Syntheses, structures, and dynamic properties of $M(CO)_2(\eta^3\text{-}C_3H_5)(en)(X)$ (M = Mo, W; X = Br, N_3, CN) and $[(en)(\eta^3\text{-}C_3H_5)(CO)_2M(\mu\text{-}CN)M(CO)_2(\eta^3\text{-}C_3H_5)(en)]Br$ (M = Mo, W)

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ABSTRACT

Mononuclear compounds $M(CO)_2(\eta^3\text{-}C_3H_5)(en)(X)$ (X = Br, M = Mo(1), W(2); X = N_3, M = Mo(3), W(4); X = CN, M = Mo(5), W(6)) and cyanide-bridged bimetallic compounds $[(en)(\eta^3\text{-}C_3H_5)(CO)_2M(\mu\text{-}CN)M(CO)_2(\eta^3\text{-}C_3H_5)(en)]Br$ (M = Mo (7), W(8)) were prepared and characterized. These compounds are fluxional and display broad unresolved proton NMR signals at room temperature. Compounds 1–6 were characterized by NMR spectroscopy at −60 °C, which revealed isomers in solution. The major isomers of 1–4 adopt an asymmetric endo-conformation, while those of 5 and 6 were both found to possess a symmetric endo-conformation. The single crystal X-ray structures of 1–6 are consistent with the structures of the major isomer in solution at low temperature. In contrast to mononuclear terminal cyanide compounds 5 and 6, cyanide-bridged compounds 7 and 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 $M(CO)_2(\eta^3\text{-}C_3H_5)(L\text{–}L)(X)$ (M = Mo, W; L–L = bidentate ligand; 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 $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(CH_3CN)]^+$ [18] adopts conformation **C**, in contrast to the non-rigid chelating compounds $Mo(CO)_2(\eta^3\text{-}C_3H_5)(dmpm)(N_3)$ (dmpm = bis-(dimethylphosphino)methane) [19], $Mo(CO)_2(\eta^3\text{-}C_3H_5)(glyme)(CF_3CO_2)$ [20], and $Mo(CO)_2(\eta^3\text{-}C_3H_5)(dmpm)(CN)$ [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 $M(CO)_2(\eta^3\text{-}$ $C_3H_5)(dppe)(X)$ 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 $M(CO)_2(\eta^3\text{-}C_3H_5)(en)(X)$ (M = Mo, W; X = Br, N_3, CN) and the cyano-bridged bimetallic complexes $[(en)(\eta^3\text{-}C_3H_5)(CO)_2M(\mu\text{-}CN)M(CO)_2(\eta^3\text{-}C_3H_5)(en)]Br$ (M = Mo, W).

2. Results and discussion

2.1. Preparations and properties of $M(CO)_2(\eta^3\text{-}C_3H_5)(en)(X)$ (X = Br, M = Mo(1), W(2); X = N_3, M = Mo(3), W(4); X = CN, M = Mo(5), W(6)), and $[(en)(\eta^3\text{-}C_3H_5)(CO)_2M(\mu\text{-}CN)M(CO)_2(\eta^3\text{-}C_3H_5)(en)]Br$ (M = Mo (7), W(8))

Compounds $M(CO)_2(\eta^3\text{-}C_3H_5)(en)(Br)$ (M = Mo(1), W(2)) were prepared from the reaction of $M(CO)_2(\eta^3\text{-}C_3H_5)(CH_3CN)_2(Br)$ (M = Mo, W) with 1,2-ethylenediamine (en), according to Eq. (1).
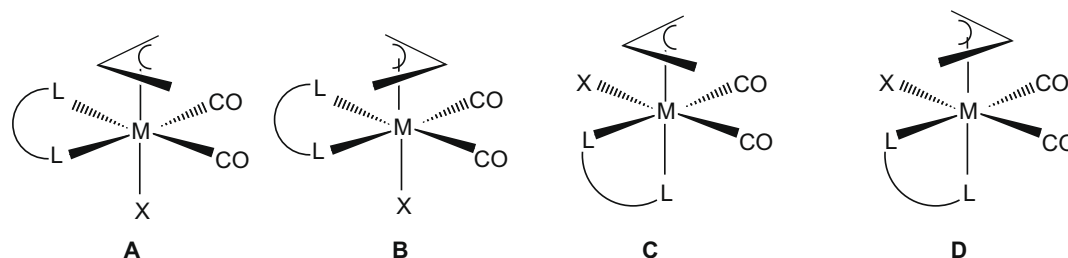
Scheme 1.

