

## Kleij Research Group



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### Abstract

Our current research activities focus on the valorization of carbon dioxide and renewable feed stocks into value-added organic matter using organocatalytic and metal-mediated catalytic approaches. We have and continue to be active in the preparation of highly functional organic carbonates, focusing on sustainable solutions and improving activity and stereo-selectivity profiles. We have recently expanded our portfolio activities to other classes of relevant compounds such as oxazolidinones, CO<sub>2</sub>-based

(bio)polymers and more complex organic matter derived from stereo-selective, multi-component coupling approaches. An important part of our work puts attention to new catalyst design and efforts to get a higher degree of understanding concerning the observed reactivity/selectivity features by means of mechanistic and computational studies. Collaborations with the industrial sector form part of our work in order to be able to potentially transfer technological advancements from bench to pilot scale and beyond.

### Carbon Dioxide Conversion

Our ongoing efforts in the area of valorization of carbon dioxide (representing a waste compound from all combustion processes) has resulted in a series of new catalytic processes based on organocatalytic or metal mediated CO<sub>2</sub> conversions to value-added organic compounds including organic carbonates, polymers and other heterocyclic compounds of academic and industrial interest. Some highlights of our work are provided below.

An effort has been made to provide a new organocatalytic solution for the formation of organic cyclic carbonates from epoxides and CO<sub>2</sub> using a recyclable system based on pyrogallol (= 1,2,3-trihydroxybenzene). The latter is a commercially available, cheap and naturally occurring polyphenol that shows exceptional epoxide activation behavior. The essence of its activation potential is the array of hydrogen bonds that are present in the key intermediates and preceding transition states (cf., *ChemSusChem* **2012**, *5*, 2032) thereby facilitating these type of transformations more easily under very mild reaction conditions (25-45°C, 2-10 bar).

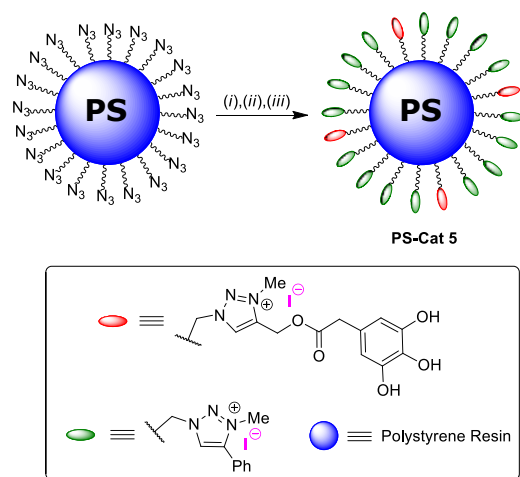


Figure 1 - PS-supported bifunctional catalyst based on pyrogallol and triazolium iodide functional groups for the formation of organic carbonates under mild conditions.

Our new design combines the use of a polystyrene (PS) support and the immobilization of both the H-bond activating group (*i.e.*, pyrogallol) and nucleophilic groups (Figure 1). This catalyst design is rather unique as it allows for predetermined ratios between the H-bond activator and nucleophilic sites and thus for

optimization of the catalytic activity and recycling features. This supported organocatalyst could be applied to the synthesis of various organic carbonates using the same batch of catalyst: the latter was conveniently filtered from the crude product and reused without any cross-contamination. Recycling of the same batch was studied and this showed good overall potential (11 cycles were successfully carried out) with a total turnover number >900.

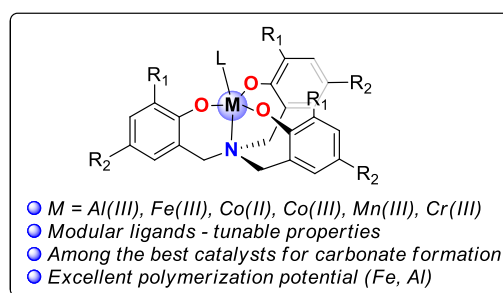


Figure 2 - Al(III) based aminotriphenolate complexes active in organic carbonate formation.

