy)(NCBH₃) (3) and W(CO)₂(η³-C₃H₅)(bipy)(NCBH₃) (4)

	3	4		3	4
M–C(1)	1.970(2)	1.958(4)	M–C(2)	1.971(2)	1.970(4)
M–N(2)	2.2392(17)	2.223(3)	M–N(1)	2.1702(19)	2.144(3)
O(1)–C(1)	1.149(3)	1.166(4)	M–N(3)	2.2387(17)	2.228(3)
N(1)–C(6)	1.114(3)	1.139(4)	O(2)–C(2)	1.151(3)	1.155(4)
B(1)–C(6)	1.595(4)	1.583(5)			
C(1)–M–C(2)	78.75(10)	78.75(15)	C(1)–M–N(3)	104.04(8)	102.16(13)
C(2)–M–N(3)	167.73(8)	170.71(12)	C(1)–M–N(1)	89.42(9)	88.29(12)
C(2)–M–N(1)	88.03(8)	89.71(13)	N(3)–M–N(1)	80.10(6)	81.09(10)
C(1)–M–N(2)	171.28(9)	167.26(12)	C(2)–M–N(2)	102.60(8)	104.14(12)
N(3)–M–N(2)	72.84(6)	72.98(10)	N(1)–M–N(2)	82.04(6)	79.37(10)
C(6)–N(1)–M	175.82(17)	176.2(3)	O(1)–C(1)–M	176.1(2)	178.2(3)
O(2)–C(2)–M	177.5(2)	176.5(3)	C(5)–C(4)–C(3)	116.1(3)	115.7(4)
N(1)–C(6)–B(1)	178.6(2)	178.4(3)			

Table 4

Selected bond distances (Å) and bond angles (°) for Mo(CO)₂(η³-C₃H₅)(en)(NCBH₃) (5) and W(CO)₂(η³-C₃H₅)(en)(NCBH₃) (6)

	5	6		5	6
M–C(1)	1.9432(16)	1.946(4)	M–C(2)	1.9604(16)	1.964(4)
M–N(1)	2.2448(14)	2.238(4)	M–N(2)	2.2945(13)	2.282(4)
M–N(3)	2.2107(14)	2.195(3)	O(1)–C(1)	1.159(2)	1.172(5)
O(2)–C(2)	1.152(2)	1.162(5)	N(1)–C(6)	1.495(4)	1.496(7)
N(1)–C(6')	1.484(6)		N(2)–C(7)	1.499(4)	1.477(6)
N(2)–C(7')	1.453(6)		C(6)–C(7)	1.499(7)	1.445(8)
N(3)–C(8)	1.138(2)	1.147(5)	C(6')–C(7')	1.487(11)	
C(8)–B(1)	1.581(3)	1.580(6)			
C(1)–M–C(2)	77.99(6)	77.88(16)	C(1)–M–N(3)	98.84(6)	99.31(15)
C(2)–M–N(3)	170.30(6)	170.15(16)	C(1)–M–N(1)	92.04(6)	92.08(15)
C(2)–M–N(1)	91.32(6)	91.55(16)	N(3)–M–N(1)	79.57(5)	79.06(14)
C(1)–M–N(2)	166.85(6)	166.59(14)	C(2)–M–N(2)	98.46(6)	98.00(14)
N(3)–M–N(2)	82.55(5)	82.57(13)	N(1)–M–N(2)	75.29(5)	75.17(12)
C(8)–N(3)–M	176.11(14)	174.7(3)	O(1)–C(1)–M	175.90(14)	176.4(3)
O(2)–C(2)–M	174.49(13)	174.6(3)	C(5)–C(4)–C(3)	115.61(16)	114.8(4)
N(3)–C(8)–B(1)	178.69(19)	179.1(5)			

Fig. 1. Molecular structure of W(CO)₂(η³-C₃H₅)(dppe)(NCBH₃) (2) showing 50% probability thermal ellipsoids.Fig. 2. Molecular structure of W(CO)₂(η³-C₃H₅)(bipy)(NCBH₃) (4) showing 50% probability thermal ellipsoids.

