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## Introduction

It is widely believed that the increasing concentration of carbon dioxide in the atmosphere, which is mainly due to anthropogenic activities, is one of the key factors behind rising global temperatures.<sup>1</sup> As a potential partial solution to this problem, extensive research has been carried out over the past several decades into the utilisation of  $CO_2$  as an abundant and cheap  $C_1$  feedstock which can be transformed into a variety of useful chemicals and fuels.<sup>2</sup> The problem here is that such transformations typically require the cleavage, or partial cleavage, of one or both of the very strong O=C(O) bonds (532 kJ mol<sup>-1</sup>) of carbon dioxide.<sup>3</sup> Despite this, much progress has been made towards the activation and multi-electron reduction of  $CO_2$  in a wide range of chemical,<sup>4</sup> photochemical,<sup>5</sup> electrochemical<sup>6</sup> and

# The reductive disproportionation of CO<sub>2</sub> using a magnesium(I) complex: analogies with low valent f-block chemistry<sup>†</sup>

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The dimeric magnesium(i) complex, [{( $^{Dip}Nacnac$ )Mg}] ( $^{Dip}Nacnac = [(DipNCMe)_{2}CH]^{-}$ , Dip = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6), reacts with 2 equivalents of CO<sub>2</sub> to give a high yield of the Mg<sup>II</sup> carbonate complex,  $[{(}^{Dip}Nacnac)Mg]_2(\mu \kappa^{2}$ : $\kappa^{2}$ -CO<sub>3</sub>)], and CO *via* a reductive disproportionation process. The Mg<sup>II</sup> oxalate, [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>( $\mu$ - $(C_2O_4)$ ], is a very low yield by-product of the reaction. Reducing the carbonate complex with elemental potassium regenerates the Mg<sup>I</sup> starting material. The carbonate complex is shown to form via a stepwise process involving the oxo-bridged intermediate,  $[{(}^{Dip}Nacnac)Mg]_2(\mu-O)]$ , which rapidly reacts with stoichiometric CO<sub>2</sub> to give [{( $^{Dip}$ Nacnac)Mg}<sub>2</sub>( $\mu$ - $\kappa^{2}$ : $\kappa^{2}$ -CO<sub>3</sub>)]. The oxo-bridged intermediate has been rationally synthesised via the reaction of  $[{(^{Dip}Nacnac)Mg}_2]$  with N<sub>2</sub>O, and treated with THF to give the adduct, [{(THF)( $^{Dip}$ Nacnac)Mg}<sub>2</sub>(µ-O)]. The complex, [{( $^{Dip}$ Nacnac)Mg}<sub>2</sub>(µ-O)], reacts with the CO<sub>2</sub> isoelectronic analogues, CS<sub>2</sub> and CyNCNCy (Cy = cyclohexyl) to give the complexes,  $[{(}^{Dip}Nacnac)Mg]_2(\mu \kappa^{2}$ : $\kappa^{2}$ -CS<sub>2</sub>O)] and [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>{ $\mu$ - $\kappa^{2}$ : $\kappa^{2}$ -C(NCy)<sub>2</sub>O}]. Rearrangement of the dithiocarbonate coordination mode of the former occurs upon treatment with diethyl ether, giving the unsymmetrical complex, [{( $^{Dip}Nacnac$ )Mg}( $\mu$ - $\kappa^{2}$ (S,S'): $\kappa^{1}$ (O)-CS<sub>2</sub>O){Mg( $^{Dip}Nacnac$ )(OEt<sub>2</sub>)}]. The majority of the complexes prepared in this study were crystallographically characterised. Taken as a whole, this study demonstrates that magnesium(i) dimers can display very similar reactivity, with respect to small molecules activations, as do Sm<sup>II</sup> and U<sup>III</sup> compounds. Accordingly, magnesium(i) compounds hold considerable potential as cheaper, less toxic, non-radioactive and diamagnetic alternatives to low valent f-block metal complexes in this realm.

