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Héloïse Dossmann Soldi-Lose, Carlos Afonso, Denis Lesage, Jean-Claude Tabet, Einar Uggerud. Formation and Characterization of Gaseous Adducts of Carbon Dioxide to Magnesium,  $(\text{CO}_2) \text{MgX}(-)$  ( $\text{X}=\text{OH}, \text{Cl}, \text{Br}$ ).. *Angewandte Chemie International Edition*, 2012, 51 (28), pp.6938-6941. 10.1002/anie.201108477 . hal-00708360

**HAL Id: hal-00708360**

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Submitted on 17 Jul 2023

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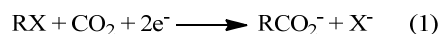
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# Formation and Characterization of Gaseous Adducts of Carbon Dioxide to Magnesium, (CO<sub>2</sub>)MgX<sup>-</sup> (X = OH, Cl and Br)

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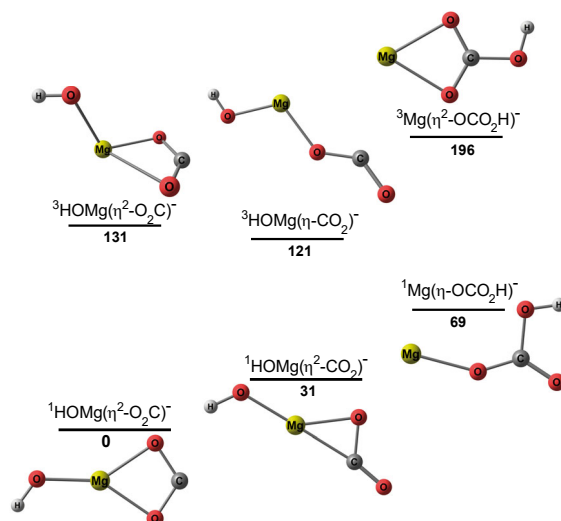
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There is great current interest in the properties and reactivity of carbon dioxide and its activated forms due to the relevance to photosynthetic CO<sub>2</sub> uptake<sup>[1]</sup> and to sequestration of CO<sub>2</sub> from flue gases formed upon the burning of fossil fuels<sup>[2]</sup> - the former process being essential to life on Earth, the latter important in sustaining it under balanced conditions.<sup>[3]</sup> Efficient fixation of carbon dioxide by covalent C-C bond formation requires two extra electrons, schematically,



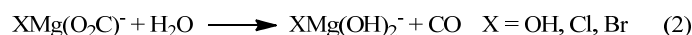
This general two-electron reduction scheme is applicable to a range of different reactions. In plant cells, the formation of a bond between the carbon atom of CO<sub>2</sub> and one carbon of the other substrate, ribulose-1,5-bisphosphate (RuBP), occurs at the magnesium centred active site of the enzyme RuBisCO,<sup>[4]</sup> the electrons being obtained from chlorophyll via NADPH<sub>2</sub>. In electrochemical and photo-electrochemical CO<sub>2</sub> fixation, they are more directly supplied by coupling to an electrochemical process, mediated by various metals.<sup>[5]</sup> Synthetic ways to fixate CO<sub>2</sub> are very often involving Grignard reaction.<sup>[6]</sup> This reaction proceeds via metals, traditionally magnesium, providing directly the electrons. In this context, we have undertaken the study of some elusive [Mg + CO<sub>2</sub>] complexes in order to characterize them and study their ability to form new C-C bonds. Mass spectrometry was an ideal tool as it makes possible to produce, isolate and probe the structures and reactivities of elusive intermediates in the rarefied gaseous state, *i.e.* in a chemical environment free from interference of neighbouring molecules, including the effects of a solvent, which otherwise would make such intermediates too short lived for observation.<sup>[7]</sup> In the following we report on the chemical characterization and reactivity of a novel and fragile structural form of carbon dioxide bonded to magnesium. The species in question are conveniently prepared by electrospray ionization of solutions containing Mg(II) salts and oxalic acid. In parallel to the experiments, quantum chemical calculations have been performed to gain more insights into the structures and mechanisms of the species under study.

