The Reductive Disproportionation of CO_2 using a Magnesium(I) Complex: Analogies with Low Valent f-Block Chemistry

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Supplementary Information (13 pages)

Contents

1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Diethyl ether was distilled over Na/K alloy (25:75), while THF, hexane, toluene and benzene were distilled over molten potassium. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either Bruker DPX300, Bruker AvanceIII 400 or Varian Inova 500 spectrometers and were referenced to the resonances of the solvent used. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates, or on solids protected with a thin layer of Nujol using an Agilent Cary 630 ATR FTIR spectrometer. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. Microanalyses were carried out at the Science Centre, London Metropolitan University. [{(^{Dip}Nacnac)Mg}$_2$] prepared by a literature procedure.[1] Ultra high purity CO_2 and $^{13}CO_2$ were used as supplied, and the latter was found to contain no detectable (by ^{13}C NMR) amounts of CO. All other reagents were used as received.

Preparation of [{(^{Dip}Nacnac)Mg}$_2$(μ-κ^2:κ^2-CO_3)] 1. CO_2 (21.8 cm^3, 0.90 mmol) was added to the head space of a Schlenk flask containing a stirred yellow solution of [{(^{Dip}Nacnac)Mg}$_2$] (400 mg, 0.45 mmol) in toluene (20 cm^3) at -30 °C, and the flask subsequently sealed. The mixture was warmed to 20 °C over 30 mins, during which time it became almost colourless. It was then concentrated *in vacuo* to *ca.* 4 cm^3 and allowed to stand at room temperature for 3 days, afforded colourless crystals of **1**. The crystals were isolated and the mother liquor concentrated to *ca.* 2 cm^3, affording a second crop of **1** (210 mg, 49 %). M.p. 325-327 °C (melts); ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 0.92 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.12 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.55 (s, 12H, C*H*$_3$), 3.11 (sept, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 4.83 (s, 2H, C*H*), 6.98-7.14 (m, 12H, Ar-*H*); ^{13}C{^{1}H}NMR (126 MHz, C_6D_6, 298 K): δ = 23.9, 24.1, 24.7 (2 x CH(*C*H$_3$)$_2$, NC*C*H$_3$), 28.3 (*C*H(CH$_3$)$_2$), 95.0 (*C*H), 124.4 (Ar-*C*), 125.7 (Ar-*C*), 142.3 (Ar-*C*), 143.9 (Ar-*C*), 168.5 (*C*O$_3$), 170.3 (N*C*CH$_3$); IR (Nujol, cm^{-1}): ν = 1616m, 1519m, 1022m, 997m, 935m, 856m, 794s, 779m, 756m; EI/MS: *m*/*z* (%): 942.6 (M$^+$-H, 10), 418.3 (^{Dip}NacnacH$^+$, 26), 403.3 (^{Dip}NacnacH$^+$-Me, 70), 202.1 (MeCCNDip$^+$, 100); elemental analysis: found: C 74.97%, H 8.82%, N 6.01%; calc. for $C_{59}H_{82}Mg_2N_4O_3$: C 75.07%, H 8.76%, N 5.94%.

N.B. [{(^{Dip}Nacnac)Mg}$_2$(μ-κ^2:κ^2-$^{13}CO_3$)] was prepared by a similar procedure, but using $^{13}CO_2$.

N.B. From one preparation of **1**, a few crystals of the magnesium oxalate complex, [{(^{Dip}Nacnac)Mg}$_2$(μ-C_2O_4)], were isolated. This is presumably a very low yield side product from

the reaction. Attempts to rationally synthesise the compound by treating THF solutions of [(^{Dip}Nacnac)MgI(OEt$_2$)] with [Na$_2$(C$_2$O$_4$)] were not successful due to the poor solubility of the latter. As a result, no spectroscopic data could be obtained for [{(^{Dip}Nacnac)Mg}$_2$(μ-C$_2$O$_4$)], though its X-ray crystal structure was determined (see below).

N.B. Stirring a toluene solution of **1** over a mirror of excess potassium led to an immediate change of the colourless solution to a yellow/green colour. After 2h, an aliquot of the reaction mixture was taken and volatiles removed *in vacuo*. The residue was re-dissolved in C$_6$D$_6$ and an ^{1}H NMR spectrum of the solution showed that **1** had been completely consumed, and resonances for [{(^{Dip}Nacnac)Mg}$_2$] and [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$] had appeared. The integration of these resonances revealed the compounds to be present in an approximately 70:30 ratio. It is not known if the hydroxide compound, [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$], was formed by hydrolysis of generated [{(^{Dip}Nacnac)Mg}$_2$] by a trace of moisture in the NMR tube, or if it originated directly from **1.**

