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ARTICLE

Easily accessible bifunctional Zn(salpyr) catalysts for the formation of organic carbonates

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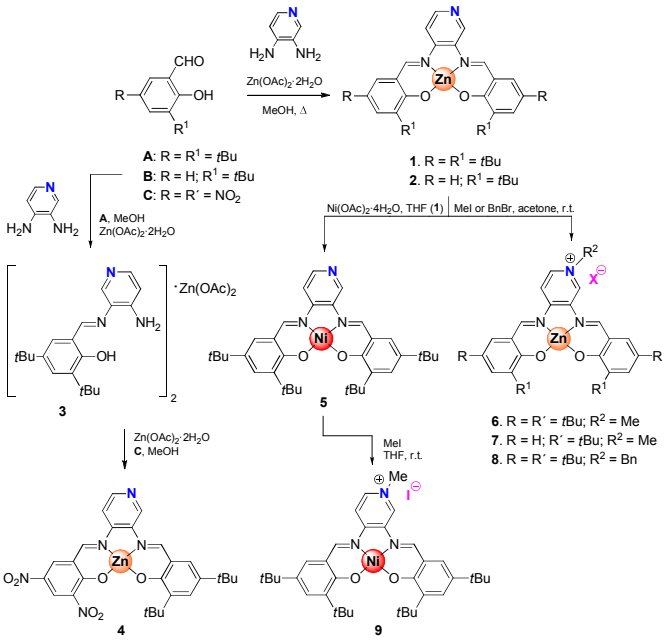
Alkylated Zn(salpyr) complexes (salpyr = *N,N′*-bis[salicylidene]-3,4-pyridinediamine) have been prepared and used as catalyst precursors for the formation of cyclic carbonates from a range of (functional) epoxides and CO_2. Reaction conditions were optimized to achieve good isolated yields of the targeted products. The molecular structure for the most active bifunctional Zn(salpyr) derivative has also been resolved using X-ray diffraction studies.

1. Introduction

The use of carbon dioxide (CO_2) as a reagent in organic synthesis is of increasing interest as it may represent a viable alternative carbon resource as opposed to fossil fuel based feed stocks.[1-4] Recent progress in the area of organic transformations employing CO_2 as key reagent has shown a true burst of new and efficient catalytic methodologies for CO_2 conversion making its use of increasing importance.[5-9] One of the most studied reactions in this context is the formation of organic carbonates from epoxides and CO_2; depending on the reaction conditions, type of catalyst and epoxide substrate, fine-tuning towards the preparation of either polymeric carbonates (in most cases the fully alternating polycarbonates)[10-15] or cyclic carbonates can be readily achieved.[16-18] Both types of organic carbonate have industrial relevance and may be employed in various applications such as aprotic solvents, engineering plastics[2,11] and precursors for (a)chiral diols.[19]

Successful examples of metal catalysts that have been developed for the preparation of cyclic carbonates include both binary[20-22] as well as bifunctional systems[23-27] with the latter category being less developed as a probable result of the more synthetically demanding characteristics of bifunctional catalyst preparation. Nonetheless, bifunctionality has proven to be highly useful in various cases to create more powerful catalyst mediators. For instance, Ema, Sakai and co-workers have developed a bifunctional metalloporphyrin catalyst that shows very high turnover frequencies and turnover numbers in cyclic carbonate formation.[28] Alternatively, various bifunctional Co(salen)s have been prepared and successfully applied in polycarbonate formation creating polymer products with increased chain lengths and/or selectivies.[29,30]

Previously we reported on Zn(salphen)/NBu_4I based binary catalysts (salphen = *N,N′*-bis-salicylidene-1,2-diaminobenzene) that are effective mediators for the conversion of various epoxides and CO_2 providing cyclic carbonates under relatively mild reaction conditions.[31-33] We were interested in the possibility of creating bifunctional (rather than binary) analogues of these catalyst systems that could be prepared in few steps from readily available materials. Herein we report the results of these investigations where the use of a pyridine-bridged salen system (Scheme 1) was key to achieving bifunctionality within the catalyst structure. This catalyst design closely follows previous reports on bifunctional systems for CO_2 conversion catalysis.[24,25,27]



Scheme 1 Synthesis of (bifunctional) salpyr-based complexes **1-9**.