Electrospray ionization (ESI) in the negative ion mode was applied to mixtures of oxalic acid (Ox) and magnesium salts MgCl<sub>2</sub> and MgBr<sub>2</sub> dissolved in CH<sub>3</sub>OH/H<sub>2</sub>O (v/v 90/10) From the recorded mass spectra we observe signals due to MgC<sub>2</sub>O<sub>5</sub>H<sup>-</sup>, MgClC<sub>2</sub>O<sub>4</sub><sup>-</sup> and MgBrC<sub>2</sub>O<sub>4</sub><sup>-</sup> ions, respectively. Upon collisional activation, these ions (Supporting Information) dissociate by loss of CO<sub>2</sub>, 2CO<sub>2</sub> and MgC<sub>2</sub>O<sub>4</sub>. The ions resulting from carbon dioxide loss, MgCO<sub>3</sub>H<sup>-</sup>, MgClCO<sub>2</sub><sup>-</sup> and MgBrCO<sub>2</sub><sup>-</sup>, will be the subject of this Communication. Accurate mass measurements and isotopic patterns confirm each of the molecular formulae. Three possible molecular structures for the [MgCO<sub>2</sub>X]<sup>-</sup> ion have been considered: XMg(η<sup>2</sup>-O<sub>2</sub>C)<sup>-</sup>, XMg(η<sup>2</sup>-CO<sub>2</sub>)<sup>-</sup> and Mg(O<sub>2</sub>CX)<sup>-</sup> (X = OH, Cl, Br). Quantum chemical calculations for X = OH show that of these isomeric forms the former is lowest in potential energy (Figure 1) and that the electronic triplet is 131 kJ.mol<sup>-1</sup> higher in energy than the singlet. A potential energy diagram (Supporting Information) shows possible mechanisms of formation of these ions from the starting oxalic acid adduct. The application of decarboxylation as a method of forming negatively charged metallic ions is known from the literature. Jacob *et al.*<sup>[8]</sup> used alkali and alkaline earth acetates to form organometallics and Curtis *et al.*<sup>[9]</sup> and Attygalle *et al.*<sup>[10]</sup> have demonstrated that metal oxalate anions, *e.g.* KC<sub>2</sub>O<sub>4</sub><sup>-</sup>, dissociate upon collisional activation by successive losses of carbon dioxide, providing a useful method for making negatively charged atomic metal ions in the gas phase. The latter authors also suggested a bidentate structure for the MCO<sub>2</sub><sup>-</sup> intermediate observed in their experiments, supported by quantum chemical calculations, in analogy with XMg(η<sup>2</sup>-O<sub>2</sub>C)<sup>-</sup> reported here.

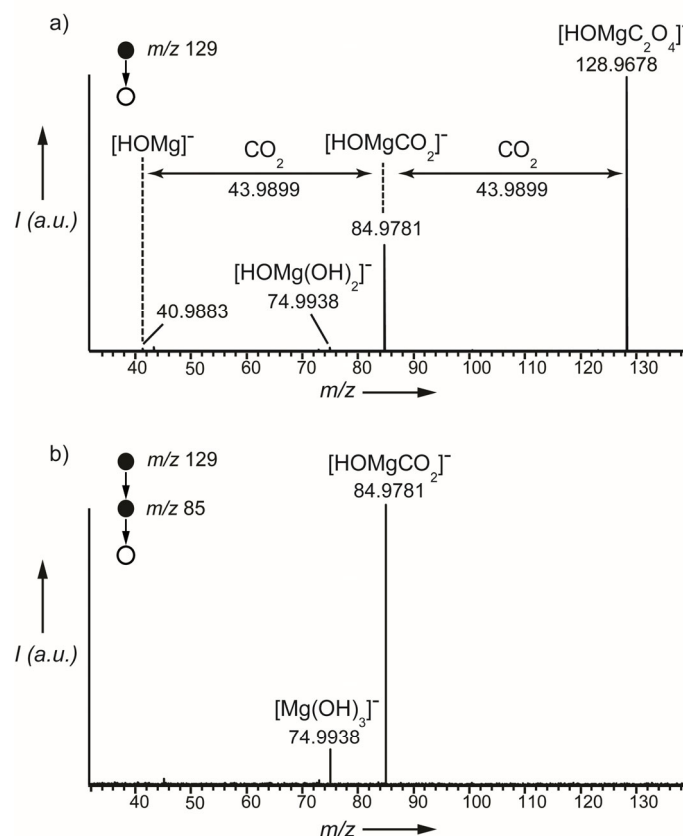


**Figure 1.** Relative energies in  $\text{kJ}\cdot\text{mol}^{-1}$  for  $\text{HOMg}(\eta^2\text{-O}_2\text{C})^-$ ,  $\text{HOMg}(\eta^2\text{-CO}_2)^-$  and  $\text{Mg}(\text{OCO}_2\text{H})^-$  in their electronic singlet and triplet forms, as indicated, obtained from G4 optimized structures.