Preparation of [{(THF)(^{Dip}Nacnac)Mg}$_2$(μ-O)] 2 and [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$]. High purity N$_2$O (6.0 cm^3, 0.25 mmol) was added to the head space of a Schlenk flask containing a stirred yellow solution of [{(^{Dip}Nacnac)Mg}$_2$] (200 mg, 0.226 mmol) in toluene (10 cm^3) at -30 °C, and the flask subsequently sealed. The mixture was warmed to 20 °C over 30 minutes, during which time the reaction mixture became colourless. All volatiles were subsequently removed *in vacuo* and the residue extracted with hexane (10 cm^3). Filtration, and removal of volatiles from the filtrate afforded compound **2** as a colourless powder (90 mg, 44 %). The hexane insoluble residue largely consisted of [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$] (100 mg, 48 %), X-ray quality crystals of which were obtained from a benzene solution. N.B. The formation of [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$] during the synthesis and work-up of **2** could not be avoided, presumably because of the high reactivity of **2**. Although the two compounds could be separated to give materials of *ca.* 90% purity (as determined by ^{1} H NMR spectroscopy), neither compound could be obtained in an analytically pure state.

Data for [{(THF)(^{Dip}Nacnac)Mg}$_2$(μ-O)] **2**: M.p. 307-310 °C (melts and turns yellow); ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ = 0.95 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.17 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.53 (s, 12 H, C*H*$_3$), 2.99 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 4.83 (s, 2H, C*H*), 7.03-7.14 (m, 12H, Ar-*H*); ^{13}C{^{1}H}NMR (126 MHz, C$_6$D$_6$, 298 K): δ = 22.8, 24.0, 25.0 (2 x CH(*C*H$_3$)$_2$, NC*C*H$_3$), 28.6 (*C*H(CH$_3$)$_2$), 94.6 (*C*H), 123.9 (Ar-*C*), 125.2 (Ar-*C*), 141.7 (Ar-*C*), 145.3 (Ar-*C*), 169.2 (N*C*CH$_3$); IR (Nujol, cm^{-1}): ν = 1521m, 1432m, 1396s, 933m, 891m, 794m, 757s, 700m; EI/MS: *m*/*z* (%): 916.8 (M$^+$+H$_2$O, 20), 898.8 (M$^+$, trace), 883.7 (M$^+$-Me, 3), 403.3 (^{Dip}NacnacH$^+$-Me, 62), 202.1 (MeCCNDip$^+$, 100).

Data for [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$]: M.p. 315-317 °C (melts and turns yellow); ^{1}H NMR (300 MHz, C_6D_6, 333 K): δ = -0.45 (s, 2H, MgO*H*), 0.90 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.51 (s, 12H, C*H*$_3$), 3.09 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 4.83 (s, 2H, C*H*), 6.98-7.13 (m, 12H, Ar-*H*); ^{13}C{^{1}H}NMR (75.5 MHz, C_6D_6, 333 K): δ = 24.1, 24.4, 24.6 (2 x CH(*C*H$_3$)$_2$, NC*C*H$_3$), 28.4 (*C*H(CH$_3$)$_2$), 94.8 (*C*H), 124.1 (Ar-*C*), 125.3 (Ar-*C*), 142.3 (Ar-*C*), 147.2 (Ar-*C*), 169.0 (N*C*CH$_3$); IR (Nujol, cm^{-1}): ν = 3743w (O-H str), 1524m, 1458s, 1400m, 1176m, 1098m, 1021m, 929m, 848m, 793m, 756s, 702s; EI/MS: *m*/*z* (%): 916.8 (M$^+$, 18), 403.3 (^{Dip}NacnacH$^+$-Me, 50), 202.1 (MeCCNDip$^+$, 100).

N.B. the related THF adduct, [{(THF)(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$], has been reported. L.F. Sanchez-Barba, D.L. Hughes, S.M. Humphrey, M. Bochmann, *Organometallics*, 2006, **25**. 1012.

Preparation of [{(THF)(^{Dip}Nacnac)Mg}$_2$(μ-O)] 3. THF (0.5 cm^3) was added to a solution of **2** (50 mg, 0.056 mmol) in hexane (2 cm^3) at 20 °C. The reaction mixture was stored overnight at -30 °C to give colourless crystals of **3** (20 mg, 34 %). M.p. 317-320 °C (melts and turns yellow); ^{1}H NMR (500 MHz, THF-d$_8$, 298 K): δ = 0.78 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 0.99 (d, $^3J_{H\text{-}H}$ =6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.36 (s, 12H, C*H*$_3$), 2.95 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 4.59 (s, 2H, C*H*), 6.87-6.97 (m, 12H, Ar-*H*); ^{13}C{^{1}H}NMR (126 MHz, THF-d$_8$, 298 K): δ = 25.1, 25.6, 27.1 (2 x CH(*C*H$_3$)$_2$, NC*C*H$_3$), 28.2 (*C*H(CH$_3$)$_2$), 94.3 (*C*H), 123.5 (Ar-*C*), 124.5 (Ar-*C*), 142.4 (Ar-*C*), 148.3 (Ar-*C*), 167.6 (N*C*CH$_3$); IR (Nujol, cm^{-1}): ν = 1654m, 1620m, 1546s, 1507m, 1440s, 1435s, 1101m, 1019m, 932m, 787s, 756s; EI/MS: *m*/*z* (%): 403.3 (^{Dip}NacnacH$^+$-Me, 95), 202.1 (MeCCNDip$^+$, 100); elemental analysis: found: 75.76%, H 9.37%, N 5.26%; calc. for $C_{66}H_{98}Mg_2N_4O_3$: C 75.92%, H 9.46%, N 5.37%.

