

Activation of CO by Hydrogenated Magnesium(I) Dimers: Sterically Controlled Formation of Ethenediolate and Cyclopropanetriolate Complexes

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Supporting Information

ABSTRACT: This study details the formal hydrogenation of two magnesium(I) dimers $\{(\text{Nacnac})\text{Mg}\}_2$ ($\text{Nacnac} = [(\text{C}_6\text{H}_3\text{R}_2-2,6)\text{NCMe}_2\text{CH}]^-$; $\text{R} = \text{Pr}^i$ ($^{\text{Dip}}\text{Nacnac}$), Et ($^{\text{Dep}}\text{Nacnac}$)) using 1,3-cyclohexadiene. These reactions afford the magnesium(II) hydride complexes, $\{(\text{Nacnac})\text{Mg}(\mu\text{-H})\}_2$. Their reactions with excess CO are sterically controlled and lead cleanly to different C–C coupled products, viz. the ethenediolate complex, $(^{\text{Dip}}\text{Nacnac})\text{Mg}\{\kappa^1\text{-O}[(^{\text{Dip}}\text{Nacnac})\text{Mg}(\kappa^2\text{-O},\text{O}-\text{O}_2\text{C}_2\text{H}_2)]\}$, and the first cyclopropanetriolate complex of any metal, $\text{cis}\{(^{\text{Dep}}\text{Nacnac})\text{Mg}\}_3\{\mu\text{-C}_3(\text{H}_3)\text{O}_3\}$. Computational studies imply the CO activation processes proceed via very similar mechanisms to those previously reported for related reactions involving f-block metal hydride compounds. This work highlights the potential magnesium compounds hold for use in the “Fischer–Tropsch-like” transformation of CO/H₂ mixtures to value added oxygenate products.

The heterogeneously catalyzed hydrogenation of CO to hydrocarbons and oxygenates via the Fischer–Tropsch (F-T) and related processes, is well established.¹ These transformations are attractive because they can be carried out on industrial scales using synthesis gas (CO/H₂) as an abundant and cheap feedstock. However, because the CO “triple bond” is one of the strongest known (257 kcal/mol), such processes are very energy intensive and typically offer low product selectivity. With the aim of improving product selectivity and potentially identifying homogeneously catalyzed alternatives to the F-T process, extensive mechanistic modeling of the fundamental steps in CO hydrogenation reactions has been carried out using organometallic complexes.² Of importance here are reactions of metal hydride systems with CO, which are thought to lead to metal formyl intermediates that undergo subsequent C–C bond forming reactions in the presence of excess CO and/or H₂. While such modeling has been carried out with late transition-metal hydride compounds, reactions of CO with the more oxophilic early d- and f-block metal hydrides have the advantage of generating, sometimes isolable, η^2 -formyl intermediates that can be stabilized by both C- and O-coordination to the metal.²

Of most relevance to the current study are reactions of f-block (and group 3) metal hydrides with CO. In the absence of H₂ these have led to isolated *cis*- and *trans*-ethenediolate

$([\text{O}(\text{H})\text{C}=\text{C}(\text{H})\text{O}]^{2-})$ complexes of Sm,³ Yb,⁴ Ce,⁵ and Th;⁶ oxomethylene $([\text{OCH}_2]^{2-})$ complexes of Y, Lu,^{7a} and Ce;⁵ etheneolate $([\text{H}_2\text{C}=\text{C}(\text{H})\text{O}]^-)$ and propeneolate $([\text{H}_2\text{C}=\text{CHC}(\text{H})_2\text{O}]^-)$ complexes of Y;⁷ and free ethylene and propene.⁷ In the presence of H₂, the formation of methoxide $([\text{OCH}_3]^-)$ complexes of both Ce⁵ and Th⁶ has also been reported. Related to this work are a number of examples of CO reductive homologations effected by uranium(III) systems, yielding complexes bearing dianionic ligands, $([(\text{CO})_n]^{2-}, n = 2-4)$.⁸ One such reaction, carried out in the presence of H₂, has given a uranium methoxide complex, albeit probably not via a uranium hydride intermediate.⁹