> enzymatic<sup>7</sup> processes. These can be stoichiometric or catalytic in nature, and while the lion's share of reductive  $CO_2$  transformations require the involvement of d-block metal reagents,<sup>2</sup> examples enlisting p- and f-block element compounds are becoming more prevalent. In this realm, and of most relevance to the current study, are reports on the reduction of  $CO_2$  to COby low oxidation state p-block element complexes,<sup>8,9</sup> and the reduction (or reductive disproportionation) of  $CO_2$  by low-valent f-block metal (Sm<sup>II</sup> or U<sup>III</sup>) systems to CO and/or oxalate, oxo, carbonate or  $[CO_2]^-$  complexes.<sup>10-13</sup>

> To the best of our knowledge, there have been no studies on the reduction of CO<sub>2</sub> to CO using well defined s-block compounds. We believed this paucity might be addressed by examining the reactivity of dimeric magnesium(1) complexes, that have been developed in our group,<sup>14</sup> towards CO<sub>2</sub> and related compounds. This seemed a reasonable proposition given that we have previously shown magnesium(1) dimers to act as versatile reducing agents in a variety of both organic and organometallic synthetic methodologies.<sup>14</sup> Furthermore, the products obtained from magnesium(1) reductions of unsaturated organic substrates, *e.g.* nitriles and isonitriles, are often closely related to the products from reductions of the same substrates with low oxidation state p- or f-block metal

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complexes. It was of interest to see if these similarities extended to the magnesium(I) reduction of CO<sub>2</sub>, and if such reductions could ultimately lead to value added organic products. Another driving force for this study was a comparison of the reactivities of magnesium(1) compounds and magnesium metal towards CO<sub>2</sub>. As is often demonstrated in undergraduate lectures, elemental magnesium reacts spectacularly, and highly exothermically, with CO2 to generate MgO and carbon soot.15 A final incentive for this study was the recent speculation that in the dark reaction of photosynthesis, the two-electron reduction of CO<sub>2</sub>, that is required for its incorporation into carbohydrates, proceeds via electron transfer from a transient quasi-magnesium(1) centre in the RuBisCo enzyme.<sup>16</sup> Details of our investigations into the reactivity of a magnesium(I) dimer and a magnesium(II) oxo complex towards CO<sub>2</sub>, and related molecules, are reported herein.

### **Results and discussion**

# (i) Magnesium(1) induced reductive disproportionation of $CO_2$

The magnesium(I) dimer that was chosen for this study,  $[\{(^{\text{Dip}}\text{Nacnac})Mg\}_2]$   $(^{\text{Dip}}\text{Nacnac} = [(\text{DipNCMe})_2CH]^-$ , Dip =  $C_6H_3Pr_2^i$ -2,6), has previously been shown by us to act as a twoelectron reductant towards a wide range of unsaturated substrates.<sup>14,17</sup> In the current study, two equivalents of CO<sub>2</sub> were added to the head space above a yellow toluene solution of [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>], held at room temperature. This led to the rapid decolouration of the solution, and the formation of the carbonate bridged magnesium(II) compound, [{(<sup>Dip</sup>Nacnac)Mg $_{12}(\mu - \kappa^2 : \kappa^2 - CO_3)$ ] **1** (Scheme 1). When the reaction was carried out at -70 °C, the solution initially took on an orange colour, which slowly faded to colourless above -30 °C. Once the mixture reached 20 °C, it was worked up to give a good isolated yield of 1. Monitoring the reaction by <sup>1</sup>H NMR spectroscopy revealed signals only for [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>] below -30 °C. These gradually reduced in intensity above this temperature and were replaced by resonances for 1, while there was no spectroscopic evidence for an intermediate in the reaction. At 20 °C, the <sup>1</sup>H NMR spectrum of the mixture closely resembled that of 1, but with very small amounts of other

Scheme 1 The magnesium(I) induced reductive disproportionation of CO2.

products present, which implies that the reaction is close to quantitative. It cannot be sure why the reaction solution is orange below -30 °C, but we propose this is due to the formation of a weak, and reversible, O-donor adduct between  $CO_2$  and  $[\{(^{Dip}Nacnac)Mg\}_2]$ . In this respect, we have previously shown that both THF and dioxane form weak and reversible orange adducts with  $[\{(^{Dip}Nacnac)Mg\}_2]$ .<sup>18</sup> Given that the <sup>1</sup>H NMR spectrum of the orange  $CO_2-[\{(^{Dip}Nacnac)Mg\}_2]$  reaction mixture exhibited signals only for the magnesium(1) compound at low temperatures, it is likely that any adduct between the two reactants would be weakly associated, and would exist in equilibrium with  $[\{(^{Dip}Nacnac)Mg\}_2]$ . Consistent with this view is the fact that all attempts to isolate such an adduct at low temperatures were unsuccessful, and instead yielded only unreacted  $[\{(^{Dip}Nacnac)Mg\}_2]$ .