Preparation of [{(^{Dip}Nacnac)Mg}$_2$(μ-κ^2:κ^2-CS$_2$O)] 4. High purity N_2O (6.0 cm^3, 0.25 mmol) was added to the head space of a Schlenk flask containing a stirred yellow solution of [{(^{Dip}Nacnac)Mg}$_2$] (200 mg, 0.226 mmol) in toluene (15 cm^3) at -30 °C, and the flask subsequently sealed. The mixture was warmed to 20 °C over 30 minutes, and subsequently concentrated to *ca.* 10 cm^3 *in vacuo* to remove excess N_2O. The mixture was then cooled to -70°C, and CS_2 (19 mg, 0.25 mmol) added to it, resulting in an immediate colour change from colourless to orange. The mixture was warmed to room temperature and further stirred for 30 mins. Concentration of the red-brown solution to *ca.* 4 cm^3, and standing overnight afforded colourless needles of **4** which were filtered off and washed with hexane (2 x 5 cm^3). The mother liquor was layered with hexane washings to obtain a second crop of **4** (65 mg, 30 %). M.p. 264-266 °C (melts and turns yellow). N.B. The ^{1}H NMR spectrum of the **4** (C_6D_6) at 298 K is complex and exhibits

many overlapping signals that are difficult to assign unambiguously. It is apparent that these correspond to at least two isomeric forms of **4**, presumably with the $[COS_2]^{2-}$ dianion bridging the two Mg centres in a μ-κ^2(O,S):κ^2(O,S')-fashion (as seen in the solid state structure), or in a less symmetrical μ-κ^2(O,S):κ^2(S,S')-fashion. Given that none of the latter isomer was detected in the crystal structure of **4**, we believe that the former isomer is more thermodynamically more stable, and that the two isomers interchange in solution. Some evidence for this proposition comes from the NMR spectra of **4** acquired at 343 K, which simplify, and can be tentatively assigned. ^{1}H NMR (400 MHz, C_6D_6, 343 K): δ = 1.05 (v. br., 24H, CH(C*H*$_3$)$_2$), 1.17 (br., 24H, CH(C*H*$_3$)$_2$), 1.64 (br., 12H, C*H*$_3$), 3.16 (v. br., 8H, C*H*(CH$_3$)$_2$), 4.90 (br. s, 1H, C*H*), 7.03-7.18 (br. m, 12H, Ar-*H*); ^{13}C{^{1}H}NMR (75.5 MHz, C_6D_6, 343 K): δ = 24.8, 25.2, 25.4 (all br., 2 x CH(*C*H$_3$)$_2$, NC*C*H$_3$), 29.2 (br., *C*H(CH$_3$)$_2$), 96.9 (br., *C*H), 124.7 (br., Ar*C*), 126.4 (br., Ar*C*), 143.3 (br., Ar*C*), 145.5 (br., Ar*C*), 171.1 (br., N*C*CH$_3$); O*C*S$_2$ resonance not observed; IR (Nujol, cm^{-1}): ν = 1532m, 1518m, 1458m, 1172m, 1155m, 1101m, 1040m, 1026s, 933m, 853m, 794s, 759s; EI/MS: *m*/*z* (%): 418.3 (^{Dip}NacnacH$^+$, 42), 403.3 (^{Dip}NacnacH$^+$-Me, 100).