Over the past several years, we have explored the chemistry of magnesium(I) dimers, LMg-MgL ($\text{L} = \beta$ -diketiminate) and have shown them to be very effective as reducing agents in both organic and inorganic syntheses.¹⁰ This work has revealed their reactivity to sometimes mirror that of low-valent f-block metal complexes in, e.g., the reduction of CO,¹¹ isocyanides and nitriles.¹² Here, we extend these analogies with f-block chemistry to magnesium(II) hydride complexes, $\text{LMg}(\mu\text{-H})_2\text{MgL}$, which are shown to be formed via the formal hydrogenation of magnesium(I) dimers. Depending on the steric bulk of the β -diketiminate ligands in these hydride species, their reactions with CO cleanly lead to the first example of a cyclopropanetriolate complex of any metal, or an unprecedented magnesium ethenediolate compound. Computational studies reveal that the mechanisms of their formations are likely to be very similar to those proposed for the reaction of f-block metal hydrides with CO.

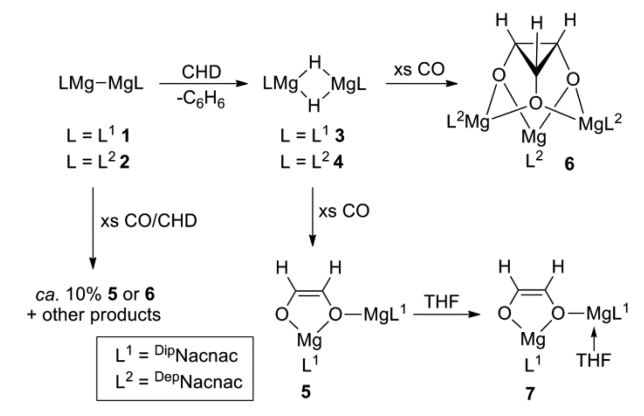
Although the main focus of this study was the “f-block metal-like” reactivity of magnesium(II) hydrides toward CO, at the outset we sought to demonstrate that the magnesium(II) hydride reactants could be generated by hydrogenation of magnesium(I) dimers. If so, this would highlight the potential Mg^{I} compounds have as reagents for the conversion of H₂/CO mixtures to value added C–C coupled products. With that said, we have previously shown that the Mg^{I} dimer, $\{(^{\text{Dip}}\text{Nacnac})\text{Mg}\}_2$ **1** ($^{\text{Dip}}\text{Nacnac} = [(\text{DipNCMe})_2\text{CH}]^-$, $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^i-2,6$) does not react with H₂ (or CO) under mild conditions, despite the hydrogenation being thermodynamically viable.¹³ Accordingly, we prepared the less hindered Mg^{I} dimer, $\{(^{\text{Dep}}\text{Nacnac})\text{Mg}\}_2$ **2** ($^{\text{Dep}}\text{Nacnac} = [(\text{DepNCMe})_2\text{CH}]^-$, $\text{Dep} = \text{C}_6\text{H}_3\text{Et}^i-2,6$; see Supporting Information (SI)), but this was also found to be unreactive

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toward H₂ (and CO) under ambient conditions. As a result, reactions of **1** and **2** with an excess of the transfer hydrogenation reagent, 1,3-cyclohexadiene (CHD), at ambient temperature, were explored. These led to the formal addition of dihydrogen to the Mg–Mg bonds of the compounds and the close to quantitative generation (>97%) of the magnesium(II) hydride compounds **3** and **4**, in addition to benzene (Scheme 1, see SI for

Scheme 1. Synthesis of Compounds 3–7



further details).¹⁴ Not surprisingly, the reaction between **2** and CHD was more rapid (complete in ca. 7 h) than that involving the more hindered dimer **1** (complete in ca. 10 h).