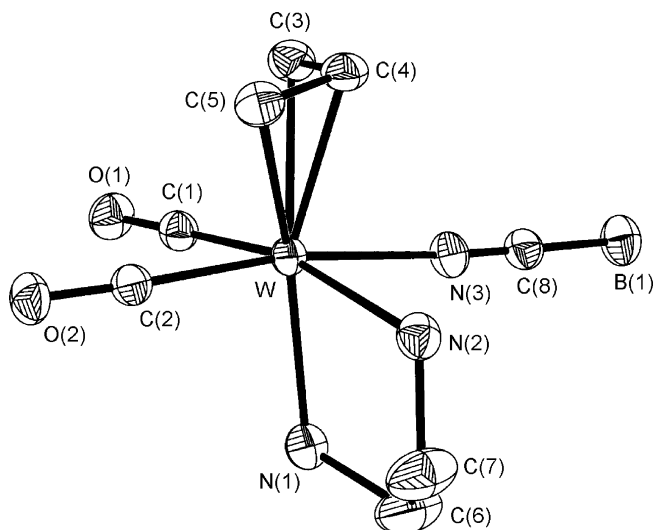


Fig. 3. Molecular structure of $W(CO)_2(\eta^3-C_3H_5)(en)(NCBH_3)$ (**6**) showing 50% probability thermal ellipsoids.

(1800 cm^{-1} for **5** and 1781 cm^{-1} for **6**) is significantly below the range generally accepted for the terminal carbonyl. This result may be attributed to the asymmetric coordination of the en ligand, which is a good σ -donor but a poor π -acceptor. The carbonyl *trans*- to the nitrogen atom of the en ligand displays a significant π -back bonding effect, resulting in a weaker absorption band. In DME solution, where fast conformational exchange takes place (*vide infra*), this carbonyl absorption band displays a significant blue shift of about 50 cm^{-1} , accompanied by a slight red shift of the other $C\equiv O$ absorption band for each compound.

2.4. NMR studies

The ^{11}B NMR signals of compounds **1–6** appear in the range of -42.9 to -44.2 ppm as broad quartets ($J_{B-H} = 90$ Hz). This is very close to the signals of $NaBH_3CN$ (-43.5 ppm, $J_{B-H} = 89$ Hz) [18] and other N-bonded cyanotrihydroborate compounds [11,16a,16b,19].

The 1H NMR spectra of compounds **1** and **2** are relatively simple. The allyl ligand hydrogens of compound **1** appear at 1.97 (H_a), 3.66 (H_s), and 3.80 (H_c) ppm. Two broad signals at 2.32 and 2.77 ppm assigned to the methylene groups of dppe correspond to two different kinds of

environment [9] relative to the cyanotrihydroborate ligand. Except for the signal of H_c , which overlaps with one of the broad signals of the dppe backbone, compound **2** displays the same pattern in its 1H NMR spectrum. Such a simple proton NMR pattern is consistent with the fluxional behavior of a typical $M(CO)_2(\eta^3-C_3H_5)(P-P)(X)$ species, for which only an averaged spectrum was observed [1c,5,9]. This is also observed in the room temperature ^{31}P NMR spectra of **1** and **2**, each of them displaying only a sharp singlet at 52.2 and 37.1 ppm, respectively. These chemical shifts are consistent with those reported for $Mo(CO)_2(\eta^3-C_3H_5)(dppe)Cl$ (53.2 ppm) [9] and $W(CO)_2(\eta^3-C_7H_7)(dppe)Cl$ (36 ppm) [12b]. The fluxional behavior of **1** was studied by the variable-temperature ^{31}P NMR. As shown in Fig. 4, the signal at 52.2 ppm became broad as the temperature was lowered, and collapsed at about $-60\text{ }^\circ C$. Upon further temperature decrease it reappeared gradually and eventually split into three broad signals at 47.1, 48.0, and 65.9 ppm in the ratio of 1:1:0.4 at $-90\text{ }^\circ C$. The variable-temperature 1H NMR spectra of **1** were also acquired; however, several broad signals were observed at $-90\text{ }^\circ C$. A trigonal twist rearrangement has been proposed