Preparation of [{(^{Dip}Nacnac)Mg}$_2${μ-κ^2:κ^2-C(NCy)$_2$O}] 5. High purity N_2O (6.0 cm^3, 0.25 mmol) was added to the head space of a Schlenk flask containing a stirred yellow solution of [{(^{Dip}Nacnac)Mg}$_2$] (200 mg, 0.226 mmol) in toluene (15 cm^3) at -30 °C, and the flask subsequently sealed. The mixture was warmed to 20 °C over 30 minutes, and subsequently concentrated to *ca.* 10 cm^3 *in vacuo* to remove excess N_2O. The mixture was then cooled to -70°C, and CyNCNCy (51 mg, 0.25 mmol) was added to it. The mixture was warmed to room temperature, stirred for 30 minutes and concentrated to *ca.* 3 cm^3. Storing the solution at room temperature overnight afforded **5** as a colourless crystalline solid. Further concentration of the supernatant solution to *ca.* 1 cm^3 yielded a second crop (140 mg, 57 %). Crystals of **5** suitable for X-ray diffraction were grown from benzene. M.p. 333-335 °C (melts and turns yellow); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.52 (q, br, 2H, Cy-*H*), 0.54 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.80-1.73 (m, 18H, Cy-*H*), 1.10 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.40 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.52 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.60 (s, 6 H, C*H*$_3$), 1.72 (s, 6H, C*H*$_3$), 2.86-2.94 (m of two overlapping sept, $^3J_{H-H}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 3.25-3.38 (m, 6H, C*H*(CH$_3$)$_2$, Cy-*H*), 4.88 (s, 2H, C*H*), 6.99-7.24 (m, 12H, Ar-*H*); ^{13}C {^{1}H}NMR (75.5 MHz, C_6D_6, 298 K): δ 22.5, 23.1, 23.8, 23.9, 24.4, 24.7, 24.8, 25.1, 25.2, 25.5, 26.0, 26.2, 26.4, 28.0, 28.2, 28.4 (8 x CH(*C*H$_3$)$_2$, 2 x NC*C*H$_3$, 4 x *C*H(CH$_3$)$_2$, 2 x Cy-*C*), 30.4 (Cy-*C*), 35.7 (Cy-*C*), 38.7 (Cy-*C*), 51.9 (Cy-N*C*), 96.2 (*C*H), 123.3 (Ar-*C*), 123.6 (Ar-*C*), 124.2 (Ar-*C*), 124.6 (Ar-*C*), 125.0 (Ar-*C*), 125.6 (Ar-*C*), 141.2 (Ar-*C*), 142.2 (Ar-*C*), 143.5 (Ar-*C*),

143.9 (Ar-*C*), 146.2 (Ar-*C*), 146.7 (Ar-*C*), 164.9 (O*C*NCy), 169.1 (N*C*CH$_3$), 169.6 (N*C*CH$_3$); IR (Nujol, cm^{-1}): ν = 1626w, 1533m, 1517s, 1459m, 1018m, 985m, 885m, 849m, 791s, 758m, 745m, 725s, 692m; EI/MS: *m*/*z* (%): 1106.0 (M$^+$, 23), 1091.0 (M$^+$ -Me, 11), 687.5 (M$^+$ -^{Dip}NacnacH, 11), 418.3 (^{Dip}NacnacH$^+$, 39), 403.3 (^{Dip}NacnacH$^+$-Me, 91), 202.1 (MeCCNDip$^+$, 100); elemental analysis: found: C 76.99%, H 9.22%, N 7.70%; calc. for $C_{71}H_{104}Mg_2N_6O$: C 77.09%, H 9.48%, N 7.60%.

[{(^{Dip}Nacnac)Mg}(μ-κ^2(S,S'):κ^1(O)-CS$_2$O){Mg(^{Dip}Nacnac)(OEt$_2$)}] 6. Compound **4**, (20 mg, 0.02 mmol) was dissolved in diethyl ether (*ca.* 0.2 cm^3) and hexane (*ca.* 0.3 cm^3) was added. This resulted in the slow deposition of colourless crystals of **6** over several hours (19 mg, 88 %). M.p. 259-260 °C (melts and turns yellow); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.43 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, (OCH$_2$C*H*$_3$), 1.05 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.21 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.49 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.60 (s, 6H, CH$_3$), 1.76 (s, 6H, CH$_3$), 3.07 (q, $^3J_{H-H}$ = 7.0 Hz, 4H, (OC*H*$_2$CH$_3$), 3.21 (sept, $^3J_{H-H}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 3.52 (sept, $^3J_{H-H}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.71 (s, 1H, C*H*), 5.01 (s, 1H, C*H*), 7.09 (br, 6H, Ar-*H*), 7.23-7.30 (m, 6H, Ar-*H*); ^{13}C{^{1}H}NMR (75.5 MHz, C_6D_6, 298 K): δ 13.3 (br., OCH$_2$*C*H$_3$), 24.5, 24.7, 24.9, 25.1, 25.2 (3 x CH(*C*H$_3$)$_2$, 2 x NC*C*H$_3$), 28.5, 28.7, 28.9 (CH(*C*H$_3$)$_2$, 2 x *C*H(CH$_3$)$_2$), 65.6 (O*C*H$_2$CH$_3$), 94.5 (*C*H), 95.1 (*C*H), 123.9 (Ar-*C*), 124.3 (Ar-*C*), 124.4 (Ar-*C*), 125.3 (Ar-*C*), 125.4 (Ar-*C*), 125.7 (Ar-*C*), 125.9 (Ar-*C*), 128.4 (Ar-*C*), 128.6 (Ar-*C*), 143.1 (Ar-*C*), 144.9 (Ar-*C*), 145.2 (Ar-*C*), 169.5 (N*C*CH$_3$), 169.6 (N*C*CH$_3$), 227.4 (O*C*S$_2$); IR (Nujol, cm^{-1}): ν = 1619m, 1541m, 1521m, 1015s, 931m, 852m, 790s, 757s; EI MS: *m*/*z* (%): 975.7 (MH$^+$-OEt$_2$, trace), 418.3 (^{Dip}NacnacH$^+$, 40), 403.3 (^{Dip}NacnacH$^+$-Me, 100); elemental analysis: found: C 72.11%, H 8.69%, N 5.42%; calc. for $C_{63}H_{92}Mg_2N_4O_2S_2$: C 72.05%, H 8.83%, N 5.34%.