Toluene solutions of the magnesium hydride compounds **3** and **4** were exposed to 1 atm. of CO, and the reaction mixtures were heated at ca. 45–50 °C overnight to give close to quantitative yields of the C–C coupled products, **5** and **6** respectively, as determined by NMR spectroscopic analyses of the mixtures (Scheme 1).¹⁵ However, the isolated crystalline yield of the very soluble compound, **6**, was variable, while **5** could not be obtained as a crystalline solid in our hands. Consequently, THF was added to a benzene solution of **5**, which afforded a good isolated yield of the adduct complex, **7**, as colorless needles. The course of each of these reactions was monitored by ¹H NMR spectroscopy, though no intermediates were observed in any case. In addition, and in an attempt to demonstrate the potential for generating C–C coupled products from reactions of H₂/CO mixtures with Mg^I dimers, compounds **1** and **2** were again treated with CHD, but under an atmosphere of CO. While these reactions yielded mixtures of products, they did give rise to small amounts (ca. 10%) of the magnesium ethenediolate and cyclopropane-bridged complexes **5** and **6**, respectively (as determined by NMR spectroscopic analyses of the reaction mixtures). The identity of the other products of these reactions is unknown at this stage. It is also of note that both **5** and **6** are resistant to reaction with excess H₂ and/or CO under ambient reaction conditions.

In view of the fact that isocyanides are isolobal with CO, and for sake of comparison with the formation of **5** and **6**, reactions of CNR (R = Bu^t or cyclohexyl (Cy)) with **3** and **4** were carried out. However, in all cases C–C bond forming reactions did not occur, and instead the alkylformimidoyl bridged complexes **8–11** were obtained in moderate isolated yields (Scheme 2). These reactions likely proceed via insertion of the isocyanide into the Mg–H bonds of **3** and **4**, in a similar fashion to that proposed for related reactions between isocyanides and lanthanide hydride complexes.¹⁶ Given this result, it seemed possible that formyl bridged dimers with structures related to **8–11** are intermediates in the reactions that ultimately afforded **5** and **6** (*vide infra*).¹⁷

Scheme 2. Synthesis of Compounds 8–11

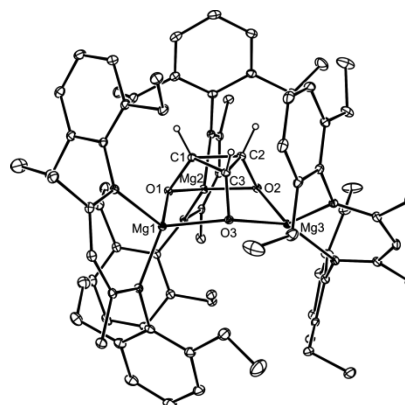
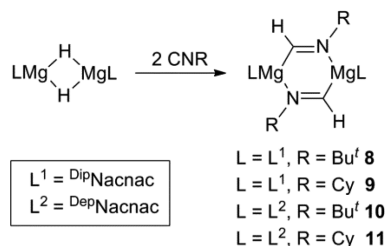


Figure 1. Thermal ellipsoid plot (20% probability surface) of **6**. Selected bond lengths (Å) and angles (deg): C(1)–C(2) 1.526(2), C(1)–C(3) 1.532(2), C(2)–C(3) 1.528(2), C–O 1.400(2)–1.411(2), Mg–O 1.991(1)–2.025(1), C(2)–C(1)–C(3) 60.0(1), C(1)–C(2)–C(3) 60.2(1), C(2)–C(3)–C(1) 59.8(1), O–Mg–O 85.91(5)–88.42(5).

