



Syntheses, structures, and dynamic properties of $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{X})$ ($M = \text{Mo}, \text{W}$; $\text{X} = \text{Br}, \text{N}_3, \text{CN}$) and $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}, \text{W}$)

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ABSTRACT

Mononuclear compounds $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{X})$ ($\text{X} = \text{Br}, M = \text{Mo}(\mathbf{1}), \text{W}(\mathbf{2})$; $\text{X} = \text{N}_3, M = \text{Mo}(\mathbf{3}), \text{W}(\mathbf{4})$; $\text{X} = \text{CN}, M = \text{Mo}(\mathbf{5}), \text{W}(\mathbf{6})$) and cyanide-bridged bimetallic compounds $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}(\mathbf{7}), \text{W}(\mathbf{8})$) were prepared and characterized. These compounds are fluxional and display broad unresolved proton NMR signals at room temperature. Compounds $\mathbf{1-6}$ were characterized by NMR spectroscopy at -60°C , which revealed isomers in solution. The major isomers of $\mathbf{1-4}$ adopt an asymmetric *endo*-conformation, while those of $\mathbf{5}$ and $\mathbf{6}$ were both found to possess a symmetric *endo*-conformation. The single crystal X-ray structures of $\mathbf{1-6}$ are consistent with the structures of the major isomer in solution at low temperature. In contrast to mononuclear terminal cyanide compounds $\mathbf{5}$ and $\mathbf{6}$, cyanide-bridged compounds $\mathbf{7}$ and $\mathbf{8}$ were found to adopt the asymmetric *endo*-conformation in the solid state.

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1. Introduction

The group 6 metal allyl complexes $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{X})$ ($M = \text{Mo}, \text{W}$; $\text{L-L} =$ bidentate ligand; $\text{X} =$ anionic monodentate ligand) have been studied for more than four decades [1–3] due to their conformational and dynamic behavior [4–6] as well as their possible application in organic synthesis [7–12]. In general, when L-L is a rigid bidentate ligand the complex adopts conformation **A** (Scheme 1) in the solid state and displays non-fluxional behavior in solution [13,14]. When L-L is a non-rigid bidentate ligand, the complex adopts conformation **C** (Scheme 1) in the solid state and is fluxional in solution [15–17]. Although most of these allyl compounds can be classified into these two categories based on the rigidity of the bidentate ligand, exceptions have been found. For example, the rigid chelating compound $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})(\text{CH}_3\text{CN})]^+$ [18] adopts conformation **C**, in contrast to the non-rigid chelating compounds $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{dmpm})(\text{N}_3)$ ($\text{dmpm} =$ bis-(dimethylphosphino)methane) [19], $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{glyme})(\text{CF}_3\text{CO}_2)$ [20], and $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{dmpm})(\text{CN})$ [19] adopting conformations **D** (Scheme 1), **A**, and a *trans*-dicarbonyl arrangement, respectively. Among these bidentate ligands, the diphosphine ligand 1,2-bis(diphenylphosphino)ethane (dppe) is the most common non-rigid bidentate ligand studied. The dppe-containing compounds $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{dppe})(\text{X})$

have always been found to adopt conformation **C** in the solid state and display fluxional behavior in solution [16–18]. A trigonal twist rearrangement involving a rotation of the triangular face formed by the ligand X and the chelating diphosphine ligand P-P with respect to the face formed by the allyl and two carbonyls has been proposed to explain their fluxional behavior in solution [15,21,22]. In contrast to the dppe-containing compounds, those with 1,2-ethylenediamine (*en*) have not been studied extensively. To our knowledge, there are only a handful of examples of *en*-containing compounds reported in literature [21,23,24]. Here we would like to report our recent findings with respect to the *en*-containing mononuclear complexes $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{X})$ ($M = \text{Mo}, \text{W}$; $\text{X} = \text{Br}, \text{N}_3, \text{CN}$) and the cyanide-bridged bimetallic complexes $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}, \text{W}$).

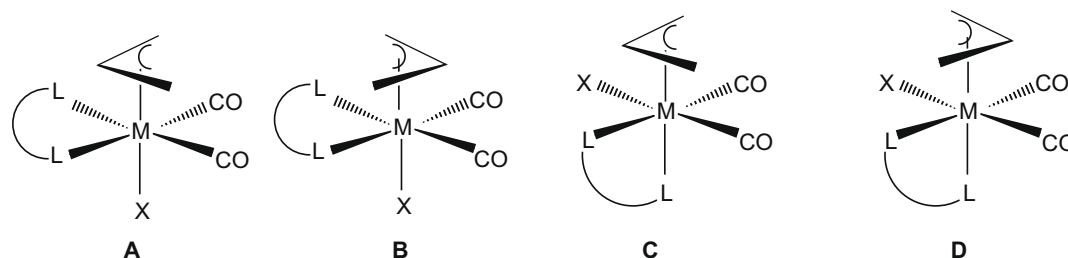
2. Results and discussion

2.1. Preparations and properties of $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{X})$ ($\text{X} = \text{Br}, M = \text{Mo}(\mathbf{1}), \text{W}(\mathbf{2})$; $\text{X} = \text{N}_3, M = \text{Mo}(\mathbf{3}), \text{W}(\mathbf{4})$; $\text{X} = \text{CN}, M = \text{Mo}(\mathbf{5}), \text{W}(\mathbf{6})$), and $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}(\mathbf{7}), \text{W}(\mathbf{8})$)

Compounds $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{Br})$ ($M = \text{Mo}(\mathbf{1}), \text{W}(\mathbf{2})$) were prepared from the reaction of $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{CH}_3\text{CN})_2(\text{Br})$ ($M = \text{Mo}, \text{W}$) with 1,2-ethylenediamine (*en*), according to Eq. (1).

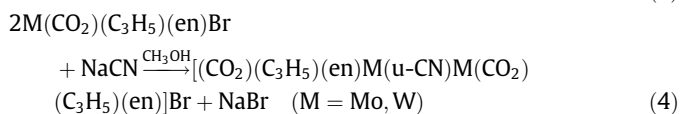
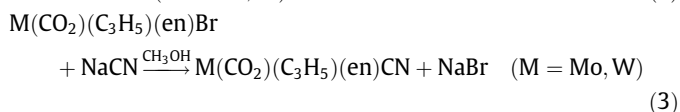
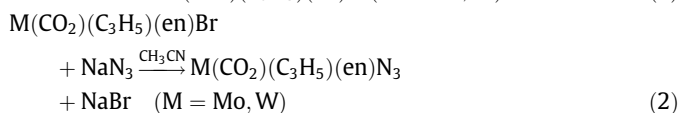
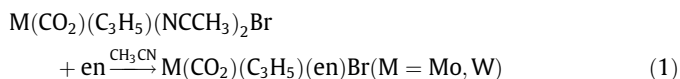
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Scheme 1.

