ChemPubSoc Europe
DOI: 10.1002/cssc.201501664
CHEMSUSCHEM Communications

Unprecedented Carbonato Intermediates in Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium(Salen) Complexes

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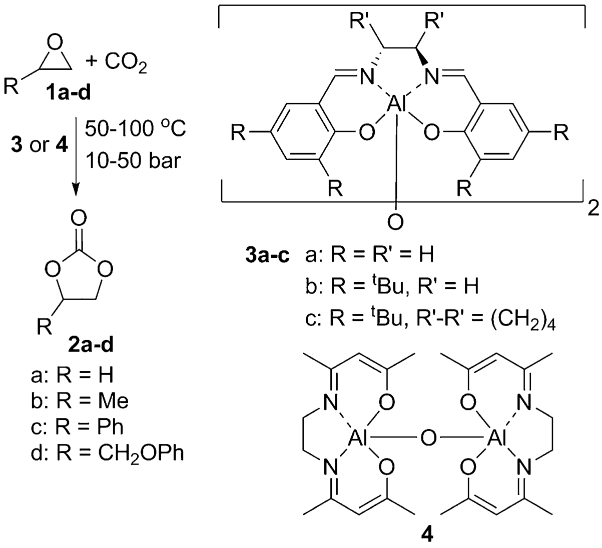
The mechanism by which $[Al(salen)]_2O$ complexes catalyse the synthesis of cyclic carbonates from epoxides and carbon dioxide in the absence of a halide cocatalyst has been investigated. Density functional theory (DFT) studies, mass spectrometry and ^1H NMR, ^{13}C NMR and infrared spectroscopies provide evidence for the formation of an unprecedented carbonato bridged bimetallic aluminium complex which is shown to be a key intermediate for the halide-free synthesis of cyclic carbonates from epoxides and carbon dioxide. Deuterated and enantiomerically-pure epoxides were used to study the reaction pathway. Based on the experimental and theoretical results, a catalytic cycle is proposed.

Utilization of carbon dioxide as a sustainable carbon source for the synthesis of organic chemicals has emerged as a major challenge.[1] One commercial process that uses carbon dioxide as a feedstock is the synthesis of cyclic carbonates **2** from epoxides **1**. Cyclic carbonates have a number of applications including as electrolytes in lithium-ion batteries.[2] Current industrial processes for the synthesis of **2** utilize inefficient quaternary ammonium or phosphonium salt catalysts and require the use of high temperatures and pressures.[3] Aluminium(salen) complexes **3**, in conjunction with a halide co-catalyst are amongst the most active catalyst systems for this reaction at or close to room temperature and one bar pressure.[4] The halide acts as a nucleophile to ring-open the epoxide. We recently reported, however, that complex **3** can act as a catalyst for the synthesis of **2** at 50–100 °C and 10–50 bar without the need for a halide co-catalyst (Scheme 1).[5] This unexpected finding is incompatible with the established mechanisms for cyclic carbonate synthesis[6] and prompted a study of the reaction mechanism using density functional theory (DFT) calculations along with spectroscopic and isotope labelling experiments. The resulting unprecedented reaction pathways are reported herein.



Scheme 1. Synthesis of cyclic carbonates from epoxides and CO_2.

DFT calculations were initially carried out using $[Al(acen)]_2O$ **4** as a model to accelerate the calculations. Accuracy and suitability of the applied DFT methodology were determined by benchmark calculations and comparison with literature data as detailed in the Supporting Information.[7] Complexes **3** and **4** are both catalysts for the reaction shown in Scheme 1.[8] First calculations focused on the interaction between complex **4** and epoxides **1 a**–**c**, carbon dioxide, and product **2 a**. These calculations indicated that complex **4** would form an adduct with carbon dioxide, but not with epoxides or cyclic carbonates.

One possible interaction between complex **4** and carbon dioxide is via an oxygen atom of carbon dioxide and an aluminium atom of **4**. However, the DFT calculations did not provide evidence for such an interaction.[7] Another possible interaction is that between the bridging oxygen of complex **4** and the carbon of carbon dioxide. DFT calculations confirmed the presence of a stable adduct of this type (adduct state in Figure 1). The molar standard entropy change ($\Delta_r S^{\ominus}$) upon adduct formation from complex **4** and carbon dioxide was $-81\ J\,mol^{-1}\,K^{-1}$,

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Supporting Information for this article can be found under http://dx.doi.org/10.1002/cssc.201501664.