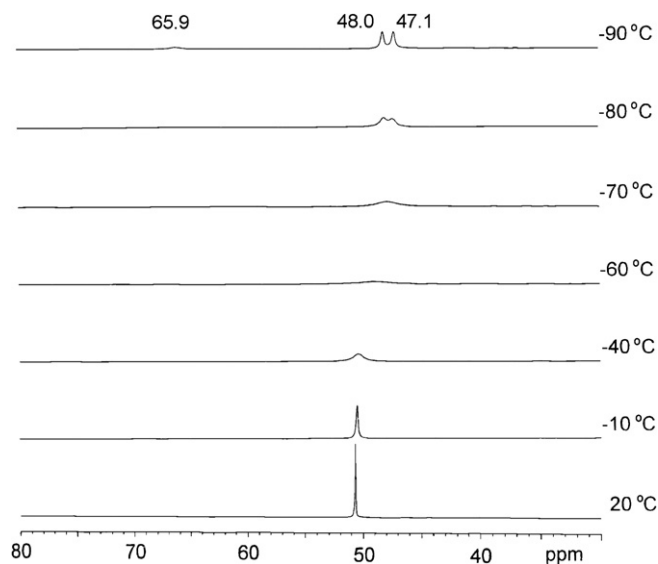


Fig. 4. Variable temperature ^{31}P NMR spectra of $Mo(CO)_2(\eta^3-C_3H_5)(dppe)(NCBH_3)$ (**1**).

Table 5

Selected Infrared data of compounds [$Mo(CO)_2(\eta^3-C_3H_5)(dppe)(NCBH_3)$] (**1**), [$W(CO)_2(\eta^3-C_3H_5)(dppe)(NCBH_3)$] (**2**), [$Mo(CO)_2(\eta^3-C_3H_5)(bipy)(NCBH_3)$] (**3**), [$W(CO)_2(\eta^3-C_3H_5)(bipy)(NCBH_3)$] (**4**), [$Mo(CO)_2(\eta^3-C_3H_5)(en)(NCBH_3)$] (**5**), [$W(CO)_2(\eta^3-C_3H_5)(en)(NCBH_3)$] (**6**), and [$N(CH_3)_4][NCBH_3]$]

Compounds	ν_{CO}	ν_{CN}	ν_{BH} (cm^{-1})				
1	1945(vs)	1863(vs)	2204(vw)	2184(m)	2329(m)	2277(vw)	1114(m)
2	1933(vs)	1844(vs)	2203(vw)	2185(m)	2338(m)	2267(vw)	1114(m)
3	1945(vs)	1861(vs)	2215(vw)	2194(m)	2347(m)	2301(w)	1117(m)
4	1935(vs)	1846(vs)	2214(vw)	2194(m)	2348(m)	2294(vw)	1118(m)
5	1944(vs)	1800(vs)	2218(vw)	2196(s)	2344(s)	2266(m)	1113(s)
6	1937(vs)	1781(vs)	2218(vw)	2194(m)	2346(m)	2260(vw)	1110(s)
[$N(CH_3)_4][NCBH_3]$			2230(w)	2172(s)	2339(s)	2301(s, sh)	1132(m)

[12b] for this type of compound. The mechanism involves rotation of the triangular face formed by the cyanotrihydroborate and two phosphorus atoms with respect to the face formed by the allyl and two carbonyls. Both the ^{31}P and ^1H NMR spectroscopy observations suggest a fast rotation to occur at room temperature. The rearrangement involves three isomers: **A**, **B**, and **B'**. It is possible that the broad signal at 65.9 ppm is due to conformation **A**, where both phosphorous atoms are in the equatorial positions. The two phosphorous atoms in **B**, and **B'** are in different environments; however, since the ^{31}P NMR is not able to distinguish these two isomers, they display the same chemical shifts. Thus, at low temperature the asymmetric conformations consistent with the solid state structures of compounds predominate. The low temperature NMR study has also suggested compound $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)\text{-}(\text{dppe})(\text{X})$ ($\text{X} = \text{halide}$) [9] to exist as conformation **B** (**B'**).

For compound **3** two isomers coexist in solution in a 3:2 ratio. Their NMR signals were assigned through $^1\text{H}\text{-}^1\text{H}$ COSY and $^1\text{H}\text{-}^{13}\text{C}$ HMQC 2D NMR studies. As three allyl group signals were found for each isomer, these isomers were assigned to **A** and **A'**. A recent theoretical calculation has suggested conformations **A** and **A'** of $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})(\text{NCCCH}_3)]^+$ to be in equilibrium in solution [3]. The structure of the only isomer found for compound **4** has been assigned to conformation **A**.

