Rapid Communication

Open Access

Jamie Hicks, Martin Juckel, and Cameron Jones*

X-ray crystal structures of carbonate and hydroxide bridged Mn^{II}/Mg^{II} heterobimetallic complexes formed by reduction of CO₂ or H₂O by a Mn⁰–Mg^{II} bonded compound

<https://doi.org/10.1515/mgmc-2021-0027>

received August 06, 2021; accepted August 28, 2021

Abstract: The previously reported Mn⁰–Mg^{II} bonded heterobimetallic compound [L⁺Mn–Mg^{(Mes)Nacnac}] (L⁺ = –N(Ar⁺)(SiPrⁱ), Ar⁺ = C₆H₂{C(H)Ph₂}₂Prⁱ-2,6,4; MesNacnac = [(MesNCMe)₂CH]; Mes = mesityl) forms an adduct complex, [L⁺Mn–Mg(THF)^{(Mes)Nacnac}], when dissolved in THF. Adventitious water is shown to be reduced by [L⁺Mn–Mg^{(Mes)Nacnac}] to give the hydroxide bridged heterobimetallic, [L⁺Mn(μ-OH)₂Mg^{(Mes)Nacnac}]. The Mn⁰–Mg^{II} bonded heterobimetallic reductively disproportionates CO₂, affording the carbonate bridged species, [(L⁺Mn(μ-CO₃)Mg(THF)^{(Mes)Nacnac})]₂, in the presence of THF. The three new compounds have been crystallographically characterized.

Keywords: heterobimetallic, magnesium, manganese, metal-metal bond, carbonate

The chemistry of metal-metal bonded complexes has been intensively studied for decades (Liddle, 2015). This is true for both homo- and heterobimetallic systems, numerous examples of which have found applications in areas as varied as catalysis, small molecule activation, materials science, and enzyme mimicry (Buchwalter et al., 2015; Cooper et al., 2012; Lorion et al., 2017). A degree of advantageous cooperativity between the metal centers in bimetallics is often observed in these applications, which is not possible for their mono-metallic counterparts. Although the field has been dominated by species incorporating d-block metals, compounds

containing unsupported main group metal-metal bonds are becoming more wide-spread (Liddle, 2015). In this arena, we reported the first stable s-block metal-metal bonded compounds, LMg–MgL (L = bulky guanidinate or β-diketiminato) in 2007 (Green et al., 2007), and have since shown these magnesium(I) compounds to be invaluable as reducing agents in both organic and inorganic synthetic methodologies (Jones, 2017).

With regard to inorganic synthesis, one of the most fascinating applications of magnesium(I) complexes has been their use in the formation of compounds bearing unprecedented examples of unsupported Mg–metal bonds (Dange et al., 2019; Hicks et al., 2015). Most relevant to this study is the Mn⁰–Mg^{II} bonded compound **1** (Scheme 1), which was prepared by Mg^I reduction of a bulky amido manganese(II) bromide precursor (Hicks et al., 2014). Compound **1** contains a two-coordinate, high-spin, formally manganese(0) center, that is covalently bonded to a β-diketiminato magnesium(II) fragment. In preliminary work, the high reactivity of **1** was demonstrated by reductive insertion of a carbodiimide into its Mn–Mg bond to give [L⁺Mn{μ-κ¹-C:κ²-N,N'-C(NPrⁱ)₂}Mg^{(Mes)Nacnac}] (L⁺ = –N(Ar⁺)(SiPrⁱ), Ar⁺ = C₆H₂{C(H)Ph₂}₂Prⁱ-2,6,4; MesNacnac = [(MesNCMe)₂CH]; Mes = mesityl); and by its oxidation with N₂O, affording the oxo-bridged system [L⁺MnOMg(THF)^{(Mes)Nacnac}] (Hicks et al., 2014). Here, we show that CO₂ (isoelectronic to carbodiimides) undergoes reductive disproportionation when reacted with **1**, yielding a bimetallic carbonate complex, while partial hydrolysis of **1** gives a hydroxide bridged heterobimetallic. A THF adduct of **1** is also prepared. The X-ray crystal structures of all compounds are discussed.

In order to demonstrate the electrophilicity of low-coordinate **1**, it was dissolved in THF, which afforded the blue-green crystalline adduct complex **2** in an isolated yield of 87% (Scheme 1). Interestingly, the two-coordinate

* Corresponding author: Cameron Jones, School of Chemistry, Monash University, P.O. Box 23, Melbourne, Victoria, 3800, Australia, e-mail: cameron.jones@monash.edu

Jamie Hicks and Martin Juckel: School of Chemistry, Monash University, P.O. Box 23, Melbourne, Victoria, 3800, Australia

Scheme 1: Synthesis of compounds 2-4.