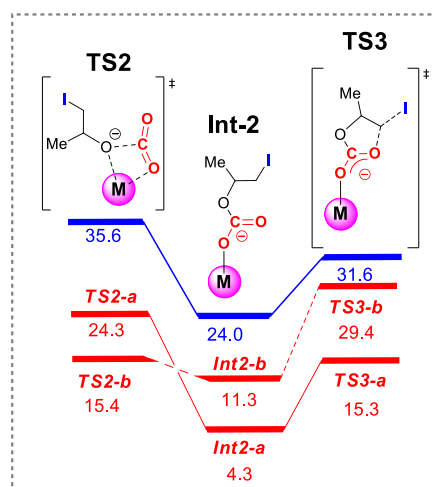


Figure 3 - Part of the calculated mechanistic cycle for both Zn(salen) (blue trace) as well as Al(aminotriphenolate) based catalysts (red trace). The lower barriers for the Al complex (only those pertinent to CO<sub>2</sub> insertion and ring-closing steps are shown here) are indicative for the higher reactivity observed. M stands for the metal in the complexes, all relative free energies are in kcal/mol.

Separately, we have studied in detail the use of Al(III) centered aminotriphenolate complexes (Figure 2) as catalysts for organic carbonate formation and estimated their activities through initial kinetic data. Benchmarking studies with known active Zn and Al based catalysts revealed

that the Al(aminotriphenolate) complexes are among the most active reported to date with initial turnover numbers up to 36,000 h<sup>-1</sup> and TONs exceeding 120,000. This novel, unprecedented reactivity has allowed using these catalysts in organic transformations beyond the state of the art including (highly) challenging internal epoxides, oxetanes and functional substrates (*cf.*, *JACS* **2013**, 135, 1228). Initial kinetic data are also in line with first order in Al complex and DFT studies (Figure 3) have clearly shown the underlying reasons for this Al system being more active than our previously reported Zn(salen) catalyst (*Chem. Commun.* **2010**, 46, 4580).

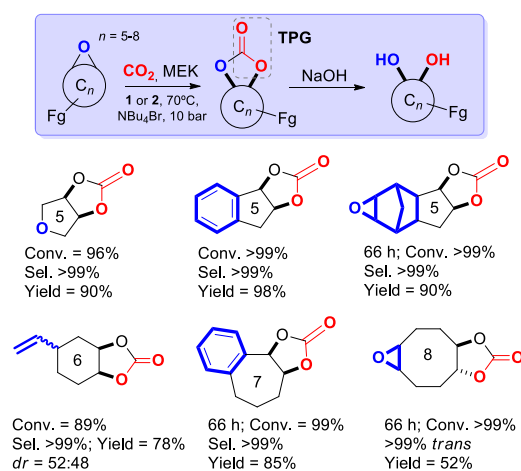


Figure 4 - Using CO<sub>2</sub> as a TPG and carbonates as intermediates towards *cis*-diol formation with part of the substrate scope investigated.

The formation of organic carbonates from epoxides and CO<sub>2</sub> also allows capitalizing on the use of these compounds as precursors in organic synthesis. A clear example was provided by the use of carbon dioxide as a temporary protecting group (TPG) in the formation of *cis*-diol scaffolds derived from internal epoxides (Figure 4). The diastereo-selective formation of these *cis*-diols is based on the chemo-selective conversion of internal epoxide into their cyclic carbonates under conditions that do not allow for competitive polycarbonate synthesis. The use of the right catalyst/nucleophile ratio and the appropriate medium (MEK) turned out to be extremely fruitful to achieve high *dr* values (up to >99%) in this chemistry and with amplified substrate scope (*ACIE* **2014**, 53, 10416).

### New Catalyst Design

Further to the formation of organic carbonates, a new bifunctional Zn(salen) type complex has

been designed and used in catalytic and kinetic studies (Figure 5). The design takes advantage of the presence of a pyridyl group that can be alkylated by suitable alkyl halide providing a pyridinium group flanked by an internal nucleophile needed in the catalytic conversion of epoxide and CO<sub>2</sub>.