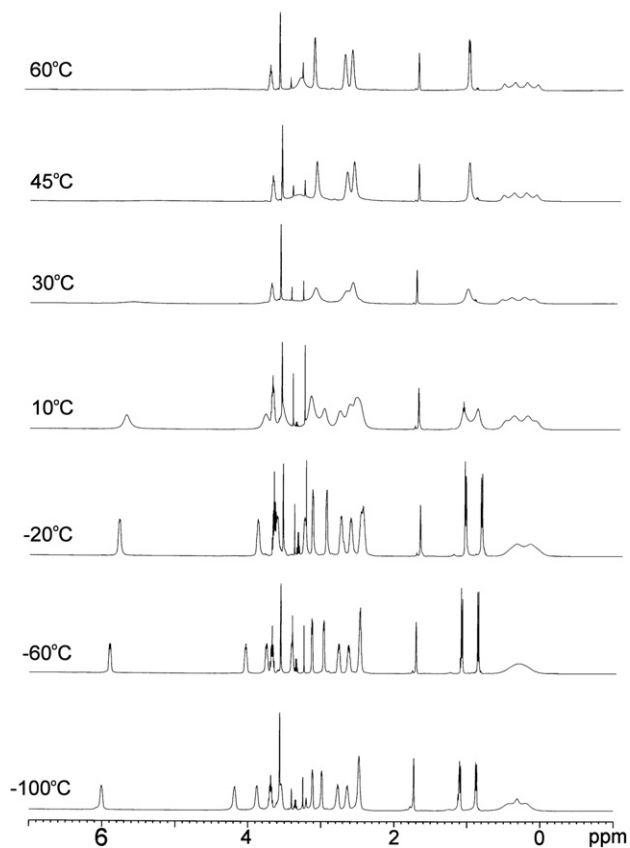


Fig. 5. Variable temperature ^1H NMR spectra of $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{NCBH}_3)$ (**5**).

The ^1H NMR spectra of **5** and **6** display broad signals at room temperature. Their assignments are based on the $^1\text{H}\text{-}^1\text{H}$ COSY and $^1\text{H}\text{-}^{13}\text{C}$ HMQC 2D NMR studies at -40°C . In solution, both compounds adopt asymmetric conformation **B** (**B'**) at low temperature, which is consistent with their solid state structures. The variable-temperature ^1H NMR spectra of **5** are shown in Fig. 5. A static state is obtained at about -40°C . As the temperature increased, the signals broadened at first and collapsed later at about 30°C . As the temperature increased further, the signals sharpened; however, a fast rotation has not been reached yet at 60°C . Compared with the fluxional behavior observed for **1**, the rotation energy barriers for these two compounds containing en ligand are higher.

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, and solvents were dried and freshly distilled prior to use. $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{CH}_3\text{CN})_2\text{Br}$ and $\text{W}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{CH}_3\text{CN})_2\text{Br}$ were prepared by the literature procedures [20]. Elemental analyses were recorded on a Hitachi 270-30 spectrometer. Proton spectra ($\delta(\text{TMS}) = 0.00$ ppm) were recorded either on a Bruker Avance DPX300 or a Varian Unity Inova 600 spectrometer operating at 300.130 and 599.948 MHz, respectively. ^{11}B spectra (externally referenced to $\text{BF}_3 \cdot \text{OEt}_2$ ($\delta 0.00$ ppm)) were recorded on the same instruments operating at 96.293 and 192.481 MHz, respectively. 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 **2–6** were mounted and sealed inside glass capillaries under nitrogen. Crystallographic data collections were carried out on a Nonius KappaCCD diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 150(1) K. Unit cell parameters were retrieved and refined using DENZO-SMN [21] software on all reflections. Data reduction was performed with the DENZO-SMN [21] software. An empirical absorption was based on the symmetry-equivalent reflections and was applied to the data using SORTAV [22] program. The structure was solved using the SHELXS-97 [23] program and refined using SHELXL-97 [24] 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 **2** were located and refined isotropically and other hydrogen atoms were fixed at calculated positions and refined using a riding mode. Crystallographic data of **2–6** are summarized in Tables 1–4.