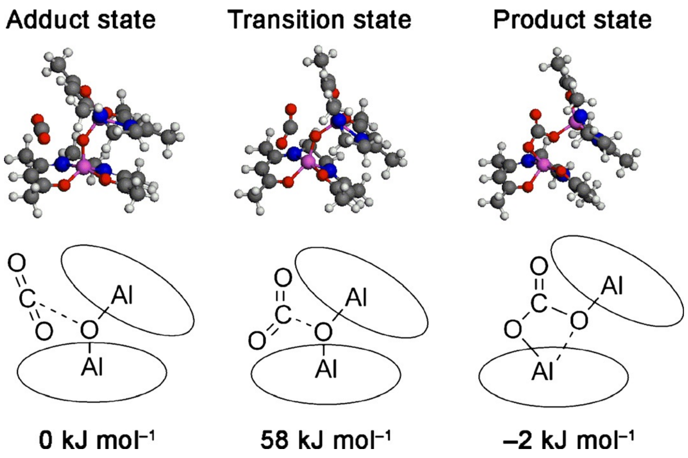


Figure 1. Models and free energies at standard conditions ($\Delta G^{\ominus}$) of the calculated adduct, transition, and product states of CO_2 insertion into the Al-μ-O-Al unit of **4**. Colour coding: hydrogen white, carbon grey, oxygen red, nitrogen blue and aluminium pink.

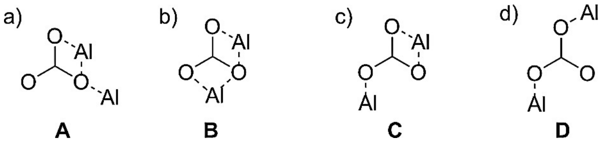


Figure 2. Possible bonding arrangements of the Al-OC(O)O-Al-unit in $[Al(acen)]_2CO_3$.

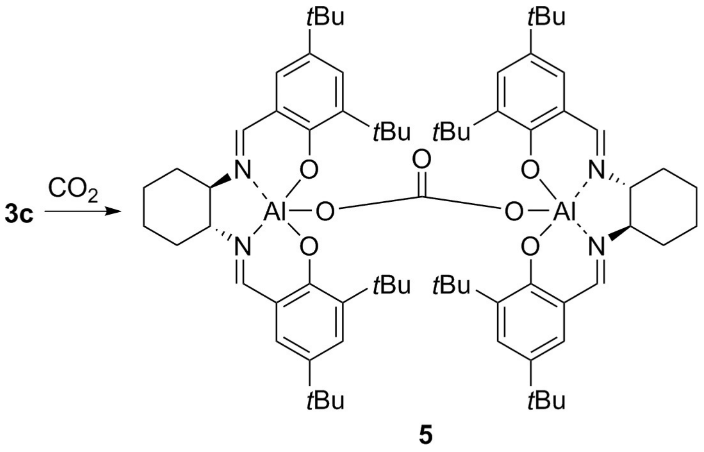
which is consistent with formation of an associative adduct. Adduct formation was exothermic with a molar standard enthalpy change ($\Delta_\mathrm{r}H^{\ominus}$) of −38 kJ mol^{-1}. This led to a molar standard free energy change ($\Delta_\mathrm{r}G^{\ominus}$) of −13 kJ mol^{-1}. So the adduct formation is exergonic at standard conditions. Significantly therefore, DFT calculations indicate that $[Al(acen)]_2O$ is a better Lewis base than Lewis acid with respect to carbon dioxide.

