Short Communication

Open Access

K. Yuvaraj and Cameron Jones*

Reduction of a 1,4-diazabutadiene and 2,2'-bipyridine using magnesium(I) compounds

<https://doi.org/10.1515/mgmc-2020-0021>

Received August 13, 2020; accepted August 23, 2020.

Abstract: β -diketiminato coordinated magnesium(I) compounds, $[(^{\text{Ar}}\text{Nacnac})\text{Mg}]_2$ ($^{\text{Ar}}\text{Nacnac} = [(\text{ArNCMe})_2\text{CH}]^-$ (Ar = 2,6-diisopropylphenyl (Dip) or mesityl (Mes)), have been utilized as reducing agents in reactions with the redox active 1,4-diazabutadiene, $(\text{Bu}^t\text{NCH})_2$ ($^{\text{Bu}^t}\text{DAB}$), and 2,2'-bipyridine (bipy). These reactions led to one-electron reductions of the unsaturated substrate, and formation of the highly colored radical complexes, $[(^{\text{Ar}}\text{Nacnac})\text{Mg}(^{\text{Bu}^t}\text{DAB}^\bullet)]$ and $[(^{\text{Mes}}\text{Nacnac})\text{Mg}(\text{bipy}^\bullet)(\text{bipy})]$. The X-ray crystal structures of the compounds reveal each to possess one singly reduced $^{\text{Bu}^t}\text{DAB}$ or bipy ligand.

Keywords: magnesium(I); diazabutadiene; bipyridine; reduction; radical

s-Block metals have been widely utilized as reagents for the reduction of organic substrates, yielding synthetically useful organometallic and inorganic products, for well over a century (Yamamoto and Oshima, 2004). Such reactions are often difficult to control because they are typically two-phase processes, and/or because the s-block metal involved is highly reducing. In 2007 we developed the first stable magnesium(I) compounds, e.g. LMg-MgL (L = β -diketiminato), and have since shown these to be widely applicable as soluble, stoichiometric, and safe reducing agents for the controlled reduction of numerous inorganic and unsaturated organic substrates (Green et al., 2007; Jones, 2017).

Two organic compound types we have not attempted to reduce using magnesium(I) compounds are redox non-innocent 1,4-diazabutadienes and 2,2'-bipyridines. While the one and two-electron reductions of such compounds have previously been achieved by a number of methods

(e.g. reaction with activated elemental magnesium, and alkali metal reductions of magnesium halides in the presence of the unsaturate), product selectivity can be a problem (Freeman et al., 2019; Gao et al., 2011; Gardiner et al., 1994; Liu et al., 2009; Ren et al., 2017). We believed that the unique combination of properties that magnesium(I) reagents hold could lend them to the selective one-electron reduction of 1,4-diazabutadienes (DAB) and 2,2'-bipyridine (bipy). Indeed, the radical products of these reductions could themselves be synthetically useful, as has previously shown to be the case for related radical systems (Ren et al., 2017). Here, we describe the synthesis and structural characterization of three such magnesium complexes of DAB and bipy radicals.

The β -diketiminato coordinated magnesium(I) compounds, $[(^{\text{Ar}}\text{Nacnac})\text{Mg}]_2$ ($^{\text{Ar}}\text{Nacnac} = [(\text{ArNCMe})_2\text{CH}]^-$ (Ar = 2,6-diisopropylphenyl (Dip) or mesityl (Mes)) (Bonyhady et al., 2010; Hicks et al., 2018), were treated with two equivalents of the 1,4-diazabutadiene, $(\text{Bu}^t\text{NCH})_2$ ($^{\text{Bu}^t}\text{DAB}$), in toluene, yielding the radical complexes, **1** and **2**, in low to moderate isolated yields as red-orange crystalline solids, after work-up (Scheme 1). Similarly, treating $[(^{\text{Mes}}\text{Nacnac})\text{Mg}]_2$ with 2,2'-bipyridine gave rise to a low isolated yield of the purple crystalline compound, **3**, which incorporates one singly reduced and one neutral bipy ligand. It should be noted that the closely related radical complex, $[(^{\text{Dip}}\text{Nacnac})\text{Mg}(\text{bipy}^\bullet)]$, has been reported to arise from the reduction of $[(^{\text{Dip}}\text{Nacnac})\text{MgBr}]$, using KC_8 in the presence of bipy (Ren et al., 2017). It is possible that only one bipy ligand coordinates the Mg center in that complex because of its sterically bulkier β -diketiminato, relative to that in **3**.