It was presumed that the by-product from the reaction that gave 1 was CO, and that this was formed by a net reductive disproportionation of CO<sub>2</sub>. This was confirmed by carrying out the reaction of [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>] with <sup>13</sup>CO<sub>2</sub>, and following the reaction by 13C NMR spectroscopy. The most prominent signals in the spectrum of the mixture appeared at  $\delta$  184.5 and 168.1 ppm, and were assigned to 13CO and the 13C enriched carbonate ligand of 1, respectively. Similar reductive disproportionations of CO<sub>2</sub> using samarium(II) and uranium(III) compounds have been reported,<sup>11-13</sup> and it has been proposed that they could proceed via one of two routes. That is, either decomposition of an initially formed oxalate complex (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, arising from the reductive coupling of CO<sub>2</sub>) to carbonate and CO, or reductive deoxygenation of  $CO_2$  to yield CO and an oxide  $(O^{2-})$  complex, which subsequently reacts with a second equivalent of CO<sub>2</sub> to give carbonate. The latter mechanism has been recently confirmed by Meyer et al. for the reduction of CO<sub>2</sub> with U<sup>III</sup> complexes.<sup>12a,b</sup> Despite this, either of the two routes proposed for CO2 reduction by low valent f-block metal complexes could be responsible for related magnesium(1) reductions. To test this, the reaction between [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>] and CO<sub>2</sub> was carried out in a 1:1 stoichiometry, in an attempt to isolate a magnesium oxide intermediate. However, this yielded only an approximately 50 : 50 mixture of **1** and unreacted [{(<sup>Dip</sup>Nacnac)-Mg<sub>2</sub>], suggesting the intermediate reacts more rapidly with  $CO_2$ , than does [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>].<sup>19</sup> It is noteworthy that the reaction of  $[{(^{Dip}Nacnac)Mg}_2]$  with a large excess of CO<sub>2</sub> was also investigated. This led to an intractable mixture of many products at room temperature (as determined by NMR spectroscopy), which clearly indicates that in situ generated 1 reacts with CO<sub>2</sub>, by unknown pathways, to give a number of products.

It seemed unlikely that the magnesium(1) induced reductive disproportionation of CO<sub>2</sub> involves a magnesium(1) oxalate intermediate, [{( $^{Dip}Nacnac$ )Mg}<sub>2</sub>( $\mu$ -C<sub>2</sub>O<sub>4</sub>)], given that magnesium oxalate complexes are typically thermally stable species.<sup>20</sup> Indeed, a very small amount of thermally stable [{( $^{Dip}Nacnac$ )-Mg}<sub>2</sub>( $\mu$ -C<sub>2</sub>O<sub>4</sub>)] was isolated from one preparation of **1**, and its structure confirmed by X-ray crystallography (see ESI†). Instead, a magnesium oxide intermediate that is reactive towards CO<sub>2</sub> seemed more probable, especially considering Meyer's aforementioned studies with U<sup>III</sup> complexes.<sup>12</sup> To assess this possibility, [{( $^{Dip}Nacnac$ )Mg}<sub>2</sub>] was reacted with N<sub>2</sub>O, which gave rise



to a moderate isolated yield of the unsupported oxo-bridged dimagnesium complex,  $[\{(^{Dip}Nacnac)Mg\}_2(\mu-O)]$  2, as a highly reactive microcrystalline powder (Scheme 1).<sup>21</sup> Although such complexes are unprecedented in magnesium chemistry, it is of note that a variety of closely related oxo-bridged f-block metal complexes have resulted from the reactions of Sm<sup>II</sup> or U<sup>III</sup> compounds with N<sub>2</sub>O.<sup>12,22</sup> It is also worthy of mention that attempts to prepare 2 *via* the reaction of  $[\{(^{Dip}Nacnac)Mg\}_2]$  and O<sub>2</sub> were not successful and instead gave a low yield of the magnesium peroxide complex,  $[\{(THF)(^{Dip}Nacnac)Mg\}_2(\mu-O_2)]$  (see ESI† for details).<sup>23</sup> Because the identity of microcrystalline 2 could not be confirmed by X-ray crystallography, it was treated with THF to form the adduct complex,  $[\{(THF)(^{Dip}Nacnac)-Mg\}_2(\mu-O)]$  3, the structural elucidation of which (*vide infra*) implied that the proposed formulation of 2 is correct.