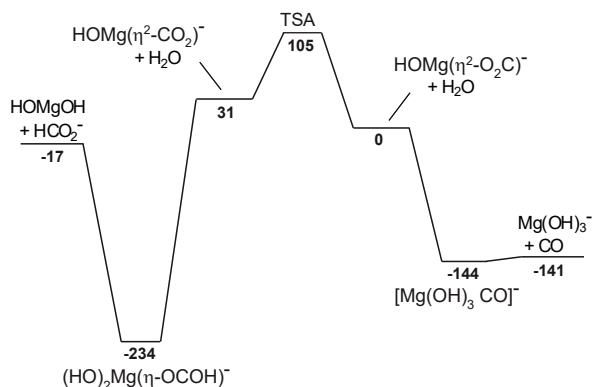
Isolation of  $\text{XMg}(\text{O}_2\text{C})^-$  inside the cell of an FT-ICR mass spectrometer leads to loss of the elements of carbon monoxide upon water addition, Figure 2.



The same reaction is observed during tandem mass spectrometry collisional activation at extended times and slightly elevated background water pressures using either a triple quadrupole mass spectrometer or a Paul ion trap. The reaction appears to be efficient, although the experimental setups provide no accurate estimates of the bimolecular rate coefficients. Figure 3 shows the computed potential energy diagram relevant to the case where  $\text{X} = \text{OH}$ . The right hand side of the diagram, which is most relevant to the experimental observation, shows that water addition essentially occurs in one step, however in a concerted but clearly non-synchronous sequence of bond formation and dissociation that is best explained as a dissociative hydration reaction. In the first stage the incoming water forms an O-Mg bond to the central magnesium atom, whereupon one of the water hydrogen atoms gradually transfers to one of the basic oxygen atoms of the  $\text{CO}_2$  moiety. At the G4 level of theory, this hydrogen transfer proceeds without barrier, explaining why no  $[\text{HOMgCO}_2\text{H}_2\text{O}]^-$  intermediate complex is displayed on the potential energy diagram in Figure 3. A weakly bonded  $[\text{Mg}(\text{OH})_3\text{-CO}]^-$  complex is thus formed, which finally dissociates. The driving forces of the reaction are formation of a strongly bonded magnesium oxide form and the concurrent hydration. The former is similar to the well-known highly exothermic reaction between magnesium metal and  $\text{CO}_2$ .<sup>[11]</sup> As a consequence, the  $\text{Mg}(\text{OH})_3^-$  product is extremely stable. A related mechanism was found in reactions between  $[\text{CH}_3\text{MgL}_2]^-$  and water.<sup>[12]</sup> The left hand side of Figure 3 shows an alternative route, namely the possible reaction between the isomeric  $\text{HOMg}(\eta^2\text{-CO}_2)^-$  and water, which indicates that the expected reaction ionic product would be formate anion rather than the observed  $\text{Mg}(\text{OH})_3^-$ , substantiating our structural and mechanistic assignment. Figure 3 also shows that the two isomers are separated by a considerable energy barrier of  $105 \text{ kJ}\cdot\text{mol}^{-1}$ .

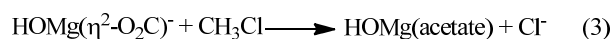


**Figure 2.** SORI-CID spectrum of (a)  $\text{HOMg}(\text{C}_2\text{O}_4)^-$   $m/z$  129 and (b)  $\text{HOMg}(\text{CO}_2)^-$   $m/z$  85 reacting with water. The  $\text{HOMg}(\text{H}_2\text{O})^-$  ion  $m/z$  75 is produced through loss of  $\text{CO}$  from  $\text{HOMg}(\text{CO}_2)^-$  upon addition of  $\text{H}_2\text{O}$ .