3.3. Preparation of complexes

3.3.1. $Mo(CO)_2(\eta^3-C_3H_5)(dppe)(NCBH_3)$ (**1**)

$Mo(CO)_2(\eta^3-C_3H_5)(NCCH_3)_2Br$ (360.2 mg, 1.00 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (402.5 mg, 1.01 mmol) were placed in a 50 mL flask. After degassing, about 25 mL of CH_2Cl_2 was transferred into the flask at $-78^\circ C$. The system was warmed to room temperature and stirred for 2 h resulting in a red solution. A solution of sodium cyanotrihydroborate (63.1 mg, 1.00 mmol) in 3.0 mL of methanol was added dropwise to the red solution. The reaction mixture was stirred for additional 9 h changing color to orange-red with precipitation. The solvent was removed under a dynamic vacuum, and the resulting orange-red solid was extracted several times with 20.0 mL portions of CH_2Cl_2 . The CH_2Cl_2 extracts were combined and stripped off the solvent *in vacuo*. The resulting red solid was dissolved in CH_2Cl_2 and layered with CH_3OH for crystallization. The product was isolated as orange-red crystals (520.3 mg, 82.4%). ^{11}B NMR (CH_2Cl_2): δ -43.6 ppm (br, q, $J_{B-H} = 90$ Hz). ^{31}P NMR (CH_2Cl_2): δ 52.2 ppm (s). 1H NMR ($CDCl_3$): δ 7.36 – 7.79 (m, 20H, Ph), 3.80 (m, 1H, H_c), 3.66 (br, m, 2H, H_s), 2.77 (m, 2H, PCH_2CH_2P), 2.32 (m, 2H, PCH_2CH_2P), 1.97 (d, $J_{H-H} = 10.8$ Hz, 2H, H_a), and 0.29 ppm (br, 3H, BH_3). ^{13}C NMR ($CDCl_3$): δ 223.22 (CO), 133.16 , 132.11 , 131.20 , 130.83 , 129.10 (C_6H_5), 87.11 (C_c), 60.08 (C_i), 26.50 , and 26.27 ppm (PCH_2CH_2P). IR (KBr): 3079 (vw), 3059 (w), 3023 (vw), 3002 (vw), 2968 (vw), 2923 (vw), 2329 (m), 2277 (vw), 2204 (vw), 2184 (m), 1945 (vs), 1863 (vs), 1587 (vw), 1575 (vw), 1483 (m), 1469 (vw), 1459 (vw), 1435 (s), 1410 (w), 1398 (vw), 1389 (vw), 1334 (vw), 1308 (vw), 1261 (vw), 1234 (vw), 1187 (vw), 1163 (vw), 1114 (m), 1071 (m), 1025 (m), 999 (w), 968 (vw), 925 (vw), 874 (w), 853 (vw), 823 (w), 746 (m), 694 (s), 678 (m), 654 (w), 615 (vw), 597 (w), 564 (vw), 529 (s), 515 (m), 481 (m), 462 (w), 446 (vw), 432 (w), and 418 (m) cm^{-1} . Anal. Calc. for $C_{32}H_{32}BNO_2P_2Mo$: N, 2.22; C, 60.88; H, 5.11. Found: N, 2.24; C, 60.67; H, 5.07%.

3.3.2. $W(CO)_2(\eta^3-C_3H_5)(dppe)(NCBH_3)$ (**2**)

A procedure similar to the one described for the preparation of **1** was used. The reaction of $W(CO)_2(\eta^3-C_3H_5)(NCCH_3)_2Br$ (448.0 mg, 1.01 mmol) with 1,2-bis(diphenylphosphino)ethane (400.7 mg, 1.01 mmol) and sodium cyanotrihydroborate (63.1 mg, 1.00 mmol) followed by layering the CH_2Cl_2 solution of the product with methanol produced 562.7 mg (78.2% yield) of **2** as orange-red crystals. ^{11}B NMR (CH_2Cl_2): δ -43.6 ppm (br, q, $J_{B-H} = 86$ Hz). ^{31}P NMR (CH_2Cl_2): δ 37.1 ppm (s, $J_{W-P} = 202$ Hz). 1H NMR ($CDCl_3$): δ 7.38 – 7.82 (m, 20H, Ph), 3.40 (br, s, 2H, H_s), 2.82 (m, 3H, PCH_2CH_2P , H_c), 2.32 (m, 2H, PCH_2CH_2P), 1.89 (d, $J_{H-H} = 9.9$ Hz, 2H, H_a), and 0.29 ppm (br, 3H, BH_3). ^{13}C NMR ($CDCl_3$): δ 213.25 (CO), 133.50 , 133.43 , 131.90 , 130.98 , 130.66 , 129.15 (C_6H_5), 75.74 (C_c), 51.31 (C_i), 27.23 , and 26.70 ppm (PCH_2CH_2P). IR (KBr): 3080 (vw), 3061 (w), 3026 (vw), 3004 (vw), 2990 (vw), 2944 (vw), 2923 (vw), 2338 (m), 2267 (vw), 2203 (vw), 2185 (m), 1933 (vs), 1844 (vs), 1586 (vw), 1574 (vw), 1484 (w),