Mn⁰ center of the compound resists coordination by THF, probably due to its sterically protected and electron rich nature. Compound 2 is paramagnetic, exhibiting a magnetic moment of $5.3 \mu_{\text{B}}$, consistent with it containing a high-spin Mn centre, as is the case for 1 ($\mu_{\text{eff}} = 5.3 \mu_{\text{B}}$). It is of note that, on several occasions, when toluene solutions of 1 were exposed to small amounts of adventitious water, a few yellow crystals of the hydroxide bridged bimetallic compound 3 were obtained. As this compound could not be obtained in higher yields by rational syntheses, no spectroscopic data could be obtained for it. However, its X-ray crystal structure is included here due to its novelty (see below). In light of the synthesis of 2, it seems likely that 3 is formed by initial nucleophilic attack of water at the Mg center of 1, followed by reduction of the coordinated water, and generation of dihydrogen gas.

With respect to reaction of 1 with electrophiles, when toluene solutions of the compound are placed under an atmosphere of CO_2 , the carbonate bridged heterobimetallic complex 4 is obtained as a yellow solid in very isolated low yield (<2%), after treatment of the reaction solution with THF. While it cannot be sure what the mechanism of formation of 4 entails, the reaction is closely related to that of CO_2 with a magnesium(I) dimer, $[\{(\text{DipNacnac})\text{Mg}\}_2]$, which yields the carbonate bridged species, $[\{(\text{DipNacnac})\text{Mg}\}_2(\mu\text{-CO}_3)]$, via elimination of

CO (Lalrempuia et al., 2013). In that case, experimental evidence suggested the initial reduction of CO_2 to CO yielded the oxo-bridged intermediate, $[\{(\text{DipNacnac})\text{Mg}\}_2(\mu\text{-O})]$, which cleanly reacts with CO_2 to give the carbonate product (Boutland et al., 2015; Lalrempuia et al., 2013). With that said, a later computational study indicated that a more concerted process is also possible (Kefalidis, 2014). As was the case with 3, the very low yield of 4 precluded the acquisition of meaningful spectroscopic data.

The X-ray crystal structures of 2-4 were determined and their molecular structures are shown in Figures 1-3 (see also Table 1). The structure of 2 (Figure 1) is closely related to that of 1, and the compound represents only the second Mn-Mg covalently bonded system. The THF coordinated Mg center of 2 has a distorted tetrahedral coordination geometry, as opposed to a distorted trigonal planar Mg geometry in 1. The increase in the Mg coordination sphere also leads to a longer Mn-Mg bond in 2 ($2.921(2) \text{ \AA}$) compared to that in 1 ($2.824(1) \text{ \AA}$, cf. Σ covalent radii for Mg and high spin Mn = $3.02 \text{ \AA}$; Cordero et al., 2008). Moreover, the Mn center in 2 is not linear, and exhibits an Mg-Mn-N angle ($158.0(1)^\circ$) that is marginally narrower than that in 1 ($160.85(9)^\circ$).

The structure of 3 (Figure 2) reveals it to have distorted tetrahedral Mg, and distorted trigonal planar Mn, centers,

though there is a weak arene-interaction between one of the amido ligand's phenyl groups and the Mn atom (closest contact: $\text{Mn}(1) \cdots \text{C}(9) = 2.837(2) \text{ \AA}$). This likely enhances the geometry distortion at that metal center. Although there are no examples of discrete monomeric complexes with hydroxide ligands bridging both Mg and Mn centers, comparisons can be drawn with hydroxy

bridged β -diketiminato magnesium(II) systems, in which the Mg–O distances (e.g., $1.960 \text{ \AA}$ mean in $[\{(\text{DipNacnac})\text{Mg}\}_2(\mu\text{-OH})_2]$; Lalrempuia *et al.*, 2013; Sarish *et al.*, 2011)

Figure 1: Thermal ellipsoid plot (20% probability surface) of the molecular structure of **2** (hydrogen atoms omitted; Ar^t, Mes and isopropyl groups shown as wireframe for clarity). Selected bond lengths (Å) and angles (°): Mn(1)–N(1) 2.039(5), Mn(1)–Mg(1) 2.921(2), Mg(1)–N(2) 2.075(5), Mg(1)–N(12) 2.082(5), Mg(1)–O(1) 2.098(4), N(1)–Mn(1)–Mg(1) 158.00(14), N(2)–Mg(1)–N(12) 90.1(2), O(1)–Mg(1)–Mn(1) 113.67(12).