The reactivity of the adduct was further investigated by DFT calculations, which indicated that carbon dioxide can insert into one of the aluminium μ-oxygen bonds to form a carbonato bridged bimetallic aluminium complex through the transition state shown in Figure 1. The energetics of this incorporation at standard conditions and with respect to the adduct state were calculated as −2 kJ mol^{-1}, −13 kJ mol^{-1}, and −38 J mol^{-1} K^{-1}, for free energy ($\Delta_\mathrm{r}G^{\ominus}$), enthalpy ($\Delta_\mathrm{r}H^{\ominus}$), and entropy change ($\Delta_\mathrm{r}S^{\ominus}$), respectively. Hence, there is a thermodynamic driving force for the formation of $[Al(acen)]_2CO_3$ from complex **4** and CO_2. The transition state for the incorporation was located and characterised. The free activation energy ($\Delta_\mathrm{r}^{\ddagger}G^{\ominus}$) was only 58 kJ mol^{-1} with respect to the adduct state. Hence, the modelling revealed that the incorporation is feasible and facile at standard conditions. Since it was shown that the free energy changes were nearly pressure and temperature independent,[7] we can assume that the free energy changes also apply to CO_2 incorporations under the experimental conditions specified in Scheme 1.

The carbonato bridge formed through CO_2 insertion can be bound to the aluminium atoms in four different ways (**A**–**D**), as indicated in Figure 2. The $\mu^2\kappa^1{:}\kappa^2$-CO_3 complex, **A**, reflects the product state, depicted in Figure 1. This complex was calculated to isomerize to complexes **B** and **C**.[7] For the $\mu^2\kappa^1{:}\kappa^1$-CO_3 complex, **D**, a stable minimum could not be located as the compound transformed to **C** upon geometry optimization. The free energy changes ($\Delta_\mathrm{r}G^{\ominus}$), relative to parent complex **4** and non-interacting carbon dioxide, were found to be −15, −13, and −6 kJ mol^{-1} for **A**–**C**, respectively. Thus, the differences in $\Delta_\mathrm{r}G^{\ominus}$ values are small. The Gibbs energies of activation ($\Delta_\mathrm{r}^{\ddagger}G^{\ominus}$) were calculated to be 24 and 19 kJ mol^{-1} for the transformation of **A** to **B** and from **B** to **C**, respectively. Since the isomeric states **A**-**C** are close in free energy and since they can easily interconvert, they provide extra stability to the carbonato bridged complex.

To confirm that the modelling on acen complexes was relevant to salen complexes, the three states shown in Figure 1 were recalculated as the corresponding salen complexes derived from complex **3a**.[7] Essentially identical structures and energetics for the transition state and the carbonato bridged complex **5a** were obtained. The transition state again had a free activation energy ($\Delta_\mathrm{r}^{\ddagger}G^{\ominus}$) of 58 kJ mol^{-1} and formation of the carbonato complex had free energy ($\Delta_\mathrm{r}G^{\ominus}$), enthalpy ($\Delta_\mathrm{r}H^{\ominus}$), and entropy changes ($\Delta_\mathrm{r}S^{\ominus}$) of 6 kJ mol^{-1}, −7 kJ mol^{-1} and −45 J mol^{-1} K^{-1} at standard conditions relative to the initial carbon dioxide adduct.

There is no precedent for carbon dioxide insertion into the bridging metal-oxygen-metal bond of an oxo-bridged bis-metal(salen) complex or into an oxo-bridged aluminium complex.[9] However, the insertion of carbon dioxide into metal-oxygen bonds in general is well-known.[10] The insertion of carbon dioxide into complex **3c** (Scheme 2) was experimentally confirmed when complex **3c** as a solid was treated with carbon dioxide at 50–100 °C and 50 bar pressure. The resulting carbonato complex **5** was found to be metastable, slowly loosing carbon dioxide to reform complex **3c**. Nevertheless, **5** was characterised by ^{1}H NMR, infrared and mass spectrometry.[7] The ^{13}C labelled complex was also prepared in situ by passing ^{13}C labelled carbon dioxide into a $CDCl_3$ solution of complex



Scheme 2. Formation of carbonato bridged bis-aluminum(salen) complex **5c**.