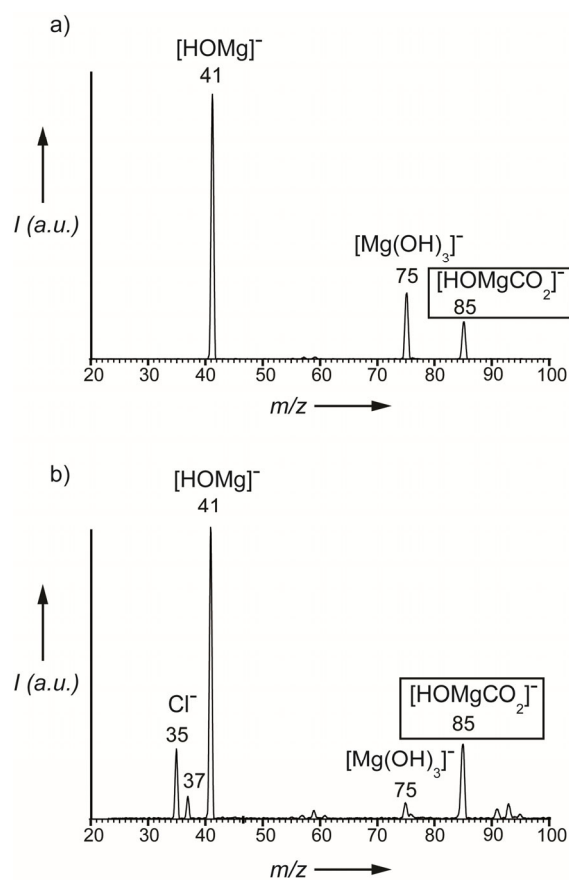


**Figure 3.** Potential energy diagram of  $\text{HOMg}(\text{CO}_2)^-$  reacting with water.

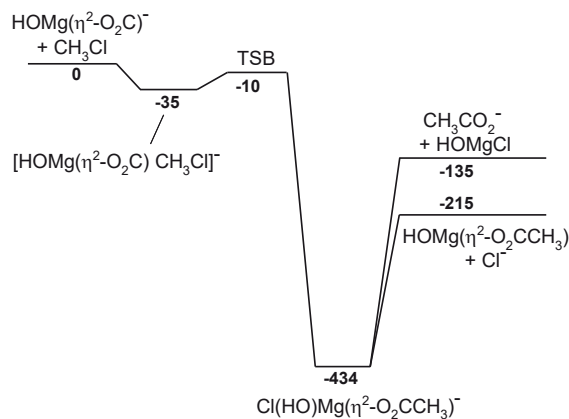
Evidence for carbon-carbon bond formation is found in reactions between  $\text{XMg}(\text{CO}_2)^-$  and alkyl halides, which is supported by quantum chemical model calculations. Figure 4 shows that the product ion in this reaction is  $\text{Cl}^-$ . In the case of the reaction with  $\text{CH}_3\text{I}$  the ionic product is  $\text{I}^-$ . In addition, depending on the ion translational energy and observation time window (which are different in the triple quadrupole, the FT-ICR and the Paul trap), variable amounts of  $\text{XMg}^-$  due to collision-induced  $\text{CO}_2$  loss are observed. Only small amounts of acetate ion are observed, *vide infra*. The computed energy diagram of Figure 5 reveals the interesting details. The calculations substantiate the idea that the reaction is due to a C-C forming  $\text{S}_{\text{N}}2$  reaction, via the transition structure TSB (see Figure 6) at  $-10 \text{ kJ}\cdot\text{mol}^{-1}$  relative to the separated reactants, demonstrating the increased nucleophilic character of the carbon atom of  $\text{HOMg}(\eta^2\text{-O}_2\text{C})^-$  compared to  $\text{CO}_2$ . The ion displaces the chloride upon which the complex of magnesium acetate hydroxide and  $\text{Cl}^-$  is formed, whereupon  $\text{Cl}^-$  separates:



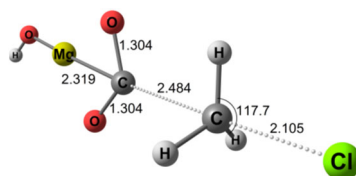
The alternative loss of acetate from the product complex is energetically less favourable and entropically more demanding, evident from the insignificant peaks at  $m/z$  59 in the product mass spectra, as reported above.



**Figure 4.** (a) CID of  $[\text{HOMgCO}_2]^-$   $m/z$  85 and (b) CAR of  $[\text{HOMgCO}_2]^-$   $m/z$  85 with  $\text{CH}_3\text{Cl}$  introduced into the collision cell using the triple quadrupole mass spectrometer.