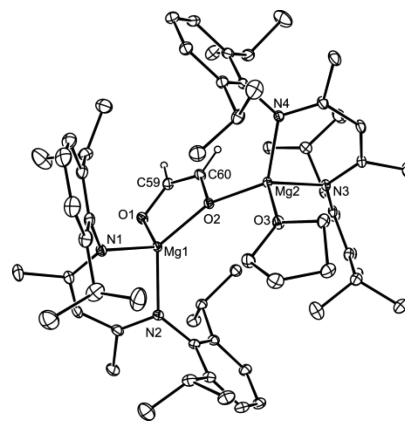


Figure 2. Thermal ellipsoid plot (20% probability surface) of **7**. Selected bond lengths (Å) and angles (deg): C(59)–C(60) 1.333(2), O(1)–C(59) 1.331(2), O(2)–C(60) 1.414(2), Mg(1)–O(1) 1.944(1), Mg(1)–O(2) 2.017(1), Mg(2)–O(2) 1.940(1), Mg(2)–O(3) 2.000(1), O(1)–Mg(1)–O(2) 88.79(5), O(2)–Mg(2)–O(3) 101.70(6).

Compounds **5–7** are all thermally stable in the solid state. In solution, their NMR spectral patterns imply more symmetrical structures than those found in the solid state for **6** and **7** (*vide infra*), and that proposed for **5**. This suggests that fluxional processes are in operation in solution, though attempts to shed light on these using variable-temperature NMR spectroscopic studies were thwarted by low compound solubility (**7**) or NMR spectra not resolving at low temperatures (**5** and **6**). Although it cannot be sure what the structure of **5** is in the solid state, that proposed seems reasonable based on the elucidated structure of the adduct complex, **7**. Moreover, a very similar structure has been suggested for the ethenediolato product,

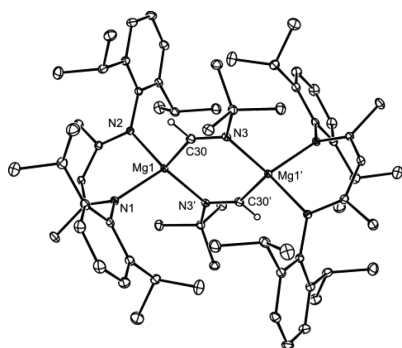


Figure 3. Thermal ellipsoid plot (20% probability surface) of **8**. Selected bond lengths (Å) and angles (deg): Mg(1)–N(3)′ 2.123(11), Mg(1)–C(30) 2.194(11), N(3)–C(30) 1.288(2), N(3)′–Mg(1)–C(30) 111.69(5).

$\text{Cp}^*_2\text{Sm}\{\kappa^1\text{-O-}[\text{Cp}^*_2\text{Sm}(\kappa^2\text{-O,O-O}_2\text{C}_2\text{H}_2)]\}$ ($\text{Cp}^* = \text{C}_5\text{Me}_5^-$), that arises from the reaction of Cp^*_2SmH with CO.³ All of the alkylformimidoyl complexes, **8–11**, are thermally stable in the solid state, and in benzene solutions do not decompose or undergo further reactions at temperatures of up to 70 °C. The NMR spectra of the compounds are consistent with their proposed formulations.

The molecular structures of the representative complexes, **6–8**, are depicted in Figures 1, 2, and 3, while full details of the crystallographic characterization of other compounds can be found in the SI. Compound **7** represents the first example of a cyclopropanetriolate complex, structurally characterized or otherwise. The trianionic $[\text{H}_3\text{C}_3\text{O}_3]^{3-}$ ligand is essentially symmetrical, with all of its O-centers *cis*-relative to each other. It chelates three $\text{Mg}(\text{Dip}^{\text{Dep}}\text{Nacnac})$ fragments, giving rise to an overall “bowl-like” structure. The complex can be compared to Cloke’s CO homologated, planar deltate compound $\{\text{Cp}^*[\text{C}_8\text{H}_6(\text{SiPr}_3)_2]\text{U}^{\text{IV}}\}_2(\mu\text{-C}_3\text{O}_3)$,^{8c} which has been proposed as a precursor to 1,2,3-cyclopropanetriol (i.e., the conjugate acid of the triolate ligand in **6**), via its hydrogenation.¹⁸