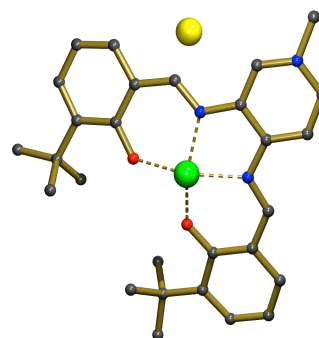


Figure 5 – A bifunctional Zn(salen) (pre)catalyst (X-ray structure) active in organic carbonate formation. Zn = green, N = blue, O = red, I = yellow.

Interestingly, comparative kinetic studies carried out with the bifunctional Zn(salen) catalyst and a binary type system comprising of a Zn(salphen)/NBU<sub>4</sub>I couple revealed a second order rate dependence in organic carbonate formation for the bifunctional system, whereas the binary type catalyst showed a first-order rate dependence. This is in contrast with what has been previously observed with Co(salen) systems in the context of poly(carbonate) formation. The rationale behind the second order rate dependence in the case of the bifunctional catalyst is the tight ion pairing between the pyridinium cation and iodide counter-ion requiring a second molecule of catalyst acting as the “nucleophile” upon conversion of the epoxide. This was further supported by addition of an external nucleophile (NBU<sub>4</sub>I) to the bifunctional system rendering it a binary one with an expected first order rate dependence in this latter case.

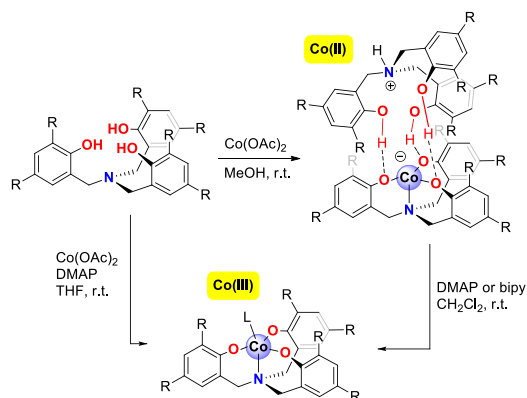


Figure 6 - Cobalt-centered aminotriphenolate complexes in different oxidation states potentially useful for catalytic applications.

Further new potential catalyst designs were probed using the aforementioned aminotriphenolate ligand systems and probing the metalation thereof by Co(II) salts. The reasoning behind this is that Co(salen)s (*i.e.*, another type of aminophenolate ligand) have been shown to be among the best catalysts for polycarbonate formation reported to date. Although previously unknown for these kind of ligands, we have been able to isolate both Co(II) as well as Co(III) derivatives of various aminotriphenolate ligands.

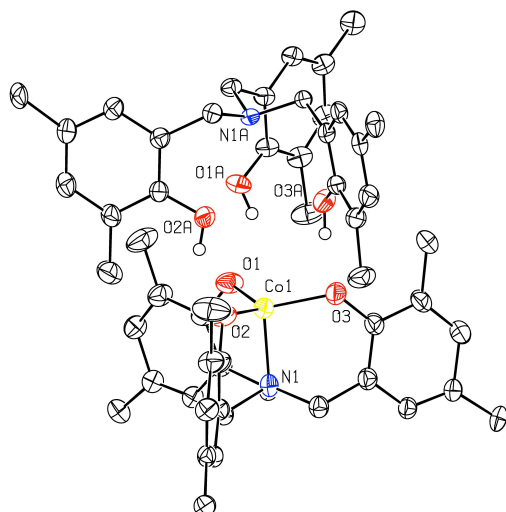


Figure 7 - A stabilized Co(II)aminotriphenolate complex forming an unusual capsular like structure. The upper hemisphere “protects” the Co(II) center through the formation of three hydrogen bonds and ion-pairing with the formerly cationic Co(aminotriphenolate) part of the complex.