[{(THF)(^{Dip}Nacnac)Mg}$_2$(μ-O$_2$)]. Dry air was slowly bubbled through a solution of [{(^{Dip}Nacnac)Mg}$_2$] (100 mg, 0.113 mmol) in toluene (6 cm^3) and THF (3 cm^3) for one min and the mixture subsequently warmed to room temperature and stirred for 5 minutes. The reaction mixture was concentrated to *ca.* 5 cm^3 *in vacuo* and stored at -30°C to afford colourless blocks of the title compound (35 mg, 27%). M.p. at *ca.* 110 °C colour change towards brown, darkens at elevated temperatures, then at *ca.* 220 °C melts to a red-brown oil. N.B. Crystalline samples of the highly reactive compound in C_6D_6 consistently exhibited complicated ^{1}H NMR spectra, suggesting the presence of a mixture of products, including [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$], despite the rigorous exclusion of moisture. As a result, meaningful solution state NMR data could not be assigned for the compound. IR (Nujol, cm^{-1}): ν = 1538m, 1517m, 1462s, 1033s, 922m, 884m, 791m, 760m,

728m; EIMS: *m*/*z* (%): 914.3 (M^+ - 2 THF, 10), 418.3 (^{Dip}NacnacH$^+$, 35), 403.3 (^{Dip}NacnacH$^+$-Me, 85), 202.2 (MeCCNDip$^+$, 100).

2. X-Ray Crystallography

Crystals of two structural modifications of **1**, **3**-**6**, [{(^{Dip}Nacnac)Mg}$_2$(μ-C_2O_4)], [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$], and [{(THF)(^{Dip}Nacnac)Mg}$_2$(μ-O_2)] suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either Oxford Gemini Ultra or Bruker Apex X8 diffractometers using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (1.54180 Å, **1**·(benzene)); or the MX1 beamline of the Australian Synchrotron (λ = 0.71080 Å, **4**). The software package Blu-Ice[2] was used for synchrotron data acquisition, while the program XDS[3] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97[4]) using all unique data. Hydrogen atoms are included in calculated positions (riding model), except the hydroxide proton of **2S**, the positional parameters of which were freely refined. Two molecules of **6** were refined in the asymmetric unit of its crystal structure. As there are no significant geometric differences between them, metrical parameters for only one are given in Figure 4 of the main text. The absolute structure parameter for the crystal structure of **1**·(benzene) is 0.00(2). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Crystal data for two structural modifications of **1**, **3-6**, [{(^{Dip}Nacnac)Mg}$_2$(μ-C_2O_4)] **1S**, [{(^{Dip}Nacnac)Mg}$_2$(μ-$OH)_2$] **2S**, and [{(THF)(^{Dip}Nacnac)Mg}$_2$(μ-O_2)] **3S**

	1	**1**·(benzene)	**3**·(benzene)	**4**	**5**·(benzene)$_2$
empirical formula	$C_{59}H_{82}Mg_2N_4O_3$	$C_{65}H_{88}Mg_2N_4O_3$	$C_{65}H_{88}Mg_2N_4O_3$	$C_{59}H_{82}Mg_2N_4OS_2$	$C_{83}H_{116}Mg_2N_6O$
formula weight	943.91	1022.01	1122.21	976.03	126.44
crystal system	monoclinic	orthorhombic	triclinic	orthorhombic	trigonal
space group	*C*2/*c*	$P2_12_12_1$	*P*-1	*Pbca*	$P3_121$
a (Å)	48.559(3)	10.8296(2)	12.1680(13)	14.860(3)	12.0374(17)
b (Å)	13.6700(9)	22.4623(2)	12.6241(14)	17.210(3)	12.0374(17)
c (Å)	17.5247(11)	24.9069(3)	13.176(2)	45.300(9)	44.799(9)
α (º)	90	90	98.046(11)	90	90
β (º)	103.460(3)	90	111.433(12)	90	90
γ (º)	90	90	109.680(10)	90	120
V (Å^3)	11313.4(12)	6058.80(14)	1692.2(4)	11585(4)	5621.6(16)
Z	8	4	1	8	3
T (K)	123(2)	123(2)	123(2)	100(2)	123(2)
ρ_{calcd} (g·cm^3)	1.108	1.120	1.101	1.119	1.119
μ (mm^{-1})	0.087	0.708	0.083	0.154	0.080
F(000)	4096	2216	612	4224	2064
reflns collected	48150	55425	15548	146059	30360
unique reflns	9945	10721	8169	10405	8072
R_{int}	0.0645	0.0230	0.0228	0.1193	0.0413
R1 [I > 2σ(I)]	0.0524	0.0283	0.0448	0.0989	0.0389
wR2 (all data)	0.1347	0.0732	0.1230	0.2218	0.0900
largest peak and hole (e·Å^{-3})	0.48, -0.30	0.19, -0.24	1.04, -0.21	1.08, –0.60	0.22, –0.18
CCDC no.	955168	955167	955171	955173	955174