The ethenediolate ligand of compound **7** chelates one $\text{Mg}(\text{Dip}^{\text{Dep}}\text{Nacnac})$ fragment, while coordinating to the other Mg center in a κ^1 -fashion. It is worthy of note that no ethenediolate chelated metal complexes have been previously structurally characterized, despite the existence of a number of known ethenediolate bridged bimetallic systems.^{3,5} The structure of compound **8** is very similar to those of **9–11**, in that the alkylformimidoyl ligands bridge two magnesium centers by coordination through both their N- and alkenyl C atoms. This arrangement is closely related to that in $\text{Bu}^t_2\text{Al}\{\mu\text{-C}(\text{H})\text{N}(\text{Bu}^t)\}_2\text{AlBu}^t_2$, prepared via the hydroalumination of CNBu^t .¹⁹

In order to gain an understanding of the mechanisms of the magnesium(I) dimer hydrogenations and the formation of the CO activated compounds, **5** and **6**, DFT calculations (B3PW91) were enlisted (see Figure 4). The former was found to proceed via a similar route to that recently described for the transfer hydrogenation of a germanium(I) dimer, $\text{L}'\text{GeGeL}'$ ($\text{L}' =$ bulky amide), by CHD.²⁰ That is, CHD inserts into the Mg–Mg bond of **1** or **2**, yielding $\text{LMg}(\mu\text{-1,4-C}_6\text{H}_8)\text{MgL}$, with two subsequent β -hydride eliminations from the bridging ligand to give **3** or **4** and benzene. Both reactions were calculated to be similarly exothermic ($\Delta H = -21.4$ kcal/mol **3**; -30.7 kcal/mol **4**).

With regards to the CO activation products, **5** and **6**, the possibility that the compounds were generated via hydro-magnesiation of CO, yielding formyl bridged dimeric intermediates, *cis*- or *trans*- $[(\text{Nacnac})\text{Mg}\{\mu\text{-C}(\text{H})\text{O}\}]_2$ (cf. **8–11**), was initially explored. However, no pathway from these to ethenediolate or cyclopropanetriolate compounds was found. Instead, calculations suggest that **5** and **6** are formed by very similar mechanisms to those proposed for the synthesis of f-block ethenediolate complexes (Figure 4, see SI for full reaction pathways).^{3,5,6,21} That is, the magnesium hydride dimers **3** and **4** react with one molecule of CO to give transient $\kappa^2\text{-C,O}$ -formyl complexes, e.g., **VI** (from **3**), the C–O bonds of which insert into the Mg–H bond of magnesium hydride fragments, e.g., **IV** (from **3**), to give bridged oxomethylene compounds, e.g., **VIII** (from **3**). A second molecule of CO inserts into one Mg–C bond of the