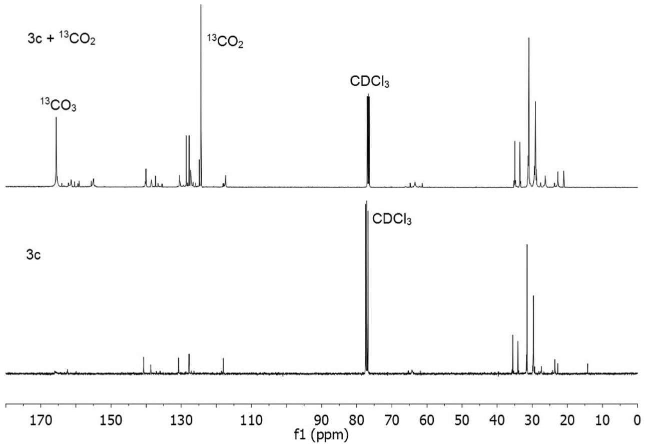
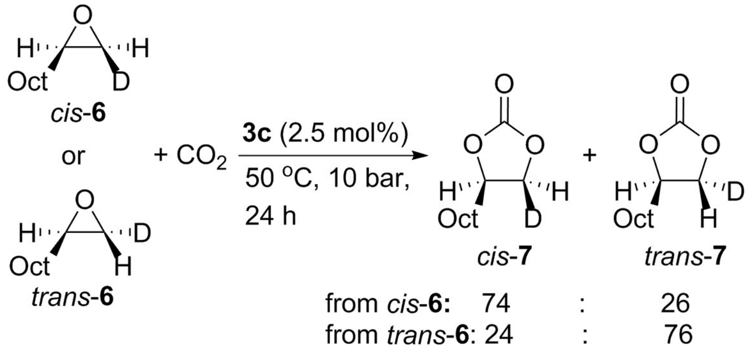


Figure 3. ^{13}C NMR spectrum of complex **3c** in CDCl$_3$ in the presence of ^{13}CO$_2$ (top) in comparison to parent **3c** in CDCl$_3$ (bottom).

3c at −78 °C, confirming that the insertion is feasible and facile, as predicted by DFT calculations. The resulting ^{13}C NMR spectrum (Figure 3) showed a resonance at 165.60 ppm, characteristic of a carbonato bridged complex,[11] and a shift in the other resonances relative to **3c**. ^{13}C NMR exchange spectroscopy (EXSY) experiments showed that complex **5** was in equilibrium with **3c** and magnetisation transfer was observed between the carbonato group of complex **5** (165.60 ppm) and dissolved ^{13}CO$_2$ (124.83 ppm).[7]

To investigate the relevance of carbonato complex **5** to the catalytic cycle, it was dissolved together with tetrabutylammonium bromide in epoxide **1b** under nitrogen at room temperature. ^{1}H NMR and GC analysis[7] confirmed the formation of carbonate **2b**, showing that complex **5** is catalytically active and that the carbonato bridge acts as a source of carbon dioxide.

The reaction mechanism in the absence of tetrabutylammonium bromide was then studied using monodeuterated *cis*- and *trans*-decylene oxide[12] **6** as substrates at 50 °C and 10 bar carbon dioxide pressure to investigate the stereochemistry of the reaction (Scheme 3). The results indicate that the reaction proceeds mainly with retention of epoxide stereochemistry, giving a 3:1 ratio of retention to inversion products. Formation of both *cis*- and *trans*-cyclic carbonate **7** in the absence of tetrabutylammonium bromide indicates that two different reaction pathways are operative.



Scheme 3. Cyclic carbonate synthesis from deuterated epoxides **6**.

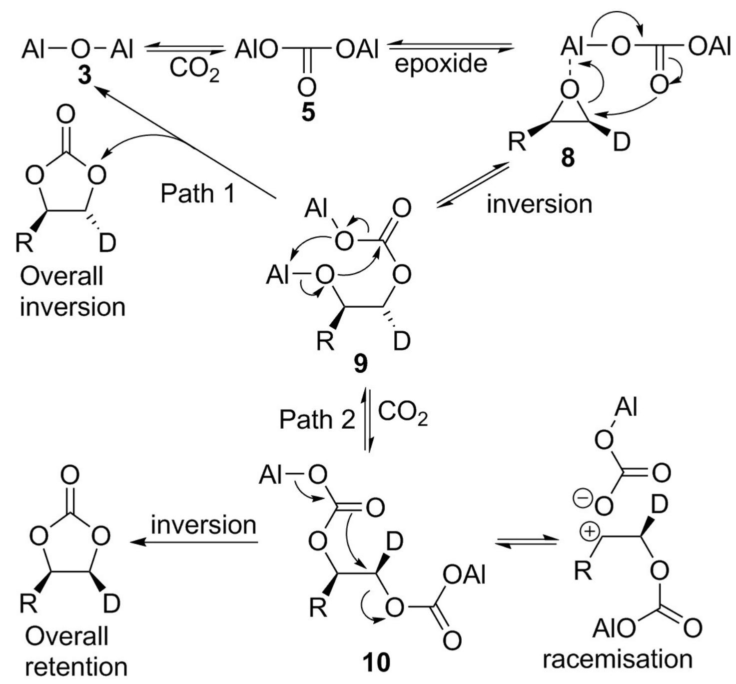
Two control experiments were also carried out. Complex **3c** and tetrabutylammonium bromide were used as catalysts for the reaction of substrates **6** at room temperature and one bar pressure, and 100 % retention of the epoxide stereochemistry was observed.[7] *Cis*-**6** was also treated with one equivalent of carbonato complex **5** at 50 °C under 1 bar nitrogen in the absence of carbon dioxide. Exclusive formation of *trans*-**7** was observed, indicating that this reaction proceeded with complete inversion of epoxide stereochemistry.