Azides $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{N}_3)$ ($M = \text{Mo}$ (**3**), W (**4**)) were obtained from bromides **1** and **2**, respectively, via a metathesis reaction with sodium azide (Eq. (2)). Whether the terminal or bridging cyanide complex is formed depends on the ratio of the reactants. Reactions of **1** and **2** with excess sodium cyanide furnished terminal cyanides $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{CN})$ ($M = \text{Mo}$ (**5**), W (**6**)), respectively (Eq. (3)). When only half equivalent of sodium cyanide was used, the bridging cyanide complexes $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2M(\mu\text{-CN})M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ ($M = \text{Mo}$ (**7**), W (**8**)) were isolated (Eq. (4)). The terminal cyanide compounds can function as metalloligands through the nitrogen atom of the cyanide ligand [25–28]. Thus, bridging cyanide complexes **7** and **8** were formed from the reaction of initially formed terminal cyanides **5** and **6**, with excess **1** and **2**, respectively. Substitutions of a halide ligand X^- ($X = \text{Cl}, \text{Br}, \text{I}$) of a metal-halide complex by a neutral metal cyanide complex have been reported [29–31]. These en-containing complexes are poorly soluble in common organic solvents. They are slightly soluble in methanol, acetonitrile, THF, and DME.



2.2. Spectroscopic studies

Among the group 6 metal allyl complexes $M(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L})(\text{X})$ with a non-rigid bidentate ligand those with 1,2-bis(diphenylphosphino)ethane (dppe) are the most studied [15,22,32]. Due to their fluxional behavior one could observe only averaged NMR signals for these compounds at room temperature, the fluxional behavior being observed even at -100°C [15]. The energy rotation barriers of the en complexes are significantly higher than those of their dppe counterparts. The en complexes **1–6** are fluxional displaying unresolved broad proton NMR signals at room temperature. They were characterized by $^1\text{H}-^1\text{H}$ COSY and $^1\text{H}-^{13}\text{C}$ HMQC 2D NMR analysis at -60°C , the NH_2 protons being further characterized by the H–D exchange in D_2O . Based on the NMR pattern of the allylic signals, a pair of isomers was found for each compound at low temperature. The spectra of **1** and **2** display two sets of asymmetric allylic signals of 4:1 and 2:1 ratio, respectively. Theo-

retical calculations of model compounds $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{NCH}_3)_3]^+$ and $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{Cl})_3]^-$ by Curtis have suggested that *endo*-isomers are energetically more favorable [33]. Azevedo and co-workers have arrived at the same conclusion in their calculation of the model compound $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})(\text{NCH}_3)]^+$ [18]. The results of these calculations are consistent with the general observation that most of group 6 metal allyl complexes adopt the *endo*-conformation. Thus, asymmetric *endo*-conformation (**C**) and *exo*-conformation (**D**) were assigned to the major and minor isomers, respectively, observed in the spectra of **1** and **2**. Due to the H–D exchange in deuterated methanol, the integration of NH_2 resonances in each isomer is less than expected. Indeed, the H–D exchange of NH_2 protons was also observed in the spectra of **3–8** at different rates. As time elapsed, the intensity of the NH_2 signals decreased gradually.

Based on the asymmetry of the allylic signal pattern conformation **C** was also assigned to the major isomers observed in the spectra of azides **3** and **4**. Conformational assignments could not be made for the minor isomers due to the paucity of the isomers (40:3 in **3** and 20:3 in **4**) and their signals being partially obscured by those of the major isomers. The spectra of both **5** and **6** indicate the presence of two isomers in a ratio of 5:2. Symmetric *endo*-conformation **A** was assigned to the major isomers of **5** and **6**, unlike to those of **1–4**, due to the symmetry of their allylic signal patterns. Conformation **C** was assigned to the minor isomers due to the asymmetry of their allylic signal patterns. In the ^{13}C NMR spectra weak cyanide signals were observed for **6** (158.71 and 157.25 ppm) and the major isomer of **5** (157.10 ppm), while that of the minor isomer of **5** was not observed.

The bridging cyanide bimetallic compounds **7** and **8** also display broad proton signals at room temperature. Their low temperature spectra could not be assigned unambiguously due to their complexity. However, those taken at above 50°C displayed a well-resolved pattern for **7** (Fig. 1). Signals gradually turn sharper upon temperature increase, with an averaged pattern being displayed at 50°C . Two sets of allylic signals found correspond to a fast trigonal twist rotation around each Mo center. The NH_2 signals are weaker than expected, possibly due to a faster H–D exchange at higher temperature. The energy barrier of the tungsten analog, complex **8**, turned out to be higher than that of **7**. The fast rotation has not been reached yet at 60°C resulting in a broad proton spectrum. However, these NMR signals can be assigned with the assistance of $^1\text{H}-^1\text{H}$ COSY and $^1\text{H}-^{13}\text{C}$ HMQC 2D NMR at 60°C . The broad carbon signals at 61.41 (C_c), 48.66 (C_t), 46.09 (C_i , en), and 45.38 ppm (en) are consistent with a slower exchange rate for **8** at this temperature. In this case an attempted study of the fast allyl rotation in CD_3CN did not succeed due to the decomposition of **8** in CD_3CN at elevated temperatures.

Consistent with a presence of a *cis*- $M(\text{CO})_2$ unit [18,34], with the exception of **5**, two carbonyl absorption bands of about equal intensity were observed in the IR spectra of all mononuclear complexes. Three carbonyl absorption bands at 1926, 1852, and 1819 cm^{-1} were observed for complex **5** in the solid state. The sig-

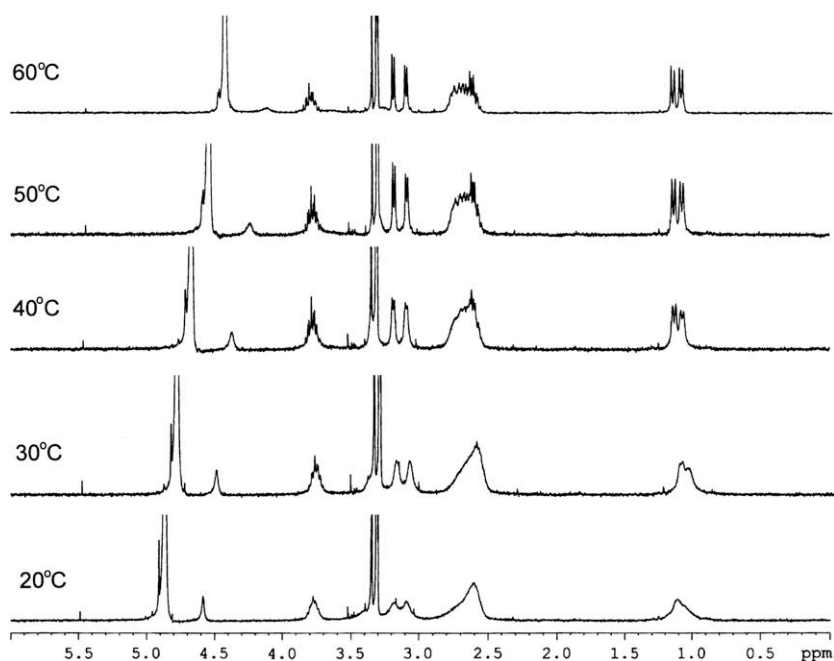


Fig. 1. Variable-temperature ^1H NMR spectra of $[(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})\text{Mo}(\mu\text{-CN})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}\cdot\text{CH}_3\text{OH}$ (**7**) in d_4 -methanol.