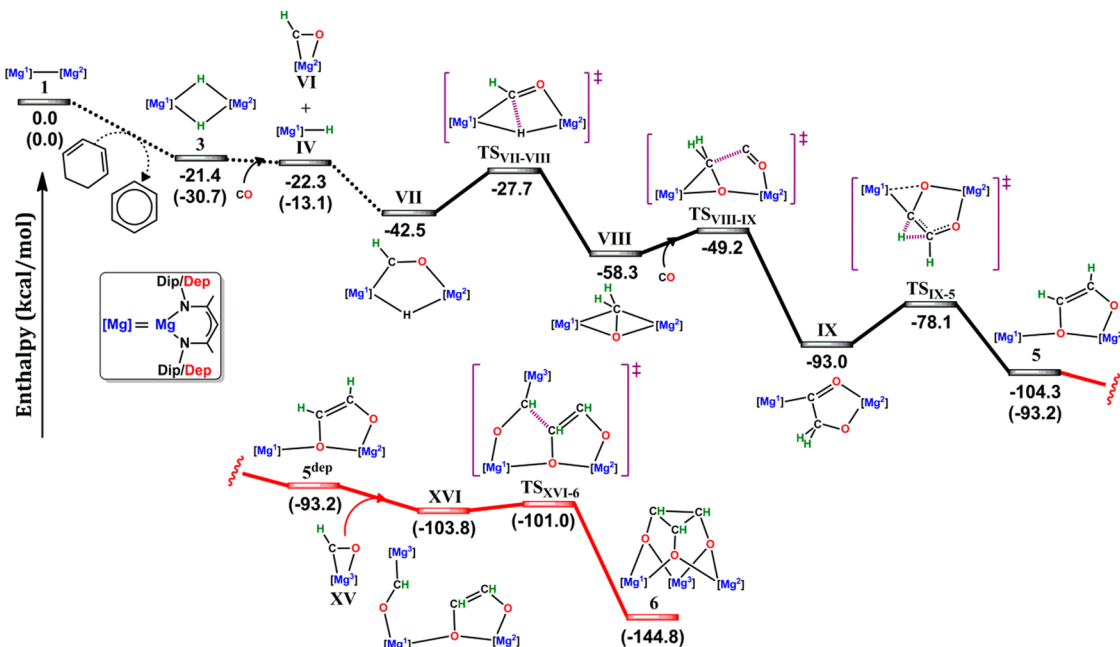


Figure 4. Simplified reaction profiles for the formation of **5** from **1** (top, black line) and **6** from **5^{Dep}** (bottom, red line). Enthalpies in parentheses correspond to processes involving $\text{Dip}^{\text{Dep}}\text{Nacnac}$ -substituted species. See SI for further details.

oxomethylene compounds, and subsequent 1,2-hydrogen migrations within the coordinated $C_2H_2O_2$ fragments occur to give the magnesium ethenediolate chelate complexes, **5** and **5^{Dep}**. In the case of the reaction involving the bulkier (^{Dep}Nacnac)Mg fragments, the conversion of **5** to a cyclopropanetriolate complex was found to be not kinetically viable, and its formation from **3** and two molecules of CO was determined to be moderately exothermic ($\Delta H = -82.9$ kcal/mol). In contrast, the ethenediolate incorporating the less bulky (^{Dep}Nacnac)Mg fragments, viz. **5^{Dep}**, can react with a molecule of the ^{Dep}Nacnac substituted analogue of formyl complex **VI**, viz. **XV**, the O-center of which attacks the κ^1 -O-coordinated Mg atom of **5^{Dep}**, followed by two C–C bond formations, to give the cyclopropanetriolate complex, **6**. The formation of this compound from 1.5 molecules of **4** and three molecules of CO is exothermic by 114.1 kcal/mol. Several other possible pathways to **5** and **6** were examined, though all were found to be kinetically less viable than those proposed above (see SI for further details).

In summary, the formal hydrogenation of two magnesium(I) dimers has been achieved. Unprecedented reactions of CO with the magnesium(II) hydride products of these hydrogenations led cleanly to C–C coupled species, the nuclearity of which is dependent upon the steric bulk of the magnesium hydride reactant. These coupled products include the first cyclopropanetriolate complex of any metal. Computational studies imply that the CO activation reactions proceed via very similar mechanisms to those previously proposed for related reactions involving f-block metal hydride compounds. Accordingly, and further to previous work from our group, this study highlights the potential magnesium hydride compounds possess as cheap, non-toxic, nonradioactive, and diamagnetic alternatives to analogues derived from the lanthanide and actinide elements. In addition, and considering that the transfer hydrogenation of magnesium(I) dimers carried out under an atmosphere of CO leads to C–C coupled alkoxy products, we believe that more reactive examples of such dimers could find use for the stoichiometric or catalytic “F–T-like” transformation of CO/H₂ mixtures to value added oxygenate products. We are currently exploring this possibility.

■ ASSOCIATED CONTENT

Supporting Information

Details of the synthesis and characterizing data for all new compounds. Full details and references for the crystallographic and computational data. Crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06439.

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Notes

The authors declare no competing financial interest.

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