Compounds **1-3** are thermally stable in solution and the solid state, but all are extremely air sensitive. No signals were observed in their solution state NMR spectra, presumably due to their paramagnetic nature. Moreover, the extreme air sensitivity of the compounds hindered the acquisition of meaningful EPR spectroscopic data for them. However, all compounds were crystallographically characterized, and their molecular structures are shown in Figures 1 and 2 (see also Table 1). The magnesium centers

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

K. Yuvaraj, School of Chemistry, Monash University, P.O. Box 23, Melbourne, Victoria, 3800, Australia

Scheme 1: Synthesis of compounds 1-3.

Figure 1: Thermal ellipsoid plot (25% probability surface) of the molecular structures of (a) **1** and (b) **2** (hydrogen atoms omitted; Dip, Mes and *tert*-butyl groups shown as wireframe for clarity). Selected bond lengths (Å) and angles (°) for **1**: Mg(1)-N(4) 2.044(3), Mg(1)-N(2) 2.044(3), Mg(1)-N(1) 2.058(3), Mg(1)-N(3) 2.097(4), N(3)-C(30) 1.326(5), N(4)-C(31) 1.320(5), C(30)-C(31) 1.403(6), N(2)-Mg(1)-N(1) 92.45(13), N(4)-Mg(1)-N(3) 83.41(13). Selected bond lengths (Å) and angles (°) for **2**: Mg(1)-N(3) 2.032(5), Mg(1)-N(2) 2.033(5), Mg(1)-N(1) 2.034(5), Mg(1)-N(4) 2.064(5), N(3)-C(28) 1.318(7), N(4)-C(29) 1.324(7), C(28)-C(29) 1.397(8), N(2)-Mg(1)-N(1) 91.68(18), N(3)-Mg(1)-N(4) 83.25(19).

of **1** and **2** possess distorted tetrahedral coordination geometries, being chelated by both ^{Ar}Nacnac and radical ^{Bu^t}DAB ligands. The N–C and C–C bond lengths within the backbone of the ^{Bu^t}DAB ligands are strongly suggestive of electronic delocalization over those backbones, and are comparable to the N–C and C–C distances in other Mg complexes bearing singly reduced ^{Bu^t}DAB ligands, e.g. 1.32(1) Å and 1.40(1) Å respectively in [Mg(^{Bu^t}DAB•)]₂ (Gardiner et al., 1994).

The molecular structure of **3** reveals it to have a distorted octahedral geometry, with the magnesium atom

Figure 2: Thermal ellipsoid plot (25% probability surface) of the molecular structure of **3** (hydrogen atoms omitted; Mes groups shown as wireframe for clarity). Selected bond lengths (Å) and angles (°): Mg(1)-N(1) 2.1583(14), Mg(1)-N(3) 2.1783(13), Mg(1)-N(4) 2.1803(13), Mg(1)-N(2) 2.1890(13), Mg(1)-N(6) 2.2890(14), Mg(1)-N(5) 2.2892(13), N(3)-C(28) 1.389(2), N(4)-C(29) 1.386(2), N(5)-C(38) 1.343(2), N(6)-C(39) 1.347(2), C(28)-C(29) 1.426(2), C(38)-C(39) 1.486(2), N(3)-Mg(1)-N(4) 75.61(5), N(1)-Mg(1)-N(2) 86.05(5), N(6)-Mg(1)-N(5) 71.46(5).

being chelated by one ^{Mes}Nacnac and two bipy ligands. The N–C and C–C distances over the NCCN fragments of the two bipy ligands differ significantly, and suggest that the ligand incorporating the N(1) and N(2) centers is not reduced, while the ligand containing the N(3) and N(4) atoms is a singly reduced radical anion. This becomes apparent when those distances are compared to those in unreduced and singly reduced bipy ligands in related complexes, e.g. C–C 1.487(3) Å and N–C 1.349 Å (mean) in [(^{Dip}Nacnac)Mg(SePh)(bipy)]; and C–C 1.425(3) Å and 1.392 Å (mean) in [(^{Dip}Nacnac)Mg(bipy•)] (Ren et al., 2017).