1435 (s), 1420 (w), 1408 (w), 1396 (vw), 1382 (vw), 1334 (vw), 1309 (vw), 1266 (vw), 1187 (vw), 1158 (vw), 1114 (m), 1097 (m), 1071 (vw), 1027 (vw), 999 (vw), 955 (vw), 872 (vw), 825 (w), 743 (m), 703 (s), 692 (s), 677 (w), 653 (w), 624 (vw), 616 (vw), 598 (vw), 568 (vw), 544 (m), 526 (m), 515 (m), 485 (w), 472 (w), 456 (vw), 441 (vw), 431 (w), 423 (w), 418 (vw), 413 (vw), and 401 (w) cm^{-1} . Anal. Calc. for $C_{32}H_{32}BNO_2P_2W$: N, 1.95; C, 53.44; H, 4.48. Found: N, 1.96; C, 53.33; H, 4.45%.

3.3.3. $Mo(CO)_2(\eta^3-C_3H_5)(bipy)(NCBH_3)$ (**3**)

In a dry box, 361.1 mg (1.00 mmol) of $Mo(CO)_2(\eta^3-C_3H_5)(NCCH_3)_2Br$ and 158.3 mg (1.01 mmol) of 2,2'-bipyridine were added into a 50 mL flask. The flask was evacuated and about 25 mL of CH_2Cl_2 was transferred into the flask. After stirring for 1 h a red-purple solution was obtained. A solution of sodium cyanotrihydroborate (62.4 mg, 0.99 mmol) in 3.0 mL of methanol was added dropwise to this red-purple solution. This reaction mixture was stirred for additional 8 h changing color to red with precipitation. The solvent was removed *in vacuo*, and the resulting red solid was extracted several times with 20.0 mL portions of DME. The combined DME extracts were concentrated and layered with hexane for crystallization. The product was isolated as red crystals (253.6 mg, 65% yield). ^{11}B NMR (CH_2Cl_2): δ -44.2 ppm (br, q, $J_{B-H} = 91$ Hz). 1H NMR (CD_2Cl_2): isomer A, δ 8.88 – 7.68 (m, bipy), 3.31 (d, $J_{H-H} = 6.0$ Hz, H_s), 3.11 (m, H_c), 1.60 (d, $J_{H-H} = 9.6$ Hz, H_a), and 0.12 ppm (br, BH_3). isomer B, δ 9.10 – 7.79 (m, bipy), 3.88 (m, H_c), 3.59 (br, H_s), 1.54 (m, H_a), and 0.01 ppm (br, BH_3). ^{13}C NMR (CD_2Cl_2): isomer A, δ 224.08 (CO), 153.66 , 152.34 , 139.45 , 126.62 , 122.62 (bipy), 73.65 (C_c), and 57.41 ppm (C_i). isomer B, 224.08 (CO), 153.66 , 152.32 , 138.53 , 126.82 , 122.73 (bipy), 71.57 (C_c), and 57.41 ppm (C_i). IR (KBr): 3106 (vw), 3081 (vw), 3069 (vw), 3026 (vw), 3004 (vw), 2960 (vw), 2920 (vw), 2856 (vw), 2357 (m), 2347 (m), 2301 (w), 2215 (vw), 2194 (m), 2039 (vw), 2017 (vw), 1945 (vs), 1861 (vs), 1600 (m), 1470 (vw), 1457 (w), 1441 (m), 1424 (w), 1419 (vw), 1364 (vw), 1339 (vw), 1311 (w), 1260 (w), 1248 (vw), 1226 (vw), 1173 (vw), 1151 (vw), 1145 (vw), 1117 (m), 1103 (w), 1072 (w), 1046 (vw), 1024 (w), 865 (vw), 852 (vw), 818 (vw), 802 (w), 760 (s), 733 (m), 669 (vw), 648 (vw), 630 (vw), 603 (vw), 575 (vw), 569 (vw), 555 (vw), 545 (w), 513 (vw), 510 (w), and 504 (vw) cm^{-1} . Anal. Calc. for $C_{16}H_{16}BN_3O_2Mo$: N, 10.80; C, 49.39; H, 4.14. Found: N, 10.60; C, 48.71; H, 4.21%.