The presence of strong field ligands (*cf.*, DMPA, 4-dimethylamino-pyridine) allows for stabilization of the Co<sup>III</sup> oxidation state in these complexes whereas weaker field ligands typically result in stabilization of the Co<sup>II</sup> oxidation state. Unexpectedly, these Co(II) complexes turned out to be rather (air)stable, with a clear dependence of their oxidation chemistry (probed by cyclic voltammetry studies) on the nature of the ligand present. Unique capsular-like complexes were isolated and crystallographically characterized, and further studies showed that the second hemi-sphere comprising an additional, protonated aminotriphenolate ligand helps to (further) stabilize the Co(II) towards oxidation (Figure 7). When replacing the large, trialkylammonium cation by a less “coordinating” one (*i.e.*, PPN<sup>+</sup>; PPN = bis(triphenylphosphine)iminium) the Co(II) center could be more facile oxidized reinforcing the stabilization potential of the formerly mentioned ammonium type cation (see Figure 7).

Other trivalent metal ions including Cr(III) and Mn(III) have also been coordinated to these aminotriphenolate ligands and their structures supported by X-ray analysis. Preliminary studies have revealed that these systems possess high catalytic activity for the formation of polyesters and further details will follow in due course, together with a more detailed studies towards the potential of the Co systems in redox-based catalytic conversions.

## Articles

“Conversion of Oxiranes and CO<sub>2</sub> to Organic Cyclic Carbonates using a Recyclable, Bifunctional Polystyrene-Supported Organocatalyst”

*Green Chem.* (2014) 16, 1552-1559  
Whiteoak, C. J.; Henseler, A. H.; Ayats, C; Kleij, A. W.\*; Pericàs, M. A.\*

“Highly Active Aluminium Catalysts for the Ring-Expansion Addition of CO<sub>2</sub> to Oxiranes”

*Chem. Eur. J.* (2014) 20, 2264-2275  
Whiteoak, C. J.; Kielland, N.; Laserna, V.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W.\*

“Spectroscopic Properties of Zn(Salphenazine) Complexes and their Application in Small Molecule Organic Solar Cells”

*Dalton Trans.* (2014) 43, 210-221  
Salassa, G.; Ryan, J. W.; Escudero-Adán, E. C.; Kleij, A. W.\*

“Easily accessible bifunctional Zn(salpyr) Catalysts for the formation of organic carbonates”

*Catal. Sci. Technol.* (2014) 4, 1615-1621  
Martín, C.; Whiteoak, C. J.; Martin, E.; Martínez Belmonte, M.; Escudero-Adán, E. C.; Kleij, A. W.\*

“Exploring the Building Block Potential of Readily Accessible Chiral Zn(salen) Complexes”

*Eur. J. Inorg. Chem.* (2014) 4632-4641  
Martin, E.; Martínez Belmonte, M.; Escudero-Adán, E. C.; Kleij, A. W.\*

“Catalytic Conversion and Use of Carbon Dioxide”

*Catal. Sci. Technol.* (2014) 4, 1481-1481  
Kleij, A. W.\*

“Comparing kinetic profiles between bifunctional and binary type of Zn(salen) based catalysts for organic carbonate formation”

*Beilstein J. Org. Chem.* (2014) 10, 1817-1825  
Martín, C.; Kleij, A. W.\*

“Preparation of CO<sub>2</sub>-diene copolymers: advancing carbon dioxide based materials”

*Angew. Chem. Int. Ed.* (2014) 53, 7402-7404  
Fiorani, G.; Kleij, A. W.\*

“Synthesis and Structural Features of Co(II) and Co(III) Complexes Supported by Amino-trisphenolate Ligand Scaffolds”

*Inorg. Chem.* (2014) 53, 11675-11681

Martín, C.; Whiteoak, C. J.; Martin, E.; Escudero-Adán, E. C.; Galán-Mascarós, J. R.; Kleij, A. W.\*

“Carbon Dioxide as a Protecting Group: Highly Efficient and Selective Catalytic Access to Cyclic Cis-Diol Scaffolds”

*Angew. Chem. Int. Ed.* (2014) 53, 10416-10419  
Laserna, V.; Fiorani, G.; Whiteoak, C. J.\*; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W.\*