In summary, reductions of either a 1,4-diazabutadiene or 2,2'-bipyridine with magnesium(I) compounds lead to single electron transfers to the redox active substrate, and formation of three magnesium radical complexes. The crystal structures of these highly air sensitive compounds show them all to possess one singly reduced radical ligand. We are currently exploring the use of these compounds as one electron reducing agents in both organic and inorganic synthesis.

Experimental

General

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Toluene and hexane were

Table 1: Summary of crystallographic data for 1-3.

	1	2	3
empirical formula	C ₃₉ H ₆₁ MgN ₄	C ₃₃ H ₄₉ MgN ₄	C ₄₃ H ₄₅ MgN ₆
formula weight	610.22	526.07	670.16
crystal system	tetragonal	monoclinic	monoclinic
space group	<i>P</i> -42 ₁ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	19.7631(10)	14.2357(18)	11.4360(1)
<i>b</i> (Å)	19.7631(10)	11.0941(13)	15.9104(2)
<i>c</i> (Å)	19.5886(13)	20.187(3)	20.1083(2)
<i>a</i> (deg.)	90	90	90
<i>β</i> (deg.)	90	92.692(6)	91.424(1)
<i>γ</i> (deg.)	90	90	90
vol (Å ³)	7650.9(9)	3184.7(7)	3657.60(7)
<i>Z</i>	8	4	4
<i>ρ</i> (calcd) (g·cm ⁻³)	1.060	1.097	1.217
<i>μ</i> (mm ⁻¹)	0.076	0.082	0.716
<i>F</i> (000)	2680	1148	1428
reflections collected	101429	13675	36004
unique reflections	7524	7067	6651
<i>R</i> _{int}	0.0982	0.1813	0.0639
<i>R</i> ₁ indices [<i>i</i> > 2σ(<i>i</i>)]	0.0547	0.1137	0.0416
<i>wR</i> ₂ indices (all data)	0.1514	0.2364	0.1147
largest peak/hole (e/Å ³)	0.60, -0.21	0.35, -0.41	0.30, -0.22
CCDC No.	2023080	2023078	2023079

distilled over molten potassium, while pentane was distilled over 1:1 Na/K alloy. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid-state probe. FTIR spectra were collected as Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. The starting materials ^{Bur}DAB (Haaf et al., 1998) and [{(^{Ar}Nacnac)Mg}₂] (^{Ar} = Dip or Mes) (Bonyhady et al., 2010; Hicks et al., 2018), were prepared by literature procedures. All other reagents were used as received.

Preparation of [(^{Dip}Nacnac)Mg(^{Bur}DAB•)] 1

[{(^{Dip}Nacnac)Mg}₂] (200 mg, 0.226 mmol) and ^{Bur}DAB (76 mg, 0.452 mmol) were dissolved in 6 mL of toluene, which resulted in generation of an orange-red solution. The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed in vacuo and the residue was

extracted with *n*-hexane (15 mL). The extract was then concentrated to ca. 2 mL, and placed at -30°C overnight to give **1** as red-orange crystals (102 mg, 37%). M.p. 127-131°C; IR ν/cm⁻¹ (Nujol): 1532 (m), 1507 (m), 926 (s), 847 (s), 791 (s), 752(s); MS (EI, 70 eV): *m/z* (%) = 609.6 (^{M+}, 100), 441.4 (^{Dip}NacnacMg⁺, 73); anal. calc. for C₃₉H₆₁MgN₄: C 76.76 %, H 10.08%, N 9.18%; found: C 76.72%, H 9.94%, N 8.98%.

Preparation of [(^{Mes}Nacnac)Mg(^{Bur}DAB•)] 2

[{(^{Mes}Nacnac)Mg}₂] (150 mg, 0.210 mmol) and ^{Bur}DAB (71 mg, 0.420 mmol) were dissolved in 6 mL of toluene, yielding an orange-red solution. The reaction mixture was stirred for 2 h at room temperature. All volatiles were then removed in vacuo and the residue was extracted with *n*-pentane (10 mL). The extract was concentrated to ca. 2 mL and placed at -30°C for 5 days, after which time red-orange needles of **2** had deposited (60 mg, 27%). M.p. 115-118°C; IR ν/cm⁻¹ (Nujol): 1525 (m), 1511 (m), 1011 (s), 852 (s), 772 (s), 724 (s); MS (EI, 70 eV): *m/z* (%) = 525.4 (^{M+}, 100), 357.2 (^{Mes}NacnacMg⁺, 67); a satisfactory microanalysis could not

be obtained due to the highly air sensitive nature of the compound.