nal at 1854 cm^{-1} contains a broad shoulder suggesting an overlap with another band. Upon dissolution of **5** in methanol two carbonyl absorption bands at 1945 and 1857 cm^{-1} were observed. The more complicated solid state IR spectrum appearance has been attributed to a lower symmetry of the molecule in the crystal compared to the isolated molecule in solution [35]. Four carbonyl absorption bands were observed in the IR spectra of both cyano-bridged compounds **7** and **8**, which is consistent with the presence of two *cis*- $\text{M}(\text{CO})_2$ moieties in these compounds. Due to the electron-rich nature of the third row transition metals [36], the carbonyl absorption bands of the tungsten compounds appear at lower wavenumbers compared with their Mo analogs. In general, terminal carbonyl absorption bands occur in the $1850\text{--}2120\text{ cm}^{-1}$ range [37]. For complexes **1–8** there are band(s) well below this range. This result is consistent with our previous observations for en-containing complexes $\text{M}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{NCBH}_3)$ ($\text{M} = \text{Mo}, \text{W}$) [23], which have been attributed to a good σ -donor ability of the en ligand.

The strong absorption bands at 2057 and 2065 cm^{-1} in the IR spectra of **3** and **4**, respectively, are assigned to their azido-groups. These absorptions occur slightly below the frequency observed for $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{dmpm})(\text{N}_3)$ (2072 cm^{-1} in CH_2Cl_2) [19]. The cyanide absorption bands for **5** and **6** appear at 2099 and 2110 cm^{-1} , respectively. These absorptions are comparable to that observed for $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{phen})(\text{CN})$ (2113 cm^{-1}) [38]. The bridging cyanide absorption bands for **7** (2127 cm^{-1}) and **8** (2124 cm^{-1}) occur at higher frequencies than those of the terminal cyanide compounds **5** and **6**. A similar blue shift has been observed in other bridging cyanide compounds [38–42], the frequency increase being primarily attributed to the cation electronic field and the concomitant relaxation [43].

2.3. X-ray studies

The molecular structures of **1–8** were determined by single crystal X-ray diffraction analyses. The crystallographic data and selected bond distances and angles are summarized in Tables 1–6. The molecular structures of **1**, **3**, **5**, and **7** are provided in Figs. 2–5 while the molecular structures of their tungsten analogs **2**, **4**, **6**, and **8** are included in the supporting information. Each metal pos-

sesses a *pseudo*-octahedral structure, being surrounded by an allyl group, two carbonyls, an anionic ligand X^- ($\text{X} = \text{Br}, \text{N}_3, \text{CN}$), and a bidentate ligand en. Both carbonyls are equatorial and *cis*- to each other. The allyl ligand occupies an axial position, with its open face eclipsing the two carbonyls (*endo*-isomer). These solid state structures are consistent with the conformations of their major isomers in solution at low temperature. The molecular structures of **1–4** possess an asymmetric *endo*-form **C**, in which one of the nitrogen atoms of the en ligand is in the axial position and *trans*- to the allyl group, and the other is in the equatorial position and *trans*- to a carbonyl. Conformation **C** is commonly observed for non-rigid bidentate ligand complexes, and all of the dppe-containing complexes possess this type of conformation in the solid state. For each compound, the axial M–N bond distance is slightly shorter than that of the equatorial M–N bond, which is consistent with those observed for $\text{M}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{NCBH}_3)$ ($\text{M} = \text{Mo}, \text{W}$) [23]. In agreement with lower energy absorption bands observed for the tungsten complexes their C=O bond distances are slightly longer than those of their molybdenum analogs. The N–M–N biting angles are in the range of $74.32(15)\text{--}75.23(6)^\circ$. Although it is comparable with the angles observed for $\text{M}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{NCBH}_3)$ ($75.29(5)^\circ$ (Mo); $75.17(12)^\circ$ (W)) [23], it is smaller than the P–M–P biting angle in the dppe-containing compound $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{dppe})(\text{CH}_3\text{CN})]^+$ ($78.2(1)^\circ$) [18]. The C–C–C allyl angles fall within the range of $114.7(4)\text{--}116.5(4)^\circ$, which is consistent with other allyl compounds [15,44–46]. The N(3)–N(4) ($1.162(4)\text{ \AA}$ in **3**, $1.191(6)\text{ \AA}$ in **4**), N(4)–N(5) bond distances ($1.168(4)\text{ \AA}$ in **3**, $1.152(6)\text{ \AA}$ in **4**) and the N(3)–N(4)–N(5) angles ($177.7(4)^\circ$ in **3**, $177.7(6)^\circ$ in **4**) of azido- compounds **3** and **4** are comparable to those of other azido- compounds [19,47,48]. Intermolecular hydrogen bonds were found in **4** between an NH_2 proton of the en ligand and one of the oxygens of the carbonyl ligand, with two $\text{NH}_2\cdots\text{OC}$ interactions ($\text{N}(1)\cdots\text{O}(2) = 3.045\text{ \AA}$), resulting in a dimeric structure of **4**.

The molecular structures of **5** and **6** correspond to conformation **A**, in which the en ligand is in the equatorial position and each nitrogen atom is *trans*- to a carbonyl ligand. The M–N distances are $2.2780(14)$ and $2.3093(14)\text{ \AA}$ in **5**, and $2.275(3)$ and $2.297(3)\text{ \AA}$ in **6**. These distances are comparable to one of the M–

Table 1
Crystallographic data for Mo(CO)₂(η³-C₃H₅)(en)(Br) (**1**), W(CO)₂(η³-C₃H₅)(en)(Br) (**2**), Mo(CO)₂(η³-C₃H₅)(en)(N₃) (**3**), and W(CO)₂(η³-C₃H₅)(en)(N₃) (**4**).