3.3.4. $W(CO)_2(\eta^3-C_3H_5)(bipy)(NCBH_3)$ (**4**)

A procedure similar to the one described for the preparation of **3** was used. The reaction of $W(CO)_2(\eta^3-C_3H_5)(NCCH_3)_2Br$ (447.3 mg, 1.00 mmol) with 2,2'-bipyridine (156.6 mg, 1.00 mmol) and $NaBH_3CN$ (62.6 mg, 1.00 mmol) afforded 332.5 mg (70% yield) of red crystals of **4** isolated from a hexane/DME solution. ^{11}B NMR (DME): δ -44.0 ppm (br, q, $J_{B-H} = 91$ Hz). 1H NMR (CD_2Cl_2): δ 8.95 – 7.64 (m, bipy), 3.14 (d, $J_{H-H} = 6.6$ Hz, H_s), 2.27 (m, H_c), 1.86 (d, $J_{H-H} = 8.4$ Hz, H_a), and 0.10 ppm (br, BH_3). ^{13}C NMR (CD_2Cl_2): δ 216.64 (CO),

154.64, 152.69, 139.57, 127.35, 122.93 (bipy), 66.58 (C_c), and 49.39 ppm (C_t). IR (KBr): 3111(vw), 3085(vw), 3058(vw), 2975(vw), 2869(w), 2364(m), 2348(m), 2294(vw), 2214(vw), 2194(m), 1935(vs), 1846(vs), 1635(vw), 1601(m), 1559(vw), 1490(vw), 1469(m), 1442(m), 1418(w), 1383(w), 1311(w), 1281(vw), 1260(vw), 1242(vw), 1222(vw), 1143(m), 1127(m), 1118(m), 1072(w), 1047(w), 1020(w), 821(w), 805(vw), 801(vw), 760(s), 747(w), 734(m), 541(w), 457(w), 445(w), and 426(w) cm^{-1} . Anal. Calc. for $C_{16}H_{16}BN_3O_2W$: N, 8.81; C, 40.29; H, 3.38. Found: N, 8.71; C, 39.95; H, 3.41%.

3.3.5. $Mo(CO)_2(\eta^3-C_3H_5)(en)(NCBH_3)$ (**5**)