As compound 2 is the likely intermediate in the reductive disproportionation of  $CO_2$  with [{( $^{Dip}Nacnac$ )Mg}<sub>2</sub>], we followed its reaction with one equivalent of CO<sub>2</sub> by <sup>1</sup>H NMR spectroscopy. At 20 °C this rapidly, and essentially quantitatively, led to the formation of the magnesium carbonate, 1.24 When an excess of CO<sub>2</sub> was added to the reaction mixture, a spectrum resembling that obtained from the reaction of  $[{(^{Dip}Nacnac)Mg}_2]$  with excess CO2 resulted. These observations strongly suggest that the reaction of [{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>] with CO<sub>2</sub> is a stepwise process involving an initial reductive deoxygenation of CO<sub>2</sub> to give CO and 2, followed by nucleophilic attack of the oxo-bridge of 2 at the C-centre of a second molecule of  $CO_2$  to give the magnesium carbonate, 1. We have been unable to determine the mechanism of the reductive deoxygenation reaction that gave 2, but one possibility is that it proceeds via insertion of CO2 into the Mg-Mg bond of  $[{(^{Dip}Nacnac)Mg}_2]$  to give  $[{(^{Dip}Nacnac)Mg}(\mu$ - $\kappa^2$ -O,O': $\kappa^1$ -C-CO<sub>2</sub>){Mg(<sup>Dip</sup>Nacnac)}], which rapidly eliminates CO, yielding 2. This seems likely as we have previously shown that the carbodiimide, CyN=C=NCy (Cy = cyclohexyl), which is isoelectronic to CO2, undergoes a similar insertion reaction with  $[\{(^{Dip}Nacnac)Mg\}_2] \text{ to give } [\{(^{Dip}Nacnac)Mg\}\{\mu-\kappa^2-N,N':\kappa^1-C-n,N':\kappa^2-N,N':\kappa^2-$ (CyN)<sub>2</sub>C}{Mg(<sup>Dip</sup>Nacnac)}].<sup>17e</sup> It is also of note that in a recent study, a closely related transient product from the insertion of  $CO_2$  into a Ge<sup>I</sup>-Ge<sup>I</sup> bonded complex has been observed, and subsequently shown to eliminate CO, generating an oxo-bridged digermanium complex, at low temperature.8a

With the aim of recycling [{( $^{Dip}Nacnac$ )Mg}<sub>2</sub>] for further use, and thereby closing the synthetic cycle that led to the formation of CO, the magnesium carbonate complex, **1**, was treated with excess potassium metal. This resulted in the regeneration of [{( $^{Dip}Nacnac$ )Mg}<sub>2</sub>], and presumably K<sub>2</sub>CO<sub>3</sub>, though this was not characterised as a reaction product.<sup>25</sup> An attempt was also made to generate **2** from **1** in the solid state by placing the latter under conditions of reduced pressure ( $10^{-2}$  mmHg) and elevated temperature ( $200 \ ^{\circ}$ C) for two hours. However, this was not successful and led only to the partial (*ca.* 35%) decomposition of **1** to give  $^{Dip}NacnacH$ , amongst other unidentified products, which were insoluble in normal organic solvents.

The spectroscopic data for 1–3 are consistent with their proposed formulations, and do not require further comment here, except to confirm that the carbonate signal (<sup>13</sup>C NMR:  $\delta$  168.5 ppm) that was assigned based on the reaction of

[{(<sup>Dip</sup>Nacnac)Mg}<sub>2</sub>] with <sup>13</sup>CO<sub>2</sub>, was also present in the <sup>13</sup>C NMR spectrum of isolated crystals of 1. Compounds 1 and 3 were crystallographically characterised, and their molecular structures can be found in Fig. 1 and 2. That for 1, reveals it to be a bimetallic complex with a planar carbonate ligand bridging two distorted tetrahedral Mg centres in a  $\kappa^2(O,O')$ : $\kappa^2(O,O'')$ -fashion. This is an identical bonding mode to those reported by Gardiner et al.<sup>11a</sup> and Meyer et al.<sup>12</sup> for carbonate bridged samarium(III) and uranium(IV) complexes, respectively. These were similarly formed by samarium(II) or uranium(III) induced reductive disproportionations of CO2. The CO distances in 1 suggest that its carbonate ligand is partially electronically delocalised, though that involving the higher coordinate O(1)centre is longer than the other two, as might be expected. The structure of 3 shows it to have an unprecedented linear, unsupported Mg-O-Mg fragment, with Mg-O distances that are markedly shorter than those for the Mg-THF interactions. They are, in fact, amongst the shortest such bonds to have been reported.26