Empirical formula	C ₇ H ₁₃ BrMoN ₂ O ₂	C ₇ H ₁₃ BrN ₂ O ₂ W	C ₇ H ₁₃ MoN ₅ O ₂	C ₇ H ₁₃ N ₅ O ₂ W
Formula weight	333.04	420.95	295.16	383.07
T (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /n	P2 ₁ /n
a (Å)	7.0574(4)	7.0207(2)	8.3134(5)	8.3356(9)
b (Å)	9.7698(6)	9.7684(3)	12.7845(8)	12.7345(13)
c (Å)	15.6525(9)	15.5953(5)	10.6206(7)	10.5320(11)
β (°)	90	90	99.9660(10)	99.7200(10)
V (Å ³)	1079.23(11)	1069.54(6)	1111.75(12)	1101.9(2)
Z	4	4	4	4
ρ _{calc} (g/cm ³)	2.050	2.614	1.763	2.309
Crystal size (mm ³)	0.26 × 0.24 × 0.20	0.25 × 0.16 × 0.12	0.10 × 0.08 × 0.02	0.2 × 0.2 × 0.1
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ Limits (°)	2.46–28.29	2.46–28.27	2.52–28.32	2.53–25.05
Index ranges	−9 ≤ h ≤ 9 −13 ≤ k ≤ 13 −20 ≤ l ≤ 17	−9 ≤ h ≤ 9 −13 ≤ k ≤ 13 −20 ≤ l ≤ 20	−11 ≤ h ≤ 11 −17 ≤ k ≤ 17 −20 ≤ l ≤ 14	−9 ≤ h ≤ 9 −15 ≤ k ≤ 15 −12 ≤ l ≤ 12
Reflections collected	8194	16322	11688	11217
Unique reflections	2651	2644	2768	1948
Unique reflections [I > 2σ(I)]	648	776	592	720
Completeness to θ (%)	99.7	100.0	100.0	99.9
μ (mm ^{−1})	4.890	14.508	1.170	10.473
Data/restraints/parameters	2651/0/119	2644/0/118	2768/0/136	1948/0/136
R ₁ ^a [I > 2σ(I)]	0.0148	0.0145	0.0315	0.0201
wR ₂ ^b (all data)	0.0337	0.0359	0.0778	0.0485
R _{int}	0.0178	0.0297	0.0395	0.0421
Goodness of fit (GOF) on F ²	1.005	1.100	1.062	1.049

^a R₁ = Σ||F_o|| − |F_c|| / Σ||F_o||.

^b wR₂ = {Σw(F_o² − F_c²)² / Σw(F_o²)²}^{1/2}.

Table 2
Crystallographic data for Mo(CO)₂(η³-C₃H₅)(en)(CN) (**5**), W(CO)₂(η³-C₃H₅)(en)(CN) (**6**), [(CO)₂(η³-C₃H₅)(en)Mo(μ-CN)Mo(CO)₂(η³-C₃H₅)(en)]Br·CH₃OH (**7**), and [(CO)₂(η³-C₃H₅)(en)W(μ-CN)W(CO)₂(η³-C₃H₅)(en)]Br·CH₃OH (**8**).

Empirical formula	C ₈ H ₁₃ MoN ₃ O ₂	C ₈ H ₁₃ N ₃ O ₂ W	C ₁₆ H ₃₀ BrMo ₂ N ₅ O ₅	C ₁₆ H ₃₀ BrN ₅ O ₅ W ₂
Formula weight	279.15	367.06	644.24	820.03
T (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a (Å)	10.6696(7)	10.6400(4)	10.8275(4)	10.7534(3)
b (Å)	7.6145(5)	7.6017(3)	14.6271(5)	14.5892(5)
c (Å)	13.1391(8)	13.0806(6)	15.1593(5)	15.1526(5)
β (°)	91.0950(10)	91.3750(10)	98.0240(10)	97.9140(10)
V (Å ³)	1067.27(12)	1057.68(8)	2377.35(14)	2354.55(13)
Z	4	4	4	4
ρ _{calc} (g/cm ³)	1.737	2.305	1.789	2.302
Crystal size (mm ³)	0.40 × 0.40 × 0.40	0.05 × 0.03 × 0.02	0.32 × 0.32 × 0.05	0.13 × 0.13 × 0.03
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ Limits (°)	1.91–28.26	1.91–28.71	1.90–28.28°	1.91–28.71
Index ranges	−14 ≤ h ≤ 14 −10 ≤ k ≤ 9 −17 ≤ l ≤ 17	−14 ≤ h ≤ 14 −10 ≤ k ≤ 10 −17 ≤ l ≤ 17	−14 ≤ h ≤ 14 −19 ≤ k ≤ 18 −18 ≤ l ≤ 20	−14 ≤ h ≤ 14 −19 ≤ k ≤ 19 −20 ≤ l ≤ 20
Reflections collected	8557	16287	19654	32802
Unique reflections	2646	2741	5901	6095
Unique reflections [I > 2σ(I)]	560	688	1264	1520
Completeness to θ (%)	99.9	100.0	99.8	99.8
μ (mm ^{−1})	1.208	10.901	2.770	11.494
Data/restraints/parameters	2646/0/128	2741/0/131	5901/0/263	6095/0/282
R ₁ ^a [I > 2σ(I)]	0.0177	0.0210	0.0231	0.0232
wR ₂ ^b (all data)	0.0391	0.0498	0.0656	0.0588
R _{int}	0.0177	0.0385	0.0282	0.0413
Goodness of fit (GOF) on F ²	1.099	1.038	1.151	1.044

^a R₁ = Σ||F_o|| − |F_c|| / Σ||F_o||.

^b wR₂ = {Σw(F_o² − F_c²)² / Σw(F_o²)²}^{1/2}.

N distances in compounds **1–4**, in which the en nitrogen is *trans*- to a carbonyl ligand. The N–M–N bidentate biting angles are 75.16(5)° in **5** and 74.85(11)° in **6**. They are comparable to those in compounds **1–4**. The C–C–C allyl angles are 116.5(2)° in **5** and 117.2(5)° in **6**. The M–CN distances are 2.1828(7) Å in **5** and

2.1684 (4) Å in **6**, and the MC≡N distances are 1.143(2) Å in **5** and 1.136(5) Å in **6**. The Mo–CN and MoC≡N distances are comparable to those in Mo(CO)₂(η³-C₃H₅)(phen)(CN) (2.188(8) and 1.103(8) Å) [38]. Intermolecular hydrogen bonds were also found in **5** and **6**. The interaction between an NH₂ proton and a cyanide

Table 3Selected bond distances (Å) and bond angles (°) for Mo(CO)₂(η³-C₃H₅)(en)(Br) (**1**) and W(CO)₂(η³-C₃H₅)(en)(Br) (**2**).

	1	2
M–C(1)	1.940(2)	1.935(4)
M–C(2)	1.933(2)	1.931(4)
M–N(1)	2.2911(17)	2.286(3)
M–N(2)	2.2479(15)	2.245(2)
M–Br	2.7313(3)	2.7123(4)
C(1)–O(1)	1.161(3)	1.167(4)
C(2)–O(2)	1.162(3)	1.172(4)
C(1)–M–C(2)	78.36(9)	77.98(14)
C(1)–M–N(2)	93.66(8)	94.11(13)
C(1)–M–N(1)	168.72(7)	169.16(12)
C(1)–M–Br	96.86(6)	97.46(10)
C(2)–M–N(2)	87.69(8)	88.06(12)
C(2)–M–N(1)	98.91(8)	99.55(13)
C(2)–M–Br	167.00(6)	167.06(10)
N(1)–M–N(2)	75.23(6)	75.20(10)
N(2)–M–Br	80.51(5)	80.14(8)
N(1)–M–Br	83.41(5)	82.64(8)
M–C(1)–O(1)	176.2(2)	177.0(3)
M–C(2)–O(2)	175.0(2)	175.0(3)
C(3)–C(4)–C(5)	115.2(2)	114.7(4)

Table 4Selected bond distances (Å) and bond angles (°) for Mo(CO)₂(η³-C₃H₅)(en)(N₃) (**3**) and W(CO)₂(η³-C₃H₅)(en)(N₃) (**4**).