Table S1 (contd.). Crystal data for two structural modifications of **1**, **3-6**, [{(^{Dip}Nacnac)Mg}$_2$(μ-C_2O_4)] **1S**, [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$] **2S**, and [{(^{Dip}Nacnac)Mg}$_2$(μ-O_2)] **3S**

	6	**1S**	**2S**	**3S**·(toluene)
empirical formula	$C_{63}H_{92}Mg_2N_4O_2S_2$	$C_{60}H_{82}Mg_2N_4O_4$	$C_{58}H_{84}Mg_2N_4O_2$	$C_{58}H_{84}Mg_2N_4O_2$
formula weight	1050.15	971.92	917.91	1152.24
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	*P*-1	*Pccn*	*C*2/*c*	$P2_1/n$
a (Å)	13.1816(5)	14.5246(9)	22.886(5)	12.749(3)
b (Å)	16.2050(6)	15.6210(9)	14.823(3)	14.372(3)
c (Å)	31.9827(11)	25.9215(14)	16.196(3)	18.802(4)
α (º)	79.216(3)	90	90	90
β (º)	83.332(3)	90	90.65(3)	95.03(3)
γ (º)	68.828(3)	90	90	90
V (Å^3)	6249.3(4)	5881.3(6)	5493.9(19)	3431.7(12)
Z	4	4	4	2
T (K)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.116	1.098	1.110	1.115
μ (mm^{-1})	0.148	0.087	0.087	0.084
F(000)	2280	2104	2000	1256
reflns collected	46789	35432	8993	12479
unique reflns	24528	5177	4748	6667
R_{int}	0.0344	0.0513	0.1005	0.0210
R1 [I > 2σ(I)]	0.0511	0.0466	0.0775	0.0786
wR2 (all data)	0.1186	0.1159	0.2258	0.2273
largest peak and hole (e·Å^{-3})	0.55, –0.33	0.31, –0.23	0.29, -0.29	1.24, -0.52
CCDC no.	955175	955169	955170	955172

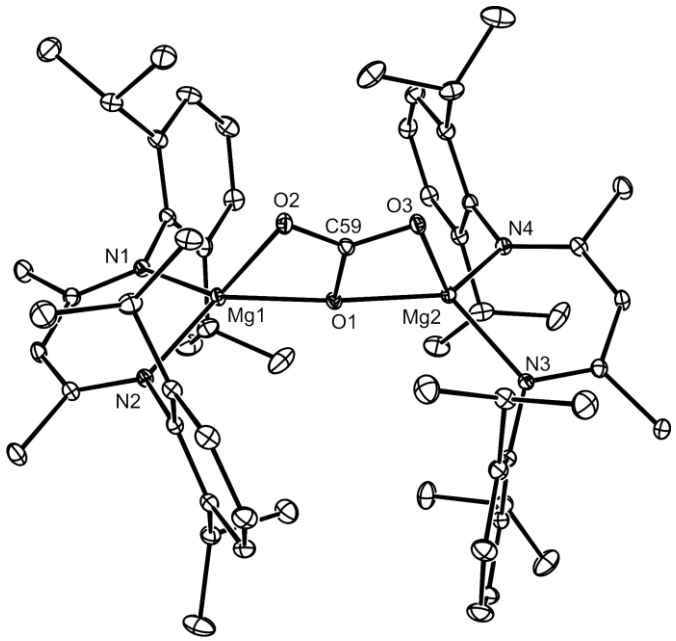

Figure S1. ORTEP diagram of a second structural modification of compound **1** (i.e. **1**·(benzene) in Table S1; 25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Mg(1)-O(2) 2.0054(10), Mg(1)-N(1) 2.0176(11), Mg(1)-N(2) 2.0240(11), Mg(1)-O(1) 2.0355(9), O(1)-C(59) 1.3527(15), O(1)-Mg(2) 2.0281(9), Mg(2)-N(3) 2.0212(11), Mg(2)-O(3) 2.0237(10), Mg(2)-N(4) 2.0240(11), O(2)-C(59) 1.2639(16), O(3)-C(59) 1.2652(15), N(1)-Mg(1)-N(2) 94.75(4), O(2)-Mg(1)-O(1) 66.58(4), N(3)-Mg(2)-N(4) 95.37(5), O(3)-Mg(2)-O(1) 66.50(4), O(2)-C(59)-O(3) 128.04(12), O(2)-C(59)-O(1) 115.89(10), O(3)-C(59)-O(1) 116.07(11).