2. Experimental section

2.1 General considerations

Carbon dioxide was purchased from PRAXAIR and used without further purification. All epoxide substrates and reagents (including 3,4-diaminopyridine) were commercially available

and were used as received. Complexes **1**,[34] **2**,[35] **5**[34] and **6**[32] were prepared as described previously. $^{1}H/^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AV-300, AV-400 or AV-500 spectrometer and referenced to the residual NMR solvent signals. Elemental analyses were performed by the Unidád de Análisis Elemental at the Universidad de Santiago de Compostela (Spain). Mass spectrometric analyses and X-ray diffraction studies were performed by the Research Support Group at the ICIQ. (±)-Indene oxide was prepared according to a procedure reported by Darensbourg and coworkers.[36]

2.2 Synthesis of complexes

2.2.1 Zn(salpyr) complex (1) and bis-monoimine salt (3): This complex was prepared on a larger scale compared to the previously reported procedure.[34] To a solution of 3,4-diaminopyridine (1.90 g, 17.4 mmol) and salicylaldehyde **A** (8.00 g, 34.14 mmol) in MeOH (150 mL) was added a solution of $Zn(OAc)_2{\cdot}2H_2O$ (3.96 g, 18.04 mmol) in MeOH (30 mL). The mixture was briefly heated to reflux and then stirred at r.t. for a further 18 h. A red solid was collected by filtration and dried in vacuo. Yield: 2.51 g (4.15 mmol, 24%). ^{1}H NMR (acetone-d_6, 400 MHz): δ = 9.11 (s, 1H, CH=N), 8.45 (s, 2H, CH=N + pyrH), 7.94 (d, $^{3}J_{H,H}$ = 4.24 Hz, 1H, pyrH), 7.73 (d, $^{3}J_{H,H}$ = 5.8 Hz, 1H, pyrH), 7.55 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.19 (s, 1H, ArH), 6.79 (s, 1H, ArH), 1.57 (s, 9H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 1.31 (2 × s, 18H, $C(CH_3)_3$); the mother liquor was then concentrated to around 100 mL after which a light yellow, crystalline solid separated. This solid was analysed and found to be complex **3** (Scheme 1) having one molecule of $Zn(OAc)_2$ associated with two monoimine molecules. Yield: 3.5 g (3.86 mmol, 44% based on diamine reagent). Crystals of compound **3** suitable for X–ray diffraction were obtained from a saturated solution in $CDCl_3$. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 12.80 (s, 1H, ArOH), 8.68 (s, 1H, pyr-H), 8.23 (d, $^{3}J_{H,H}$ = 5.9 Hz, 1H, pyr-H), 8.22 (s, 1H, CH=N), 7.52 (d, $^{4}J_{H,H}$ = 2.4 Hz, 1H, ArH), 7.30 (d, $^{4}J_{H,H}$ = 2.2 Hz, 1H, ArH), 6.69 (d, $^{3}J_{H,H}$ = 6.0 Hz, 1H, pyr-H), 4.91 (s, 2H, NH_2), 1.74 (s, 6H, OAc), 1.48 (s, 18H, $C(CH_3)_3$), 1.35 (s, 18H, $C(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ = 179.88, 166.36, 157.99, 149.04, 147.65, 141.35, 138.35, 137.08, 132.57, 129.23, 127.63, 118.22, 109.35, 35.10, 34.23, 31.41, 29.40, 22.99. MS (ESI–, MeOH): *m/z* = 711.2 $[Zn(monoimine)_2\text{-}H]^-$ (calcd. 711.3), 324.2 $[monoimine\text{-}H]^-$ (calcd. 324.21). Anal. calcd. for $C_{44}H_{60}N_6O_6Zn{\cdot}4H_2O$: C 58.30, H 7.56, 9.27; found: C 58.82, H 7.55, N 9.23.