Figure 2: Thermal ellipsoid plot (20% probability surface) of the molecular structure of **3** (hydrogen atoms, except hydroxy protons, omitted; Ar^t, Mes and isopropyl groups shown as wireframe for clarity). Selected bond lengths (Å) and angles (°): Mn(1)–O(2) 1.9921(17), Mn(1)–N(1) 2.0155(16), Mn(1)–O(1) 2.0375(16), Mg(1)–O(2) 1.9139(18), Mg(1)–O(1) 1.9471(18), Mg(1)–N(3) 2.0340(19), Mg(1)–N(2) 2.0471(19), O(2)–Mn(1)–N(1) 130.19(7), O(2)–Mn(1)–O(1) 79.25(7), N(1)–Mn(1)–O(1) 143.00(7), O(2)–Mg(1)–O(1) 83.46(7), N(3)–Mg(1)–N(2) 92.90(7).

Figure 3: Thermal ellipsoid plot (20% probability surface) of the molecular structure of **4** (hydrogen atoms omitted; Ar^t, Mes and isopropyl groups shown as wireframe for clarity). Selected bond lengths (Å) and angles (°): Mn(1)–N(1) 1.997(3), Mn(1)–O(4) 2.120(3), Mn(1)–O(2) 2.140(3), Mn(1)–O(1) 2.167(3), Mg(1)–O(3)' 1.991(3), Mg(1)–O(3) 2.017(3), O(1)–C(45) 1.293(5), O(2)–C(45) 1.253(5), O(3)–C(45) 1.289(5), N(1)–Mn(1)–O(4) 114.46(12), O(2)–Mn(1)–O(1) 61.52(11), C(45)–O(3)–Mg(1)' 151.4(3), C(45)–O(3)–Mg(1) 106.1(3), Mg(1)'–O(3)–Mg(1) 102.46(12).

Table 1: Summary of crystallographic data for 2-4

	2 •(pentane) _{1.5}	3	4 •(pentane) ₄
empirical formula	C _{78.5} H ₁₀₁ MgMnN ₃ O ₅ Si	C ₆₇ H ₈₃ MgMnN ₃ O ₂ Si	C ₁₆₄ H ₂₂₆ Mg ₂ Mn ₂ N ₆ O ₈ Si ₂
formula weight	1209.96	1069.70	2624.17
crystal system	triclinic	monoclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.7194(5)	13.954(3)	13.284(3)
<i>b</i> (Å)	14.4149(6)	31.833(6)	23.108(5)
<i>c</i> (Å)	18.7446(8)	14.154(3)	25.148(5)
α (deg.)	93.051(3)	90	90
β (deg.)	91.643(2)	104.90(3)	94.31(3)
γ (deg.)	101.609(2)	90	90
vol (Å ³)	3623.1(3)	6076(2)	7698(3)
<i>Z</i>	2	4	2
ρ (calcd) (g·cm ⁻³)	1.109	1.169	1.132
μ (mm ⁻¹)	0.251	0.292	0.244
<i>F</i> (000)	1304	2292	2836
reflections collected	38438	42252	50185
unique reflections	13443	10933	12506
<i>R</i> _{int}	0.0813	0.0827	0.0809
<i>R</i> ₁ indices [<i>I</i> > 2σ(<i>I</i>)]	0.0926	0.0479	0.0825
<i>wR</i> ₂ indices (all data)	0.2545	0.1214	0.2545
largest peak/hole (e/Å ³)	1.09, -0.54	0.34, -0.61	0.58, -0.43
CCDC No.	2101784	2101785	2101783

are slightly longer to those in **3** (1.93 Å mean). Similarly, the Mn–O distances in **3** (2.00 Å mean) are marginally shorter than those in the only characterized hydroxy bridged β-diketiminato manganese(II) system [(DipNacnac)Mn]₂(μ-OH)₂ (2.046 Å mean) (Oh et al., 2020).

Compound **4** is dimeric, with each monomeric unit consisting of a planar carbonate ligand bridging two metal centers within Mn(μ-κ²-O,O':κ¹-O-CO₃)Mg fragments. To the best of our knowledge, there are no other examples of Mn/Mg heterobimetallic systems incorporating carbonate ligands. The monomeric units of **4** dimerize through bridging O- and Mg-centers, yielding a central Mg₂O₂ four-membered ring. Both the Mn and Mg atoms have distorted tetrahedral geometries. Curiously, and as opposed to the situation in **2**, the Mn centers of **4** are coordinated by THF, while the Mg atoms are THF free. The greater affinity of the Mn center in **4** for THF is likely due to its higher oxidation state and Lewis acidity, relative to the Mn atom in **2**.