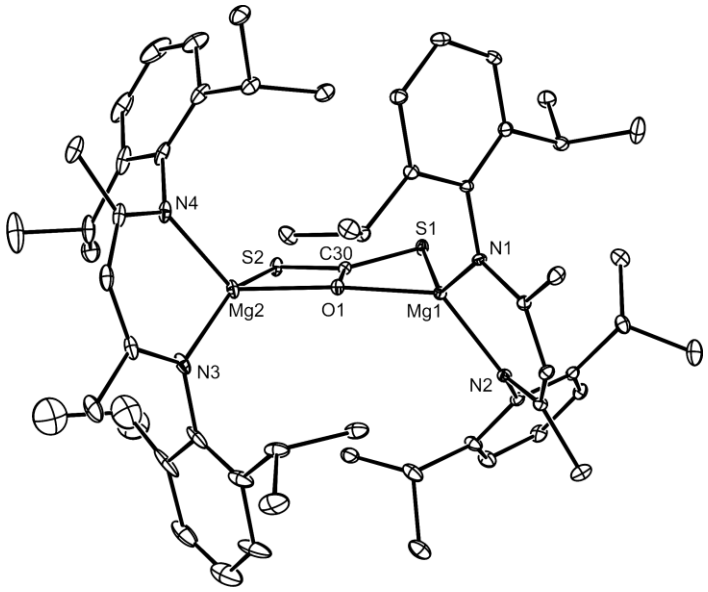

Figure S2. ORTEP diagram of compound **4** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): S(1)-C(30) 1.698(5), S(1)-Mg(1) 2.458(2), Mg(1)-N(1) 2.017(4), Mg(1)-N(2) 2.026(4), Mg(1)-O(1) 2.043(4), O(1)-C(30) 1.339(6), O(1)-Mg(2) 2.042(4), S(2)-C(30) 1.696(5), S(2)-Mg(2) 2.459(2), Mg(2)-N(3) 2.025(5), Mg(2)-N(4) 2.028(5), N(1)-Mg(1)-N(2) 95.50(16), O(1)-Mg(1)-S(1) 69.69(10), Mg(2)-O(1)-Mg(1) 164.39(19), N(3)-Mg(2)-N(4) 95.2(2), O(1)-Mg(2)-S(2) 69.85(10), O(1)-C(30)-S(2) 117.3(3), O(1)-C(30)-S(1) 116.9(3), S(2)-C(30)-S(1) 125.8(3).

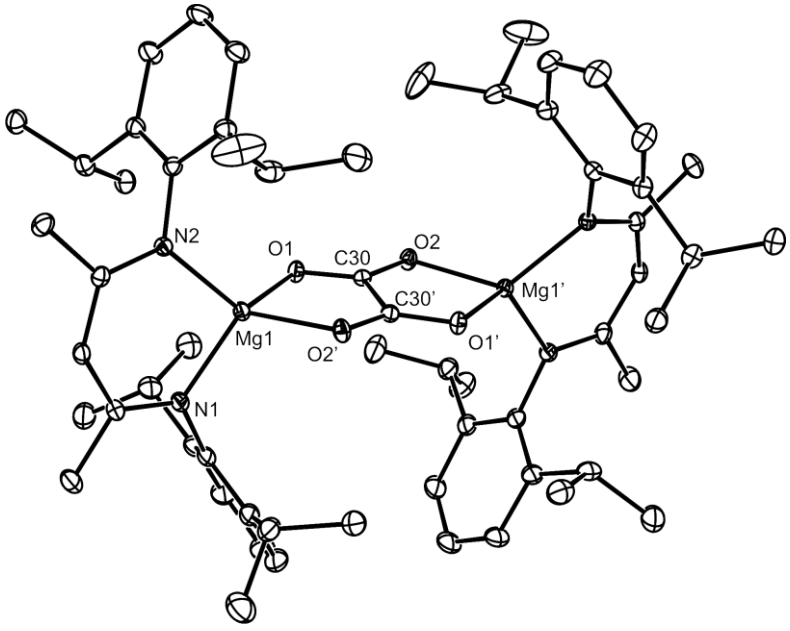

Figure S3. ORTEP diagram of compound [{(^{Dip}Nacnac)Mg}$_2$(μ-C_2O_4)] **1S** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Mg(1)-O(1) 1.9855(15), Mg(1)-O(2)' 1.9858(14), Mg(1)-N(2) 1.9936(15), Mg(1)-N(1) 2.0029(16), C(30)-C(30)' 1.547(4), O(1)-C(30) 1.258(2), O(2)-C(30) 1.252(2), O(1)-Mg(1)-O(2)' 84.35(5), N(2)-Mg(1)-N(1) 96.80(7), O(2)-C(30)-O(1) 127.08(17). Symmetry operation: ' -x+1/2, -y+1/2, z