	3	4
M–C(1)	1.946(4)	1.942(6)
M–C(2)	1.938(3)	1.942(5)
M–N(1)	2.286(3)	2.279(4)
M–N(2)	2.247(3)	2.239(4)
M–N(3)	2.233(3)	2.212(4)
C(1)–O(1)	1.154(4)	1.167(7)
C(2)–O(2)	1.161(4)	1.165(7)
N(3)–N(4)	1.162(4)	1.191(6)
N(4)–N(5)	1.168(4)	1.152(6)
C(1)–M–C(2)	79.25(15)	79.2(2)
C(1)–M–N(2)	95.51(13)	95.6(2)
C(1)–M–N(1)	169.89(13)	169.7(2)
C(1)–M–N(3)	95.13(13)	96.0(2)
C(2)–M–N(2)	87.91(13)	88.5(2)
C(2)–M–N(1)	102.12(12)	102.11(19)
C(2)–M–N(3)	165.16(13)	165.7(2)
N(1)–M–N(2)	74.61(10)	74.32(15)
N(2)–M–N(3)	78.91(11)	78.54(17)
N(1)–M–N(3)	81.07(10)	80.21(15)
M–C(1)–O(1)	178.0(4)	178.2(6)
M–C(2)–O(2)	173.5(3)	174.3(5)
M–N(3)–N(4)	126.2(2)	125.6(4)
N(3)–N(4)–N(5)	177.7(4)	177.7(6)
C(3)–C(4)–C(5)	116.5(4)	115.2(6)

nitrogen (N(1)··N(3) = 3.063 Å in **5** and N(2)··N(3) = 3.068 Å in **6**) resulted in a one dimensional polymeric extended structure for both compounds.

The bridging cyanide complexes **7** and **8** adopt asymmetric conformation **C**, where all axial M–N bond distances of the en ligands are slightly shorter than the equatorial M–N bonds. The M(1)–N(1)–C(1)–M(2) fragment is almost linear (M(1)–N(1)–C(1) = 174.19(17)° (**7**); 174.3(4)° (**8**); M(2)–C(1)–N(1) = 177.30(19)° (**7**); 176.4(4)° (**8**)). Formation of the cyanide bridges increases the M–C(1) (M–C(1) = 2.219(2) Å (**7**); 2.197(4) Å (**8**)) and C(1)–N(1) distances (1.150(3) Å (**7**); 1.152(5) Å (**8**)) compared with those of terminal cyanide compounds **5** and **6**. The u–C≡N distances in **7** and **8** are comparable with those of other bridging cyanide compounds [38,49,50]. The unit cells of both compounds contain a methanol

Table 5Selected bond distances (Å) and bond angles (°) for Mo(CO)₂(η³-C₃H₅)(en)(CN) (**5**), W(CO)₂(η³-C₃H₅)(en)(CN) (**6**).

	5	6
M–C(1)	1.9434(19)	1.945(4)
M–C(2)	1.9445(19)	1.951(4)
M–N(1)	2.2780(14)	2.297(3)
M–N(2)	2.3093(14)	2.275(3)
M–C(8)	2.1828(17)	2.168(4)
C(1)–O(1)	1.162(2)	1.174(5)
C(2)–O(2)	1.161(2)	1.153(6)
N(3)–C(8)	1.143(2)	1.136(5)
C(1)–M–C(2)	78.38(8)	78.65(18)
C(1)–M–N(2)	103.39(7)	100.85(15)
C(1)–M–N(1)	165.62(7)	171.35(14)
C(1)–M–C(8)	85.76(7)	93.09(16)
C(2)–M–N(2)	171.25(6)	165.57(16)
C(2)–M–N(1)	100.95(6)	103.59(15)
C(2)–M–C(8)	92.32(7)	86.40(16)
N(1)–M–N(2)	75.16(5)	74.85(11)
N(2)–M–C(8)	79.34(6)	79.21(13)
N(1)–M–C(8)	79.90(6)	78.80(14)
M–C(1)–O(1)	175.2(2)	177.5(4)
M–C(2)–O(2)	176.55(17)	175.7(4)
M–C(8)–N(3)	176.10(17)	177.4(4)
C(3)–C(4)–C(5)	116.5(2)	117.2(5)

Table 6Selected bond distances (Å) and bond angles (°) for [(CO)₂(η³-C₃H₅)(en)Mo(μ-CN)Mo(CO)₂(η³-C₃H₅)(en)]Br·CH₃OH (**7**) and [(CO)₂(η³-C₃H₅)(en)W(μ-CN)W(CO)₂(η³-C₃H₅)(en)]Br·CH₃OH (**8**).

	7	8
M(1)–C(2)	1.967(3)	1.967(5)
M(1)–C(3)	1.941(2)	1.943(4)
M(1)–N(11)	2.2449(19)	2.226(4)
M(1)–N(12)	2.2698(19)	2.262(4)
M(1)–N(1)	2.232(2)	2.216(4)
C(2)–O(1)	1.141(3)	1.153(6)
C(3)–O(2)	1.159(3)	1.174(5)
C(1)–N(1)	1.150(3)	1.152(5)
M(2)–C(4)	1.968(2)	1.964(4)
M(2)–C(5)	1.953(2)	1.948(4)
M(2)–N(21)	2.2404(18)	2.226(3)
M(2)–N(22)	2.2891(18)	2.272(4)
M(2)–C(1)	2.219(2)	2.197(4)
C(4)–O(3)	1.155(3)	1.162(5)
C(5)–O(4)	1.154(3)	1.163(5)
M(1)–N(1)–C(1)	174.19(18)	174.3(4)
M(2)–C(1)–N(1)	177.30(19)	176.4(4)
N(11)–M(1)–N(12)	75.56(7)	75.41(14)
N(21)–M(2)–N(22)	75.02(7)	74.81(13)
C(11)–C(12)–C(13)	116.7(3)	116.1(5)
C(21)–C(22)–C(23)	115.7(2)	115.7(5)

molecule connecting a cation and an anion through hydrogen bonding interactions (H₂N··OH and Br··HO). The N(22)··O(31) distance is 2.995 Å in **7** and the N(22)··O(5) distance is 3.07 Å in **8**, and the Br(1)··O(31) distance is 3.208 Å in **7** and the Br(1)··O(5) distance is 3.193 Å in **8**. As mentioned above, these en-containing complexes are poorly soluble in common organic solvents. It could be due to the nature of these complexes containing the en ligand. However, the intermolecular hydrogen bonding interaction found in **4–8** in the solid state could also remain in solution thereby contributing to the insolubility of these compounds.