The stereochemical consequences at the more hindered carbon atom of the epoxide was investigated using (*R*)-styrene oxide [(*R*)-**1c**] and (*S*)-glycidyl phenyl ether [(*S*)-**1d**] at 50 °C and 10 bar carbon dioxide pressure. In the presence of tetrabutylammonium bromide, cyclic carbonate synthesis from either enantiomerically pure epoxide proceeded with 100 % retention of the epoxide stereochemistry as determined by chiral HPLC.[7] However, in the absence of tetrabutylammonium bromide, (*R*)-**1c** gave a 97:3 ratio of (*R*)- and (*S*)-**2c** and (*S*)-**1d** gave a 99.5:0.5 ratio of (*S*)- and (*R*)-**2d** indicating that some cleavage of the more substituted carbon-oxygen bond of the epoxide occurred.

A catalytic cycle for cyclic carbonate synthesis catalysed by complexes **3** in the absence of tetrabutylammonium bromide consistent with the above results is shown in Scheme 4. Carbon dioxide first inserts into the aluminium-oxygen bond of complex **3** to give carbonato complex **5**. Subsequent complexation of the epoxide gives adduct **8** which undergoes intramolecular epoxide ring-opening at the less hindered carbon atom of the epoxide by the carbonate with inversion of configuration to give intermediate **9**. From complex **9** two pathways lead to the cyclic carbonate. In path 1, the alkoxide of complex **9** cyclises onto the carbonyl of the carbonato group forming the cyclic carbonate and regenerating complex **3**. This pathway involves a single inversion of configuration at the epoxide and requires no additional carbon dioxide beyond formation of **5**. Hence it accounts for the inversion of epoxide configuration observed when complex **5** is used to induce the reaction in the absence of carbon dioxide.

Pathway 2 involves a second carbon dioxide insertion into the aluminium alkoxide bond[13] of complex **9** to form biscarbonato complex **10**. The carbonato groups in complex **10** will be good nucleophiles and good leaving groups, allowing formation of the cyclic carbonate to occur by a second intramolecular substitution reaction with a second inversion of stereochemistry, giving overall retention of epoxide stereochemistry. Formation of complex **10** also provides an explanation of the partial racemization by S$_N$1 type cleavage of the carbonato group attached to the more substituted carbon atom.

Additional DFT calculations were carried out to support the routes shown in Scheme 4.[7] Thus, carbonato bridged complexes were found to coordinate epoxides as required for the formation of species **8**. The six-coordinate aluminium in complex **8** was found to exist in a *cis*-β configuration,[14] which enables the intramolecular rearrangement to form complex **9**.



Scheme 4. Proposed mechanism for the synthesis of cyclic carbonates from epoxides and CO_2 catalysed by complexes **3** in the absence of Bu_4NBr. The salen ligand attached to each aluminium ion is not shown for clarity.

In conclusion, the combination of theoretical and experimental studies have allowed key features of the mechanism of cyclic carbonate synthesis catalysed by bimetallic aluminium(salen) complexes **3** in the absence of a cocatalyst to be elucidated. The reaction proceeds by an unprecedented carbonato bridged bimetallic aluminium(salen) complex which has been characterized and shown to be catalytically active.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Programme FP7-NMP-2012 under grant agreement number 309497.

Keywords: aluminum catalyst · carbon dioxide fixation · cyclic carbonate · density functional calculations · reaction pathway

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Received: December 18, 2015