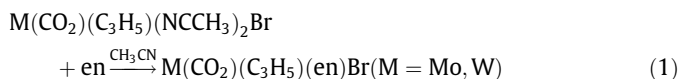Azides $M(CO)_2(\eta^3\text{-}C_3H_5)(en)(N_3)$ (M = Mo(**3**), W(**4**)) were obtained from bromides **1** and **2**, respectively, via a metathesis reaction with sodium azide (Eq. (2)). Whether the terminal or bridging cyanide complex is formed depends on the ratio of the reactants. Reactions of **1** and **2** with excess sodium cyanide furnished terminal cyanides $M(CO)_2(\eta^3\text{-}C_3H_5)(en)(CN)$ (M = Mo(**5**), W(**6**)), respectively (Eq. (3)). When only half equivalent of sodium cyanide was used, the bridging cyanide complexes $[(en)(\eta^3\text{-}C_3H_5)(CO)_2M(\mu\text{-}CN)M(CO)_2(\eta^3\text{-}C_3H_5)(en)]Br$ (M = 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 = Cl, Br, 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.

$$M(CO_2)(C_3H_5)(NCCH_3)_2Br$$
$$+ en \xrightarrow{CH_3CN} M(CO_2)(C_3H_5)(en)Br(M = Mo, W) \qquad (1)$$

$$M(CO_2)(C_3H_5)(en)Br$$
$$+ NaN_3 \xrightarrow{CH_3CN} M(CO_2)(C_3H_5)(en)N_3$$
$$+ NaBr \quad (M = Mo, W) \qquad (2)$$

$$M(CO_2)(C_3H_5)(en)Br$$
$$+ NaCN \xrightarrow{CH_3OH} M(CO_2)(C_3H_5)(en)CN + NaBr \quad (M = Mo, W) \qquad (3)$$

$$2M(CO_2)(C_3H_5)(en)Br$$
$$+ NaCN \xrightarrow{CH_3OH} [(CO_2)(C_3H_5)(en)M(u\text{-}CN)M(CO_2)$$
$$(C_3H_5)(en)]Br + NaBr \quad (M = Mo, W) \qquad (4)$$
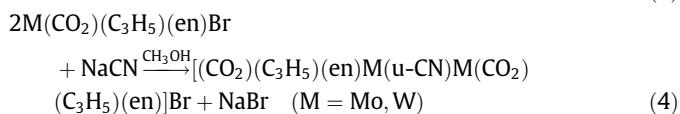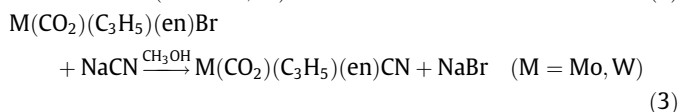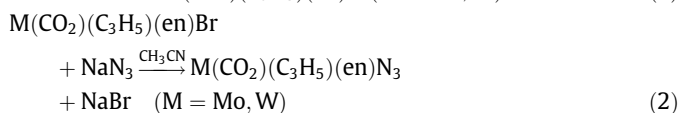
2.2. Spectroscopic studies

Among the group 6 metal allyl complexes $M(CO)_2(\eta^3\text{-}C_3H_5)(L\text{-}L)(X)$ 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 ^1H–^1H COSY and ^1H–^{13}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 $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(NCH)_3]^+$ and $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(Cl)_3]^-$ 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 $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(NCH)]^+$ [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 ^1H–^1H COSY and ^1H–^{13}C HMQC 2D NMR at 60 °C. The broad carbon signals at 61.41 (C_c), 48.66 (C_t), 46.09 (C_t, 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*-$M(CO)_2$ 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-