It is of interest to note that while terminal cyanide compounds **5** and **6** adopt symmetric conformation **A** in the solid state, their bridging cyanide counterparts **7** and **8** possess conformation **C**. Although only a few examples of en-containing compounds have

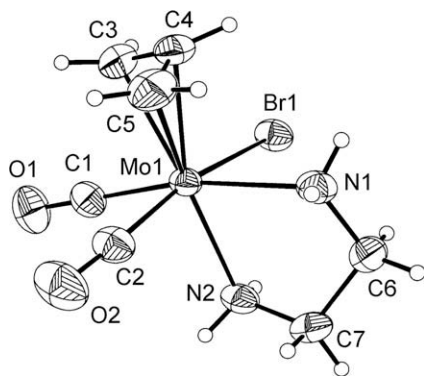


Fig. 2. Molecular structure of $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{Br})$ (**1**), with 50% probability thermal ellipsoids.

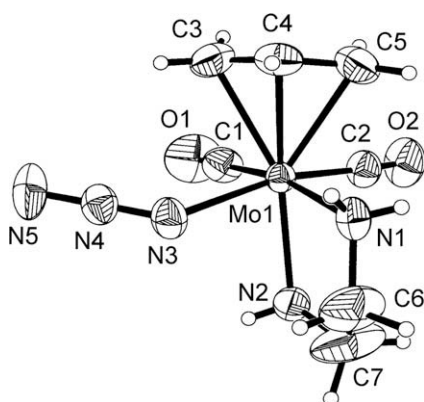


Fig. 3. Molecular structure of $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{N}_3)$ (**3**), with 50% probability thermal ellipsoids.

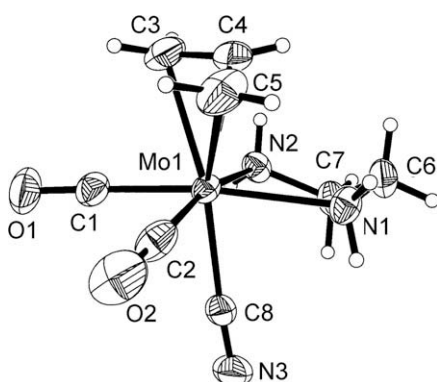


Fig. 4. Molecular structure of $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{CN})$ (**5**), with 50% probability thermal ellipsoids.

been reported, the present result suggests that the en-containing complexes would likely to adopt conformation **C** when X^- is a weak field ligand ($\text{X} = \text{BH}_3\text{CN}$, Br , N_3). Even though the cyanide is a strong field ligand, formation of the cyanide bridges will weaken its interaction with the metals. That the M-CN bond distances in **7** and **8** are slightly longer than those in compounds **5** and **6**, and the M-NC bond distances are comparable to those in azido-compounds **3** and **4** could be the evidence. Thus, decreased interaction between the cyanide ligand and the metals could result in complexes **7** and **8** adopting conformation **C** in the solid state.

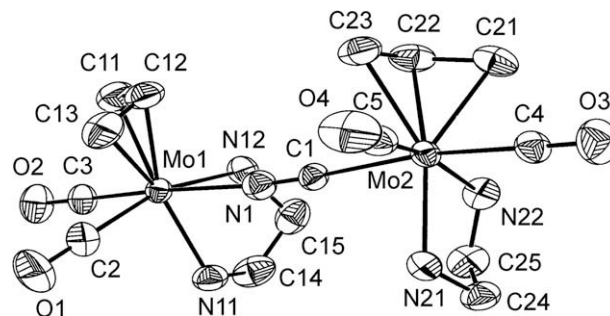


Fig. 5. Molecular structure of the cation in $[(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})\text{Mo}(\mu\text{-CN})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}\cdot\text{CH}_3\text{OH}$ (**7**), with 50% probability thermal ellipsoids.

3. Conclusions

While many group 6 metal compounds of the type $\text{M}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{L-L})(\text{X})$ have been studied, compounds **1–8** represent the rare examples of the en-containing complexes fully characterized by NMR and solid state X-ray analysis. These compounds are fluxional in solution at room temperature. The solution structures of **1–6** were analyzed by NMR spectroscopy at low temperature, with isomers being observed for each compound. The solid state structures of **1–8** appear to depend on the anionic ligand X^- . The asymmetric *endo*-forms were found for compounds containing a weak field ligand, while the symmetric *endo*-forms were found when complexes possess a strong field ligand.

4. Experimental

4.1. General procedures

All manipulations were carried out on a standard high vacuum line or in a drybox under the atmosphere of nitrogen. 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 [3]. 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 Bruker Avance II 400 spectrometer operating at 300.130 MHz and 400.132 MHz, respectively. Infrared spectra were recorded on a JASCO FT-IR 401 spectrometer with 4 cm^{-1} resolution.

4.2. X-ray structure determination

Suitable crystals of **1–8** 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 298(2) K. Unit cell parameters were retrieved and refined using DENZO-SMN [51] software on all reflections. Data reduction was performed with the DENZO-SMN [51] software. An empirical absorption was based on the symmetry-equivalent reflections and was applied to the data using SORTAV [52,53] program. The structure was solved using the SHELXS-97 [54] program and refined using SHELXL-97 [55] program by full-matrix least-squares on F^2 values. All nonhydrogen atoms in each structure were located and refined anisotropically. All hydrogen atoms were fixed at calculated positions and refined using a riding mode. Crystallographic data of **1–8** are summarized in Tables 1–6.

4.3. Preparation of complexes

4.3.1. $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{Br})$ (**1**)

In the drybox, 360.2 mg (1.0 mmol) of $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{CH}_3\text{CN})_2(\text{Br})$ and 20 mL of acetonitrile were put into a 50 mL flask. To this solution, a 60.8 mg (1.0 mmol) of 1,2-ethylenediamine (en) in 5 mL CH_3CN was added drop wise and continued to stir at room temperature for additional 6 h. The solvent was removed in *vacuo*, and the resulting yellow solid was dissolved in DME and layered with hexane for crystallization. A 230.1 mg (69.1% yield) of yellow crystals were obtained. ^1H NMR (CD_3OD , -60°C): isomer A, δ 6.50 (br, s, 0.7H, NH_2), 4.34 (br, s, 0.7H, NH_2), 3.90 (br, s, 0.7H, NH_2), 3.84 (m, 1H, H_c), 3.33 (m, 1H, H_s), 3.25 (br, s, 0.7H, NH_2), 3.14 (m, 1H, H_c), 2.75 (m, 1H, en), 2.63 (m, 2H, en), 2.27 (m, 1H, en), 1.19 (dd, $J = 9.6, 1.3$ Hz, 1H, H_a), 1.16 (dd, $J = 9.6, 1.3$ Hz, 1H, H_a) ppm. Isomer B, δ 6.22 (br, s, 0.6H, NH_2), 4.00 (br, s, 1.2H, NH_2), 3.92 (m, 1H, H_c), 3.51 (m, 1H, H_s), 3.38 (br, s, 0.6H, NH_2), 3.08 (m, 1H, H_s), 2.94 (m, 1H, en), 2.78 (m, 2H, en), 2.65 (m, 1H, en), 0.99 (d, $J = 9.5$ Hz, 1H, H_a), 0.90 (d, $J = 9.2$ Hz, 1H, H_a) ppm. ^{13}C NMR (CD_3OD , -60°C): isomer A, δ 226.99, 223.75 (CO), 69.95 (C_c) 56.66, 55.48 (C_t), 43.24, and 41.18 ppm (en). Isomer B, δ 226.59, 223.53 (CO), 69.16 (C_c), 56.39, 54.85 (C_t), 43.67, and 41.26 ppm (en). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 1926 vs, 1815 vs (CO). *Anal. Calc.* for $\text{C}_7\text{H}_{13}\text{BrN}_2\text{MoO}_2$: N, 8.41; C, 25.24; H, 3.94. Found: N, 8.40; C, 25.30; H, 3.94%.