**Figure 5.** Potential energy diagram of  $\text{HOMg}(\text{CO}_2)^-$  reacting with  $\text{CH}_3\text{Cl}$ .



**Figure 6.** G4-optimized structure of TSB (bond lengths in Å and angles in degrees).

The experimental evidence presented here together with the insights of the quantum chemical calculations indicate unique electronic properties of the  $\text{HOMg}(\eta^2\text{-O}_2\text{C})^-$  structure. Formally it is a complex of one  $\text{OH}^-$ , one  $\text{CO}_2^{2-}$  and one  $\text{Mg}^{2+}$ . In practice, the electronic situation is of course more complex but straightforward enough to describe. According to the NBO population analysis, the  $\text{CO}_2$  moiety almost carries two negative charges (-1.7), implying that magnesium is in a semi-reduced  $\text{Mg}(\text{I})$  state (+1.5). Very interestingly, a negatively charged  $\text{CO}_2$  molecule is a requirement for electrochemical conversion of  $\text{CO}_2$  to  $\text{CO}$ , in accordance with the reaction with water reported above.<sup>[13]</sup> Upon collisionally induced dissociation we observe that  $\text{XMg}(\eta^2\text{-O}_2\text{C})^-$  in all cases loses  $\text{CO}_2$ . We have not been able to establish the experimental conditions required to study the reverse association reactions  $\text{XMg}^- + \text{CO}_2$  because of the very low  $\text{XMg}^-$  signal, although in the case of  $\text{X} = \text{OH}$  our quantum chemical calculations clearly shows that formation of  $\text{HOMg}(\eta^2\text{-O}_2\text{C})^-$  is the more energetically favoured product. The addition starts with the formation of a bond between Mg and one of the oxygen atoms of the  $\text{CO}_2$ , whereupon the linear  $\text{O}=\text{C}=\text{O}$  starts to bend, eventually leading to a second Mg-O contact and formation of a four membered ring. There are no local minima or transition structures along this path.

The nucleophilic character of  $\text{XMg}(\eta^2\text{-O}_2\text{C})^-$  demonstrated in the reactions with alkyl halides reported above is also evident from an MO analysis. The highest occupied orbital (HOMO) clearly has a carbon lone pair character (Supporting Information). Although the prototypical carbene, singlet  $\text{CH}_2$ , is less stable than its triplet form in the isolated gas phase it is known to be persistent even when interacting with hydrogen bond donors in various complexes.<sup>[14]</sup> Moreover, upon substitution by electron donating substituents and protective groups singlet carbenes are stable and isolable.<sup>[15]</sup> For example, spectroscopic evidence has been presented for gas phase dihydroxymethylene,  $\text{HOCOH}$ ,<sup>[16]</sup> containing the same central structural element. We will emphasize that the compound at hand is a carbene (having one lone pair at carbon), rather than a carbon having two lone pairs,<sup>[17]</sup> since a second frontier MO having carbon lone pair character is not found.

We speculate that the findings presented here have some relevance to the mechanism of the dark reaction of photosynthesis. In the carbon-carbon bond formation step of this reaction,  $\text{CO}_2$  is incorporated into a carbohydrate catalyzed by the magnesium-centred enzyme RuBisCo. A key issue of this reaction is the difficulty by which  $\text{CO}_2$  is able to adapt a structure close to that of a carboxylate group at the transition state.<sup>[4]</sup> We propose that electron transfer (from  $\text{NADPH}_2$ ) to the magnesium atom prior to or during this event will allow this to happen via the quasi  $\text{Mg}(\text{I})$  intermediate as described here.

**Keywords:** Carbon dioxide fixation · gas phase reactions · computational chemistry · nucleophilic substitution · photosynthesis

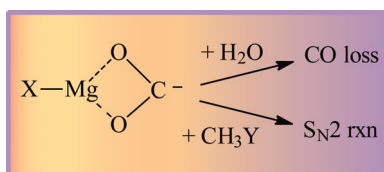
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## A key intermediate

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The structure and chemical reactivity of a novel reduced form of  $\text{CO}_2$  bonded to magnesium,  $\text{XMg}(\eta^2\text{-O}_2\text{C})^-$ , is reported. Upon reaction with water it loses  $\text{CO}$ , while it adds  $\text{CH}_3$  upon reaction with alkyl halides thereby signifying carbon nucleophilicity in  $\text{S}_{\text{N}}2$  reactions.