In summary, the second example of an Mn–Mg covalently bonded compound, and the first discrete molecular hydroxide and carbonate bridged Mn/Mg heterobimetallic compounds have been crystallographically characterized. We continue to explore the application of low oxidation state/low coordination number main group metal-metal bonded heterobimetallics to small molecule activations.

Experimental

General

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Toluene and THF were distilled over molten potassium, while pentane was distilled over 1:1 Na/K alloy. The ¹H NMR spectrum was determined on a Bruker DPX500 spectrometer and is referenced to internal C₆D₆. The FTIR spectrum was collected as a Nujol mull on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. The microanalysis was carried out at the Science Centre, London Metropolitan University. The melting point was determined in a sealed glass capillary under dinitrogen and is uncorrected. The magnetic moment was determined using the Evans method (Evans, 1959). The starting material [L⁺Mn–Mg^(Mes)Nacnac)] **1** was prepared by the literature procedure (Hicks et al., 2014). All other reagents were used as received.

Preparation of [L⁺Mn–Mg(THF)^(Mes)Nacnac)]

Blue crystals of **1** (0.200 g, 0.193 mmol) were dissolved in THF (25 mL) and the resultant solution stirred for

5 mins. Volatiles were removed *in vacuo*, the residue was dissolved in the minimum volume of pentane (*ca.* 15 mL), and the extract slowly cooled to -30°C overnight, to yield **2** as blue-green crystals (0.185 g, 87%). Mp: $147\text{--}151^{\circ}\text{C}$; IR ν/cm^{-1} (Nujol): 1599(m), 1515(m), 1492(m), 1446(s), 1429(s), 1389(s), 1257(m), 1229(m), 1195(m), 1145(m), 1125(m), 1073(m), 1030(m), 1015(m), 918(m), 856(m), 831(m), 811(m), 758(m), 743(m), 717(m), 698(s); μ_{eff} (Evans, C_6D_6 , 298 K): $5.3 \mu_{\text{B}}$; anal. calc. for $\text{C}_{71}\text{H}_{89}\text{MgMnN}_3\text{OSi}$: C 76.98%, H 8.10%, N 3.79%, found: C 76.69%, H 78.87%, N 3.69%.

Preparation of $[\text{L}^+\text{Mn}(\mu\text{-OH})_2\text{Mg}^{\text{(MesNacnac)}}]$

A few yellow crystals of the title compound deposited over several days from a solution of **1** in toluene, contaminated with a small amount of water, placed at -30°C . Due to the very low yield of the compound, no meaningful spectroscopic data could be obtained.

Preparation of $\{[\text{L}^+\text{Mn}(\mu\text{-CO}_3)\text{Mg}(\text{THF})(\text{MesNacnac})]_2\}$

To the headspace of a Schlenk flask containing a solution of **1** (0.200 g, 0.193 mmol), in toluene (15 mL), was added CO_2 (1 atm.) at -70°C . The reaction mixture was allowed to warm to room temperature, whereupon it was stirred for 2 h, then volatiles removed *in vacuo*. The residue was dissolved in the minimum volume of pentane (*ca.* 5 mL), 2 drops of THF added to the extract, and the mixture left overnight at ambient temperature, to give **4** as small yellow crystals (<2%). Due to the very low yield of the compound, no meaningful spectroscopic data could be obtained.

X-ray crystallography

Crystals of **2-4** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were carried out at 150(2) K or 100(2) K, and were made using a Bruker Apex X8 diffractometer with a graphite monochromator with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$); or the MX1 beamline of the Australian Synchrotron ($\lambda = 0.71090 \text{ \AA}$). The software package Blu-Ice (McPhillips *et al.*, 2002) was used for synchrotron data acquisition, while the program XDS (Kabsch, 1993) was employed for synchrotron data reduction. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX16) (Sheldrick, 2016) using all unique data. Non-hydrogen atoms are typically anisotropic. Hydrogen atoms were included in calculated positions (riding model), except the hydroxy protons

of **3**, the positional and isotropic atomic displacement parameters of which were freely refined. Crystal data, details of the data collection and refinement are given in Table 1. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2101783-2101785). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements: Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron, part of ANSTO.

Funding information: This research was supported by the Australian Research Council.