4.3.2. $\text{W}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{Br})$ (**2**)

A procedure similar to the one described for the preparation of **1** was used. The reaction of $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2(\text{Br})$ (443.5 mg, 1.0 mmol) with en (60.9 mg, 1.0 mmol) followed by layering the DME solution of the product with hexane produced 211.3 mg (50.2% yield) of **2** as yellow crystals. ^1H NMR (CD_3OD , -60°C): isomer A, δ 6.64 (br, s, 0.7H, NH_2), 4.64 (br, s, 0.7H, NH_2), 4.27 (br, s, 0.7H, NH_2), 3.68 (br, s, 0.7H, NH_2), 3.10 (br, s, 1H, H_s), 3.02 (m, 1H, H_c), 2.92 (br, s, 1H, H_s), 2.85 (br, s, 2H, en), 2.74 (br, s, 2H, en), 1.33 (dd, $J = 8.5, 1.7$ Hz, 1H, H_a), 1.30 (dd, $J = 8.5, 1.7$ Hz, 1H, H_a) ppm. Isomer B, δ 6.37 (br, s, 0.6H, NH_2), 4.27 (br, s, 0.6H, NH_2), 3.68 (br, s, 0.6H, NH_2), 3.45 (br, s, 0.6H, NH_2), 3.29 (br, s, 1H, H_s), 3.02 (m, 1H, H_c), 2.85 (br, s, 1H, H_s), 2.65 (br, s, 2H, en), 2.40 (br, s, 2H, en), 1.09 (dd, $J = 8.9, 1.5$ Hz, 1H, H_a), 1.03 (d, $J = 7.2$ Hz, 1H, H_a) ppm. ^{13}C NMR (CD_3OD , -60°C): isomer A, δ 218.52, 217.40 (CO), 61.09 (C_c), 48.62, 48.43 (C_t), 43.85, 41.85 (en) ppm. Isomer B, δ 219.15, 217.68 (CO), 60.62 (C_c), 49.75, 47.52 (C_t), 44.30, 42.03 (en) ppm. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 1915 vs, 1800 vs (CO). *Anal. Calc.* for $\text{C}_7\text{H}_{13}\text{BrN}_2\text{O}_2\text{W}$: N, 6.66; C, 19.97; H, 3.11. Found: N, 6.69; C, 20.03; H, 3.16%.

4.3.3. $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{N}_3)$ (**3**)

NaN_3 (65.4 mg, 1.0 mmol in 5 mL of acetonitrile) solution was added drop wise into $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{Br})$ (333.1 mg, 1.0 mmol in 20 mL acetonitrile) solution during a 5 min period. After stirred at room temperature for 8 h, the yellow solution was filtrated and the yellow solid left was washed with acetonitrile several times until none yellow species could be extracted. Solvent was removed from this yellow solution and the resulting yellow solid was dissolved in DME and layered with hexane for crystallization. The product was isolated as orange crystals (160.0 mg, 54%). ^1H NMR (CD_3OD , -60°C): δ 5.91 (br, s, 0.8H, NH_2), 3.71 (m, 1.8H, H_c and NH_2), 3.48 (br, s, 0.8H, NH_2), 3.25 (br, s, 0.8H, H_s), 3.07 (br, s, 1H, NH_2), 3.00 (br, s, 1H, H_s), 2.69 (m, 1H, en), 2.56 (m, 1H, en), 2.42 (m, 1H, en), 2.37 (m, 1H, en), 0.99 (d, 1H, $J = 10.0$ Hz, H_a), and 0.96 (d, 1H, $J = 11.7$ Hz, H_a) ppm. ^{13}C NMR (CD_3OD , -60°C): δ 226.07, 225.83 (CO), 68.28 (C_c), 55.64, 53.58 (C_t), 43.21, 41.35 (en) ppm. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 2057 s (N_3), 1924 vs, 1814 vs (CO). *Anal. Calc.* for $\text{C}_7\text{H}_{13}\text{N}_5\text{MoO}_2$: N, 23.73; C, 28.48; H, 4.45. Found: N, 23.72; C, 28.56; H, 4.44%.

4.3.4. $\text{W}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{N}_3)$ (**4**)

A procedure similar to the one described for the preparation of **3** was used. The reaction of NaN_3 (65.2 mg, 1.0 mmol) with $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{en})\text{Br}$ (421.0 mg, 1.0 mmol) afforded 188.5 mg (49.2%) orange crystals of **4**. ^1H NMR (CD_3OD , -60°C): δ 6.00 (br, s, 0.5H, NH_2), 3.95 (br, s, 0.5H, NH_2), 3.87 (br, s, 0.5H, NH_2), 3.50 (br, s, 0.5H, NH_2), 3.06 (br, s, 1H, H_s), 2.86 (m, 1H, H_c), 2.79 (m, 2H, H_s , and en), 2.68 (m, 1H, en), 2.49 (m, 2H, en), 1.07 (d, $J = 9.2$ Hz, 1H, H_a), 1.04 (d, $J = 8.9$ Hz, 1H, H_a) ppm. ^{13}C NMR (CD_3OD , -60°C): δ 219.32, 218.71 (CO), 59.54 (C_c), 47.83, 45.24 (C_t), 43.58, 41.85 (en) ppm. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 2065 s (N_3), 1914 vs, 1794 vs (CO). *Anal. Calc.* for $\text{C}_7\text{H}_{13}\text{N}_5\text{O}_2\text{W}$: N, 18.28; C, 21.95; H, 3.42. Found: N, 18.62; C, 22.07; H, 3.50%.