In a drybox a solution of 1,2-ethylenediamine (61.2 mg, 1.02 mmol) in 3.0 mL CH_2Cl_2 was added dropwise into a solution of $Mo(CO)_2(\eta^3-C_3H_5)(NCCH_3)_2Br$ (362.4 mg, 1.01 mmol) in 20 mL CH_2Cl_2 . The system was stirred for 2 h furnishing a yellow solution. A solution of sodium cyanotrihydroborate (62.7 mg, 0.99 mmol) in 3.0 mL of methanol was added dropwise to this yellow solution. After stirring for 12 h the solvents were removed under a dynamic vacuum. The resulting yellow solid was extracted several times with 20 mL portions of DME. The extracts were combined, concentrated, and layered with hexane for crystallization. The product was obtained as yellow crystals (182.2 mg, 62%). ^{11}B NMR (DME): δ -42.9 ppm (br, q, $J_{B-H} = 89$ Hz). 1H NMR (d_8 -THF, $-40^\circ C$): δ 5.85 (m, 1H, NH_2), 3.98 (m, 1H, NH_2), 3.70 (m, 2H, NH_2 , H_c), 3.35 (m, 1H, NH_2), 3.16 (m, 1H, H_s), 2.99 (m, 1H, H_s), 2.79 (m, 1H, en), 2.65 (m, 1H, en), 2.50 (m, 2H, en), 1.11 (d, $J_{H-H} = 9.6$ Hz, 1H, H_a), 0.89 (d, $J_{H-H} = 9.6$ Hz, 1H, H_a), and 0.33 ppm (br, q, 3H, BH_3). ^{13}C NMR (d_8 -THF, $-40^\circ C$): δ 226.21, 226.07 (CO), 129.09 (CN), 69.94 (C_c), 56.49, 55.79 (C_t), 44.83, and 43.22 ppm (en). IR (KBr): 3340(m), 3330(m), 3279(m), 3265(m), 3152(vw), 3069(w), 3043(vw), 3006(w), 2990(w), 2976(m), 2954(m), 2920(w), 2893(w), 2344(s), 2266(m), 2240(m), 2218(vw), 2196(s), 2147(w), 1944(vs), 1800(vs), 1583(m), 1578(s), 1558(w), 1539(w), 1472(w), 1457(m), 1399(vw), 1381(w), 1362(vw), 1315(w), 1284(m), 1261(vw), 1234(vw), 1146(m), 1134(m), 1122(m), 1113(s), 1105(m), 1081(m), 1044(s), 1027(m), 1009(m), 979(w), 954(w), 931(w), 919(w), 856(w), 844(w), 634(w), 613(vw), 587(vw), 575(m), 556(m), 503(m), 492(m), and 468(m) cm^{-1} . IR (DME, ν_{CO}): 1941 and 1849 cm^{-1} . Anal. Calc. for $C_8H_{16}BN_3O_2Mo$: N, 14.35; C, 32.80; H, 5.50. Found: N, 14.14; C, 32.39; H, 5.55%.

3.3.6. $W(CO)_2(\eta^3-C_3H_5)(en)(NCBH_3)$ (**6**)

A procedure similar to the one described for the preparation of **5** was used. The reaction of $W(CO)_2(\eta^3-C_3H_5)(NCCH_3)_2Br$ (447.9 mg, 1.00 mmol) with 1,2-ethylenediamine (60.5 mg, 1.01 mmol) and $NaBH_3CN$ (62.3 mg, 1.01 mmol) furnished 3226.4 mg (59% yield) of yellow crystals isolated from a hexane/DME solution. ^{11}B NMR (DME): δ -43.1 ppm (br, q, $J_{B-H} = 90$ Hz). 1H NMR (d_8 -THF, $-40^\circ C$): δ 5.97 (m, 1H, NH_2), 4.35 (m,

1H, NH_2), 3.96 (m, 1H, NH_2), 3.76 (m, 1H, NH_2), 2.93 (m, 1H, H_s), 2.86 (m, 2H, H_c , en), 2.79 (m, 1H, en), 2.75 (m, 1H, H_s), 2.64 (m, 1H, en), 2.53 (m, 1H, en), 1.21 (d, $J_{H-H} = 9.0$ Hz, 1H, H_a), 1.00 (d, $J_{H-H} = 8.4$ Hz, 1H, H_a), and 0.36 ppm (br, q, 3H, BH_3). ^{13}C NMR (d_8 -THF, $-40^\circ C$): δ 218.66, 218.58 (CO), 128.97 (CN), 61.22 (C_c), 48.19, 47.74 (C_t), 45.28, and 43.71 ppm (en). IR (KBr): 3337(vw), 3325(m), 3313(w), 3274(w), 3260(vw), 3146(vw), 3062(vw), 2983(vw), 2960(vw), 2894(vw), 2358(m), 2346(m), 2260(vw), 2251(vw), 2238(vw), 2218(vw), 2194(m), 1937(vs), 1781(vs), 1580(m), 1458(w), 1316(vw), 1287(w), 1261(w), 1158(w), 1110(s), 1086(m), 1049(s), 1029(m), 1008(m), 961(vw), 932(vw), 905(vw), 872(vw), 817(w), 810(w), and 803(w) cm^{-1} . IR (DME, ν_{CO}): 1932 and 1837 cm^{-1} . Anal. Calc. for $C_8H_{16}BN_2O_3W$: N, 11.03; C, 25.23; H, 4.23. Found: N, 11.10; C, 25.21; H, 4.25%.

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Appendix A. Supplementary material

CCDC 657170, 657171, 657172, 657173, and 657174 contains the supplementary crystallographic data for **2**, **3**, **4**, **5**, and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.039](https://doi.org/10.1016/j.jorganchem.2007.11.039).

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