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Investigating Alternative Catalysts for Green Cyclic Carbonate Synthesis

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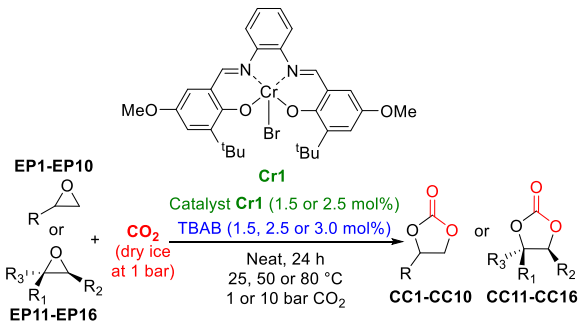
There has been a recent paradigm shift towards promoting greener and more sustainable Carbon Dioxide Utilization (CDU).[1] Consequently, research in cyclic carbonate synthesis via CDU has been focused on utilizing more sustainable metal catalysts[2] and creating catalysts that are highly active under ambient, or near-ambient, conditions. Inspired by research from Castro-Osma *et al.*, who illustrated a chromium(III) aminosalophen catalyst could ring-open epoxides using mild conditions,[3] a thorough investigation into using alternative chromium(III) salophen complexes for green cyclic carbonate synthesis was performed.

After optimizing the chromium(III) salophen catalyst structure, co-catalyst and catalytic loading, the most active catalyst **Cr1** was screened against a wide range of terminal and internal epoxides with different functionalities (Figure 1). Catalyst **Cr1** was extremely effective at ring-opening terminal epoxides and internal epoxides under near-ambient conditions (Table 1).[4]



1: R = Ph; **2**: R = Me; **3**: R = Et; **4**: R = ^{n}Bu; **5**: R = ^{n}Oct; **6**: R = CH_2Cl; **7**: R = CH_2OH; **8**: R = CH_2OPh; **9**: R = 4-ClC_6H_4; **10**: R = 4-BrC_6H_4; **11**: R_1-R_2 = $(CH_2)_4$, R_3 = H; **12**: R_1-R_2 = $(CH_2)_3$, R_3 = H; **13**: R_1=R_2 = CH_3, R_3 = H; **14**: R_1 = H, R_2=R_3 = CH_3; **15**: R_1 = H, R_2=R_3 = Ph; **16**: R_1 = H, R_2 = CH_3, R_3 = Ph

Figure 1. Screening of chromium(III) salophen complex **Cr1** in converting epoxides **EP1-EP16** to cyclic carbonates **CC1-CC16**.

Table 1. Screening results from Figure 1, using 2.5 mol% of **Cr1**, 2.5 mol% of TBAB and 1 bar CO_2.

Epoxide	Temp. (°C)	Conv. (%, 24 h)[a]	Yield (%)[b]
EP1	25	100	92
EP2[c]	0	N/A[c]	57
EP3	25	100	86
EP4	25	95	81
EP5	25	89	82
EP6	25	100	78
EP7	25	86	72
EP8	25	71	71
EP9	50	100	91
EP10	50	100	89
EP11[d]	80	80	76
EP12[d]	80	93	85
EP13[c,e]	80	N/A[c]	63
EP14[c,e]	80	N/A[c]	60
EP15[d]	80	98	89
EP16[d]	80	100	87

[a] *Conversions from ^{1}H NMR analysis of reaction mixture.*
[b] *Isolated cyclic carbonate yields after column purification.*
[c] *Due to epoxide volatility, conversion was not determined.*
[d] *Used 1.5 mol% of **Cr1**, 1.5 mol% of TBAB and 10 bar of CO_2.*
[e] *Used 1.5 mol% of **Cr1**, 3.0 mol% of TBAB and 10 bar of CO_2.*

This oral presentation will describe this work in further detail. New research into developing alternative catalysts for green cyclic carbonate synthesis via CDU will also be presented.

Acknowledgments

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