4.3.5. $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{CN})$ (**5**)

In a drybox 333.2 mg (1.0 mmol) of $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{en})\text{Br}$ and 147.3 mg (3.0 mmol) of NaCN were added into a 50 mL flask. After degassing, about 20 mL of methanol was transferred into the flask and the solution was stirred at RT overnight. The solvent was removed under a dynamic pump and the resulting orange solid was extracted with DME several times until the orange color was fade. The solution was collected and the solvent was removed under a dynamic pump. The resulting red color solids were dissolved in methanol for crystallization. A 170.2 mg (61.0% yield) of red crystals of $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{CN})$ was obtained after slow evaporation of the solution. ^1H NMR (CD_3OD , -60°C): isomer A, δ 3.64 (m, 1H, H_c), 3.43 (s, 2H, NH_2), 3.13 (br, s, 4H, H_s , and NH_2), 2.71 (m, 2H, en), 2.43 (m, 2H, en), 1.17 (d, $J = 9.6$ Hz, 2H, H_a) ppm. Isomer B, δ 5.80 (br, s, 1H, NH_2), 4.02 (br, s, 1H, NH_2), 3.84 (m, 1H, H_c), 3.77 (br, s, 1H, NH_2), 3.48 (br, s, 1H, NH_2), 3.26 (m, 1H, H_s), 2.84 (m, 2H, en), 2.62 (m, 1H, H_s), 2.57 (m, 2H, en), 0.92 (d, $J = 8.6$ Hz, 1H, H_a), 0.68 (d, $J = 8.6$ Hz, 1H, H_a) ppm. ^{13}C NMR (CD_3OD , -60°C): isomer A, δ 225.12 (CO), 157.10 (CN), 71.17 (C_c), 54.26 (C_t), 42.37 (en) ppm. Isomer B, δ 226.27, 225.98 (CO), 64.54 (C_c), 52.42, 50.97 (C_t), 44.20, 42.61 (en) ppm. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 2099 m (CN), 1926 vs, 1852 vs, 1819 vs (CO). IR (methanol): $\nu_{\text{max}}/\text{cm}^{-1}$: 2110 m (CN), 1945 vs, 1857 vs (CO). *Anal. Calc.* for $\text{C}_8\text{H}_{13}\text{N}_3\text{O}_2\text{Mo}$: N, 15.06; C, 34.42; H, 4.70. Found: N, 15.19; C, 34.36; H, 4.75%.

4.3.6. $\text{W}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})(\text{CN})$ (**6**)

A procedure similar to the one described for the preparation of **5** was used. The reaction of NaCN (148.0 mg, 3.0 mmol) with $\text{W}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{en})\text{Br}$ (421.0 mg, 1.0 mmol) afforded 227.6 mg (62.0%) red crystals of **6**. ^1H NMR (CD_3OD , -60°C): isomer A, δ 3.95 (br, s, 2H, NH_2), 3.43 (br, s, 2H, NH_2), 2.95 (d, $J = 5.7$ Hz, 2H, H_s), 2.79 (br, s, 3H, H_c , and en), 2.49 (br, s, 2H, en), and 1.24 (d, $J = 8.8$ Hz, 2H, H_a) ppm. Isomer B, δ 6.05 (br, s, 1H, NH_2), 4.45 (br, s, 1H, NH_2), 4.07 (br, s, 1H, NH_2), 3.95 (br, s, 1H, NH_2), 3.07 (m, 1H, H_c), 2.99 (m, 1H, H_s), 2.86 (br, s, 2H, en), 2.66 (br, s, 2H, en), 2.35 (br, s, 1H, H_s), 0.94 (d, $J = 8.0$ Hz, 1H, H_a), 0.72 (d, $J = 8.0$ Hz, 1H, H_a) ppm. ^{13}C NMR (CD_3OD , -60°C): isomer A, δ 218.52 (CO), 158.71 (CN), 64.16 (C_c), 47.24 (C_t), 44.60 (en) ppm. Isomer B, δ 219.19, 216.48 (CO), 157.25 (CN), 57.11 (C_c), 46.23, 45.13 (C_t), 44.33, 44.14 (en) ppm. IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 2110 m (CN), 1893 vs, 1794 vs (CO). *Anal. Calc.* for $\text{C}_8\text{H}_{13}\text{N}_3\text{O}_2\text{W}$: N, 11.44; C, 26.18; H, 3.57. Found: N, 11.40; C, 26.09; H, 3.65%.

4.3.7. $[(\text{en})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-CN})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{en})]\text{Br}$ (**7**)

In a drybox 334.3 mg (1.0 mmol) of $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{en})\text{Br}$ and 24.5.1 mg (0.5 mmol) of NaCN were added into a 50 mL flask. After degassing, about 20 mL of methanol was transferred into the flask and the solution was stirred at RT overnight. The solvent was removed under a dynamic pump. The resulting solid was extracted with 20 mL DME twice. The DME was removed from the solution and the resulting solid was dissolved in methanol for crystalliza-

tion. About 241.3 mg (75.0% yield) yellow crystals of $[(en)(\eta^3-C_3H_5)(CO)_2Mo(\mu-CN)Mo(CO)_2(\eta^3-C_3H_5)(en)]Br \cdot CH_3OH$ were obtained. 1H NMR (CD_3OD , 60 °C): δ 4.12 (br, s, 0.6H, NH_2), 3.79 (m, 2H, H_C), 3.19 (d, $J = 6.4$ Hz, 2H, H_S), 3.10 (d, $J = 6.4$ Hz, 2H, H_S), 2.67 (m, 8H, en), 1.16 (d, $J = 9.6$ Hz, 2H, H_A), and 1.09 (d, $J = 9.2$ Hz, 2H, H_A) ppm. ^{13}C NMR (CD_3OD , 60 °C): δ 224.88 (CO), 69.83 (C_C), 55.45, 54.04 (C_C), 43.06, 42.74 (en) ppm. IR (KBr): ν_{max}/cm^{-1} 2127 m (CN), 1940 vs, 1920 vs, 1845 s, 1806 s (CO). *Anal. Calc.* for $C_{16}H_{30}BrMo_2N_5O_5$: N, 10.87; C, 29.83; H, 4.69. Found: N, 10.94; C, 29.78; H, 4.71%.

4.3.8. $[(en)(\eta^3-C_3H_5)(CO)_2W(\mu-CN)W(CO)_2(\eta^3-C_3H_5)(en)]Br$ (**8**)

A procedure similar to the one described for the preparation of **7** was used. The reaction of $W(\eta^3-C_3H_5)(CO)_2(en)Br$ (420.2 mg, 1.0 mmol) and NaCN (24.6 mg, 0.50 mmol) afforded 251.1 mg (61.2% yield) yellow crystals of $[(en)(\eta^3-C_3H_5)(CO)_2W(\mu-CN)W(CO)_2(\eta^3-C_3H_5)(en)]Br \cdot CH_3OH$. 1H NMR (d_8 -THF, 60 °C): δ 4.70 (br, s, 3.2H, NH_2), 3.40 (m, 2H, H_C), 2.93 (d, $J = 6.4$ Hz, H_S), 2.88 (br, s, en), 2.69 (br, 4H, en), and 1.08 (br, 4H, H_A) ppm. ^{13}C NMR (d_8 -THF, 60 °C): δ 216.03 (CO), 62.55, 61.41 (C_C), 48.66 (C_C), 46.09 (C_C , en), and 45.38 (en) ppm. IR (KBr): ν_{max}/cm^{-1} 2124 m (CN), 1932 vs, 1909 vs, 1834 vs, 1793 vs (CO). *Anal. Calc.* for $C_{16}H_{30}BrN_5O_5W_2$: N, 8.54; C, 23.44; H, 3.69. Found: N, 8.50; C, 23.52; H, 3.71%.

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Appendix A. Supplementary data

CCDC 732782, 732783, 732784, 732785, 732786, 732787, 732788 and 732789 contains the supplementary crystallographic data for **1–8**. 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.2009.10.031](https://doi.org/10.1016/j.jorganchem.2009.10.031).

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