Author contributions: Jamie Hicks: experimental design, complex preparation, data collection, and data interpretation; Martin Juckel: complex preparation, data collection, and data interpretation; Cameron Jones: conceptualization, data interpretation, writing, funding acquisition, and supervision.

Conflict of interest: One of the authors (Cameron Jones) is a member of the Editorial Board of Main Group Metal Chemistry.

References

- Boutland A.J., Pernik I., Stasch A., Jones C., Magnesium(I) dimers bearing tripodal diimine–enolate ligands: proficient reagents for the controlled reductive activation of CO_2 and SO_2 . *Chem. Eur. J.*, 2015, 21, 15749–15758.
- Buchwalter P., Rose J., Braunstein P., Multimetallic catalysis based on heterometallic complexes and clusters. *Chem. Rev.*, 2015, 115, 28–126.
- Cooper B.G., Napoline J.W., Thomas C.M., Catalytic applications of early/late heterobimetallic complexes. *Catal. Rev.*, 2012, 54, 1–40.
- Cordero B., Gomez V., Platero-Prats A.E., Reyes M., Echeverria J., Cremades, E., *et al.*, Covalent radii revisited. *Dalton T.*, 2008, 2832–2838.
- Dange D., Gair A.R., Jones D.D.L., Juckel M., Aldridge S., Jones C., Acyclic 1,2-dimagnesiumethanes/-ethene derived from magnesium(I) compounds: multipurpose reagents for organometallic synthesis. *Chem. Sci.*, 2019, 10, 3208–3216.
- Evans D.F., The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.*, 1959, 2003–2005.
- Green S.P., Jones C., Stasch A., Stable magnesium(I) compounds with Mg–Mg bonds. *Science*, 2007, 318, 1754–1757.
- Hicks J., Hoyer C.E., Moubaraki B., Li Manni G., Carter E., Murphy D.M., *et al.*, A two-coordinate manganese(0) complex with an

- unsupported Mn–Mg bond: Allowing access to low coordinate homo- and heterobimetallic compounds. *J. Am. Chem. Soc.*, 2014, 136, 5283-5286.
- Hicks J., Underhill E.J., Kefalidis C.E., Maron L., Jones C., A mixed-valence tri-zinc complex, [LZnZnZnL] (L= bulky amide), bearing a linear chain of two-coordinate zinc atoms. *Angew. Chem. Int. Ed.*, 2015, 54, 10000-10004.
- Jones C., Dimeric magnesium(I) β -diketiminates: a new class of quasi-universal reducing agent. *Nat. Rev. Chem.*, 2017, 1, 0059.
- Kabsch W.J., Automatic processing of rotation diffraction data from crystals of initially unknown symmetry and cell constants. *Appl. Cryst.*, 1993, 26, 795-800.
- Kefalidis C.E., Stasch A., Jones C., Maron L., On the mechanism of the reaction of a magnesium(I) complex with CO₂: a concerted type of pathway. *Chem. Commun.*, 2014, 50, 12318-12321.
- Lalrempuia R., Stasch A., Jones C., The reductive disproportionation of CO₂ using a magnesium(I) complex: analogies with low valent f-block chemistry. *Chem. Sci.*, 2013, 4, 4383-4388.
- Liddle S.T. (Ed.), *Molecular Metal-Metal Bonds. Compounds, Synthesis, Properties.* Wiley-VCH, Weinheim, 2015.
- Lorion M.M., Maindan K., Kapdi A.R., Ackermann L., Heteromultimetallic catalysis for sustainable organic syntheses. *Chem. Soc. Rev.*, 2017, 46, 7399-7420.
- McPhillips T.M., McPhillips S., Chiu H.J., Cohen A.E., Deacon A.M., Ellis P.J., et al., Blu-Ice and the Distributed Control System: software for data acquisition and instrument control at macromolecular crystallography beamlines. *J. Synchrotron Rad.*, 2002, 9, 401-406.
- Oh C., Siewe J., Nguyen T.T., Kawamura A., Flores M., Groy T.L., et al., The electronic structure of a β -diketimate manganese hydride dimer. *Dalton T.*, 2020, 49, 14463-14474.
- Sarish S.P., Nembenna S., Nagendran S., Roesky H.W., Chemistry of soluble β -diketiminatoalkaline-earth metal complexes with M–X bonds (M = Mg, Ca, Sr; X = OH, Halides, H). *Acc. Chem. Res.*, 2011, 44, 157-170.
- Sheldrick G.M., SHELX-16. University of Göttingen, 2016.