#### (ii) Preliminary reactivity studies of $[{(^{Dip}Nacnac)Mg}_2(\mu-O)]$

The preparation of  $[{(^{Dip}Nacnac)Mg}_2(\mu-O)]$  2 presented the opportunity to investigate its preliminary reactivity as a novel nucleophile and potential oxo transfer reagent. For this study, the CO<sub>2</sub> isoelectronic analogues, CS<sub>2</sub> and CyN=C=NCy, were chosen as substrates. The reactions of *in situ* generated toluene solutions of 2 with either of the substrates led to low and moderate isolated yields of 4 and 5, respectively (Scheme 2). These reactions are reminiscent of that which gave 1 and likely



**Fig. 1** Molecular structure of **1** (25% thermal ellipsoids are shown; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)–O(2) 2.0035(19), Mg(1)–N(1) 2.0107(19), Mg(1)–N(2) 2.018(2), Mg(1)–O(1) 2.0223(17), O(1)–C(59) 1.352(3), O(1)–Mg(2) 2.0440(17), Mg(2)–O(3) 1.9930(18), Mg(2)–N(3) 2.0027(19), Mg(2)–N(4) 2.007(2), O(2)–C(59) 1.256(3), O(3)–C(59) 1.262(3), N(1)–Mg(1)–N(2) 96.18(8), O(2)–Mg(1)–O(1) 66.74(7), Mg(1)–O(1)–Mg(2) 173.26(9), N(3)–Mg(2)–N(4) 95.41(8), O(3)–Mg(2)–O(1) 66.55(7), O(2)–C(59)–O(3) 128.0(2), O(2)–C(59)–O(1) 116.2(2), O(3)–C(59)–O(1) 115.8(2).



**Fig. 2** Molecular structure of **3** (25% thermal ellipsoids are shown; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)–O(1) 1.8080(5), Mg(1)–O(2) 2.0905(10), Mg(1)–N(2) 2.0990(11), Mg(1)–N(1) 2.1039(12), O(1)–Mg(1)–O(2) 103.20(3), N(2)–Mg(1)–N(1) 90.36(5), O(1)–Mg(1)–N(1) 130.08(4), O(1)–Mg(1)–N(2) 127.83(4), Mg(1)–O(1)–Mg(1)' 180.00. Symmetry operation: r -x + 1, -y + 1, -z + 1.



 $\mbox{Scheme 2}$  Reactivity of the magnesium oxo complex,  $\mbox{2},$  towards  $\mbox{CS}_2$  and CyNCNCy.

involve nucleophilic attack of the O-centre of 2 at the central C-centre of the substrate. To the best of our knowledge, such reactivity is unprecedented for s-block systems, but has been observed on several occasions for f-block metal oxo compounds.<sup>12,27</sup> For sake of comparison, the reaction of two equivalents of CS<sub>2</sub> with [{( $^{Dip}Nacnac$ )Mg}\_2] was carried out with the expectation of obtaining the trithiocarbonate complex, [{( $^{Dip}Nacnac$ )Mg}\_2( $\mu$ - $\kappa^2$ : $\kappa^2$ -CS<sub>3</sub>)]. However, this led only to an intractable mixture of products and was not pursued further.

Complexes 1, 4 and 5 display very similar coordination modes for their bridging dianionic ligands. For the carbonate

and ureate complexes, **1** and **5**, this coordination was not disrupted when the complexes were treated with THF, with which they are unreactive. In contrast, treating the dithiocarbonate complex, **4**, with an excess of the weaker donor ligand, diethyl ether, led to a rearrangement of the dithiocarbonate coordination mode and ether coordination at one Mg centre in complex **6**. This complex is closely related to the samarium and uranium systems,  $[Cp_2Sm(\mu-S_2CO)SmCp_2(THF)]^{11b}$  and  $[(\kappa^1-DME)(L)U(\mu-S_2CO)$  $U(L)(\kappa^1-DME)]$  (L = N{CH<sub>2</sub>(2-C<sub>6</sub>H<sub>2</sub>MeAd-4,6)}<sub>3</sub>, Ad = adamantyl),<sup>27</sup> the former of which was formed *via* the  $[Cp_2Sm(THF)_2]$  induced reductive disproportionation of OCS. It is also of note that hydrolysis of **5**, affords the known urea, OC{N(H)Cy}<sub>2</sub>, thus demonstrating that the magnesium oxide complex, **2**, can be utilised as an oxo-transfer reagent in organic synthesis.