Preparation of [(^{Mes}Nacnac)Mg(bipy•)(bipy)] **3**

[(^{Mes}Nacnac)Mg]₂ (100 mg, 0.140 mmol) and bipy (44 mg, 0.280 mmol) were dissolved in 6 mL of toluene, yielding a dark purple solution. The reaction mixture was then stirred for 3 h at room temperature. The reaction mixture was filtered, the filtrate was concentrated to ca. 2 mL in vacuo, then placed at -30°C for 8 days. During this time, dark purple crystals of **3** deposited (12 mg, 6%, based on [(^{Mes}Nacnac)Mg]₂). M.p. 156-159°C; IR ν/cm^{-1} (Nujol): 1599 (m), 1546 (m), 1511 (m), 1009 (m), 951 (s), 854 (s), 722 (s); MS (EI, 70 eV): m/z (%) = 334.3 (^{Mes}NacnacH⁺, 35); a satisfactory microanalysis could not be obtained due to the highly air sensitive nature of the compound.

X-ray crystallography

Crystals of **1-3** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were carried out at 123(2) K, and were made using a Rigaku Synergy diffractometer using a graphite monochromator with Mo K α radiation (λ = 0.71073 Å) or Cu K α radiation (λ = 1.54184 Å). The structures were solved by direct methods and refined on F² by full matrix least squares (SHELX16) (Sheldrick, 2016) using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). The absolute structure parameter for the chiral crystal structure of **1** refined to 0.02(10). 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. 2023078-2023080). 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>).

Acknowledgement: This research was supported by the Australian Research Council.

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

References

- Bonyhady S.J., Jones C., Nembenna S., Stasch A., Edwards A.J., McIntyre G., β -Diketiminato-stabilized magnesium(I) dimers and magnesium(II) hydride complexes: synthesis, characterization, adduct formation, and reactivity studies. *Chem. Eur. J.*, 2010, 16, 938-955.
- Freeman L.A., Walley J.E., Obi A.D., Wang G., Dickie D.A., Molino A., et al., Stepwise reduction at magnesium and beryllium: cooperative effects of carbenes with redox non-innocent α -diimines. *Inorg. Chem.*, 2019, 58, 10554-10568.
- Gao J., Liu Y., Zhao Y., Yang X.-J., Sui Y., Syntheses and structures of magnesium complexes with reduced α -diimine ligands. *Organometallics*, 2011, 30, 6071-6077.
- Gardiner M.G., Hanson G.R., Henderson M.J., Lee F.-C., Raston C.L., Paramagnetic bis(1,4-di-*tert*-butyl-1,4-diazabutadiene) adducts of lithium, magnesium and zinc. *Inorg. Chem.*, 1994, 33, 2456-2461.
- Green S.P., Jones C., Stasch A., Stable magnesium(I) compounds with Mg-Mg bonds. *Science*, 2007, 318, 1754-1757.
- Haaf M., Schmiedl A., Schmedake T.A., Powell D.R., Millevolte A.J., Denk M., et al., Synthesis and reactivity of a stable silylene. *J. Am. Chem. Soc.*, 1998, 120, 12714-12719.
- Hicks J., Juckel M., Paparo A., Dange D., Jones C., Multigram syntheses of magnesium(I) compounds using alkali metal halide supported alkali metals as dispersible reducing agents. *Organometallics*, 2018, 37, 4810-4813.
- Jones C., Dimeric magnesium(I) β -diketiminates: a new class of quasi-universal reducing agent. *Nat. Rev. Chem.*, 2017, 1, 0059.
- Liu Y., Li S., Yang X.-J., Yang P., Wu B., Magnesium-magnesium bond stabilized by a doubly reduced α -diimine: synthesis and structure of [K(THF)₃][LMg-MgL] (L = [2,6-(Pr₂C₆H₃)NC(Me)]₂²⁻). *J. Am. Chem. Soc.*, 2009, 131, 4210-4211.
- Ren W., Fang X., Sun W., Gu D., Yu Y., A magnesium complex containing a reduced 2,2'-bipyridyl ligand: synthesis, structure, reactivity, and computational studies. *J. Organomet. Chem.* 2017, 842, 47-53.
- Sheldrick G.M., SHELX-16, University of Göttingen, 2016.
- Yamamoto H., Oshima K. (Eds.), Main group metals in organic synthesis. Wiley-VCH, Weinheim, 2004.