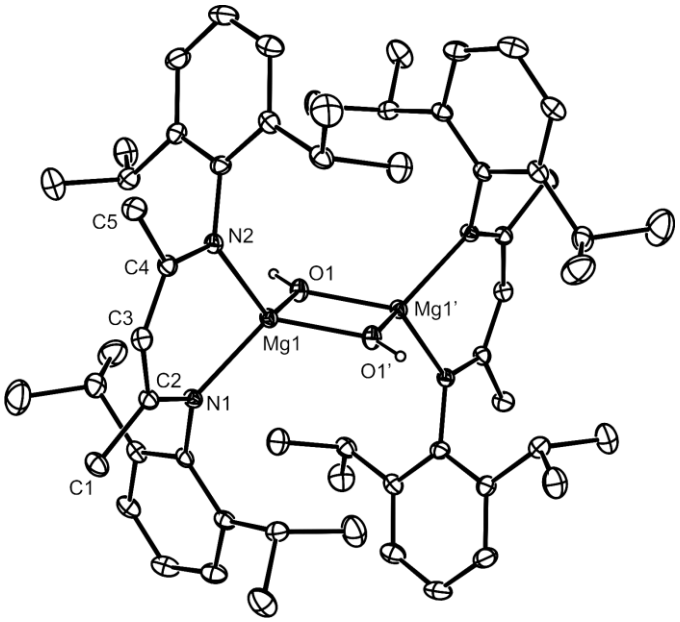

Figure S4. ORTEP diagram of compound [{(^{Dip}Nacnac)Mg}$_2$(μ-OH)$_2$] **2S** (25% thermal ellipsoids; hydrogen atoms, except hydroxide proton, omitted). Selected bond lengths (Å) and angles (º): Mg(1)-O(1) 1.957(2), Mg(1)-O(1)' 1.962(2), Mg(1)-N(1) 2.087(3), Mg(1)-N(2) 2.087(3), O(1)-Mg(1)-O(1)' 80.47(11), N(1)-Mg(1)-N(2) 92.02(10), Mg(1)-O(1)-Mg(1)' 99.53(11) .

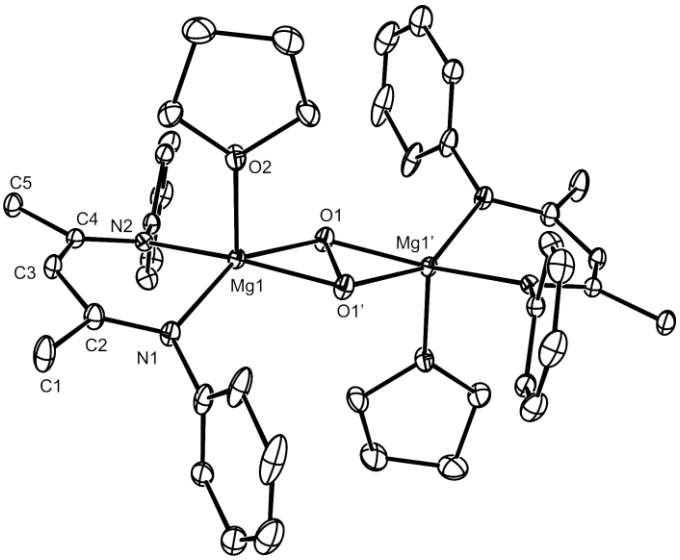

Figure S5. ORTEP diagram of compound [{(^{Dip}Nacnac)Mg}$_2$(μ-O$_2$)] **3S** (25% thermal ellipsoids; hydrogen atoms and isopropyl groups omitted). Selected bond lengths (Å) and angles (º): Mg(1)-O(1) 1.960(2), Mg(1)-O(1)' 1.961(2), Mg(1)-O(2) 2.069(2), Mg(1)-N(2) 2.096(2), Mg(1)-N(1) 2.100(3), O(1)-O(1)' 1.588(4), O(1)-Mg(1)-O(1)' 47.81(10), N(2)-Mg(1)-N(1) 89.59(9), Mg(1)-O(1)-Mg(1)' 132.19(10). Symmetry operation: ' -x, -y+2, -z.

3. References

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