Compounds 4-6 were crystallographically characterised, and the molecular structures of 5 and 6 are depicted in Fig. 3 and 4 respectively. As compound 4 is isostructural with its carbonate analogue, 1, its molecular structure is included in the ESI.† Despite this, it should be noted that the µ- $\kappa^{2}(O,S):\kappa^{2}(O,S')$ -bonding mode of its dithiocarbonate ligand has not been previously observed for any metal. Compound 5 exhibits a similar structure in which the planar, dianionic ureate ligand bridges two distorted tetrahedral magnesium centres in an  $\mu$ - $\kappa^2$ (O,N): $\kappa^2$ (O,N')-fashion. The only precedent for this form of ligation is in the titanium complex,  $[(Cp_2Ti)_2]$  $\kappa^{2}(O,N):\kappa^{2}(O,N')-OC(NPh)_{2}]$ , which was prepared by the Ti<sup>II</sup> reduction of phenylisocyanate.28 The magnitude of the C-O and C-N distances in the ureate ligand suggests that there is a degree of electronic delocalisation over its CN2O fragment. In contrast to 4, the planar  $\cos^{2^{-1}}$  ligand of 6, bridges two fourcoordinate Mg-centres in a  $\mu$ - $\kappa^2(S,S')$ : $\kappa^1(O)$ -fashion, similar to the situations in [Cp\*2Sm(µ-S2CO)SmCp\*2(THF)]<sup>11b</sup> and  $[(\kappa^1-DME)(L)U(\mu-S_2CO)U(L)(\kappa^1-DME)]$ .<sup>27</sup> The C–O and C–S bond



**Fig. 3** Molecular structure of **5** (25% thermal ellipsoids are shown; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)–O(1) 2.0334(6), Mg(1)–N(3) 2.0398(14), Mg(1)–N(1) 2.0548(13), Mg(1)–N(2) 2.0646(13), O(1)–C(30) 1.372(2), N(3)–C(30) 1.3282(14), O(1)–Mg(1)–N(3) 66.30(5), N(1)–Mg(1)–N(2) 91.92(5), Mg(1)–O(1)–Mg(1)' 178.81(9), N(3)–C(30)–O(1) 111.10(10), N(3)–C(30)–N(3)' 137.8(2). Symmetry operation: ' y, x, –z.



**Fig. 4** Molecular structure of **6** (25% thermal ellipsoids are shown; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): S(1)–C(30) 1.731(2), S(1)–Mg(2) 2.4313(9), Mg(1)–O(1) 1.9253(14), Mg(1)–N(1) 2.0197(18), Mg(1)–O(2) 2.0225(17), Mg(1)–N(2) 2.0245(17), O(1)–C(30) 1.266(2), S(2)–C(30) 1.736(2), S(2)–Mg(2) 2.4697(8), Mg(2)–N(4) 2.0387(18), Mg(2)–N(3) 2.0468(18), C(30)–O(1)–Mg(1) 144.96(15), N(1)–Mg(1)–N(2) 93.85(7), O(1)–Mg(1)–O(2) 95.33(7), N(4)–Mg(2)–N(3) 93.89(7), S(1)–Mg(2)–S(2) 75.16(3), O(1)–C(30)–S(1) 119.55(17), O(1)–C(30)–S(2) 121.28(15), S(1)–C(30)–S(2) 119.16(12).

lengths in those two compounds are very close to the equivalent bond distances in **6**.

## Conclusion

In summary, a dimeric magnesium(1) complex has been shown to effect facile reductive disproportionation of CO<sub>2</sub> to yield free CO and a carbonate bridged magnesium(II) complex in high yield. This represents the first reduction of CO<sub>2</sub> to CO by a well defined s-block compound. The mechanism of the reaction has been explored, and it seems very likely that it involves the initial reductive deoxygenation of CO<sub>2</sub>, yielding CO and an oxo-bridged dimagnesium complex. This then rapidly reacts with excess CO2 to give the magnesium carbonate, which can be reduced back to the magnesium(1) starting material using potassium metal, thereby closing the synthetic cycle. The proposed oxo-bridged dimagnesium intermediate was rationally synthesised and shown to act as a nucleophilic oxo-transfer reagent in reactions with the CO<sub>2</sub> analogues, CS<sub>2</sub> and CyNCNCy. Taken as a whole this study demonstrates that magnesium(1) dimers can display very similar reactivity, with respect to small molecules activations, as do low valent f-block compounds (specifically those of Sm<sup>II</sup> and U<sup>III</sup>). Given the emerging importance of the latter for such transformations, we believe that magnesium(1) compounds hold considerable potential as cheaper, less toxic, non-radioactive and diamagnetic alternatives to low valent f-block metal complexes in this realm.

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