2.2.2 Nonsymmetrical Zn(salpyr) complex (4): To a solution of the monoimine salt **3** (205.6 mg, 0.377 mmol) and salicyladehyde **C** (117.7 mg, 0.555 mmol) in MeOH (40 mL) was added $Zn(OAc)_2{\cdot}2H_2O$ (154.6 mg, 0.704 mmol) dissolved in MeOH (10 mL). The mixture was stirred for 18 h and then filtered to furnish a brown solid which was air-dried. Yield: 158.3 mg (0.271 mmol, 72% based on **3**). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 9.37 (s, 1H, pyrH), 9.14 (s, 1H, CH=N), 9.09 (s, 1H, CH=N), 8.82 (d, $^{4}J_{H,H}$ = 3.1 Hz, 1H, ArH), 8.73 (d, $^{4}J_{H,H}$ = 3.1 Hz, 1H, ArH), 8.56(d, $^{3}J_{H,H}$ = 5.4 Hz, 1H, pyrH), 7.84 (d, $^{4}J_{H,H}$ = 5.5 Hz, 1H, pyrH), 7.36 (d, $^{4}J_{H,H}$ = 2.6 Hz, 1H, ArH), 7.24 (d, $^{4}J_{H,H}$ = 2.6 Hz, 1H, ArH), 1.45 (s, 9H, $C(CH_3)_2$), 1.27 (s, 9H, $C(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 126 MHz): δ = 171.1, 167.6, 165.6, 165.5, 147.8, 144.2, 143.1, 141.5, 140.5, 137.0, 136.6, 134.4, 132.2, 130.3, 129.9, 124.9, 122.4, 118.7, 111.5, 35.6, 35.0, 31.7, 30.0. MS (MALDI+, pyrene): *m/z* = 581.2 $(M)^+$ (calcd. 581.1), 566.2 $(M–CH_3)^+$ (calcd. 566.1). Anal. calcd. for $C_{27}H_{27}N_5O_6Zn{\cdot}1/3H_2O$: C 55.07, H 4.74, N 11.89; found: C 55.15 H 4.86, N 11.93.

2.2.3 Alkylated Zn(salpyr) complex (7): To a suspension of Zn(salpyr) complex **2** (91.8 mg, 0.186 mmol) in acetone/THF (2:1, 6 mL) was added an excess of MeI (2 mL). The reaction mixture turned darker in time and was concentrated after 18 h to afford **6** as a brown solid. Yield: 104.2 mg (0.164 mmol, 88%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 9.38 (d, $^{4}J_{H,H}$ = 1.2 Hz, 1H, pyrH), 9.28 (s, 1H, CH=N), 9.13 (s, 1H, CH=N), 8.69 (d, $^{3}J_{H,H}$ = 7.0 Hz, 1H, ArH), 8.38 (d, $^{3}J_{H,H}$ = 7.0 Hz, 1H, ArH), 7.37 (d, $^{3}J_{H,H}$ = 7.2 Hz, 1H, ArH), 7.33 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H, ArH), 7.25 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H, ArH), 6.54-6.58 (m, 2H, ArH), 4.27 (s, 3H, pyr-NMe), 1.47 (s, 9H, $C(CH_3)_3$), 1.46 (s, 9H, $C(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 126 MHz): δ = 176.8, 174.1, 168.0, 166.1, 151.8, 143.4, 142.8, 142.1, 137.5, 136.1, 135.3, 135.1, 134.3, 132.7, 120.2, 119.6, 114.9, 113.9, 113.6, 47.7, 35.6, 29.9, 29.8; MS (MALDI+, dctb): *m/z* = 506.2 $(M–I)^+$ (calcd. 506.2). Anal. calcd. for $C_{28}H_{32}IN_3O_2Zn{\cdot}H_2O$: C 51.51, H 5.25, N 6.44; found: C 51.52 H 5.75 N 6.07.

2.2.4 Benzylated Zn(salpyr) complex (8): To a a red solution of complex **1** (0.40 g, 0.66 mmol) in acetone (30 mL) was added benzyl bromide (8.7 mL, 73.0 mol). The resulting mixture was stirred at r.t. and turned dark in time. After 3 days the solvent was evaporated under vacuum, and the crude was triturated with ether and filtered. The resulting brown, almost black powder was washed with ether and dried in vacuum to give Zn(salpyr) complex **8**. Yield: 0.41 g (0.53 mmol, 81%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 9.66 (s, 1H, pyr-H), 9.26 (s, 1H, CH=N), 9.16 (s, 1H, CH=N), 8.84 (d, $^{3}J_{H,H}$ = 7.8 Hz, 1H, pyr-H), 8.42 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H, pyr-H), 7.63 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H, ArH), 7.49 (dd, $^{3}J_{H,H}$ = 7.6 Hz, $^{3}J_{H,H}$ = 7.6 Hz, 2H, ArH), 7.44-7.47 (m, 3H, ArH), 7.42 (d, $^{4}J_{H,H}$ = 1.7 Hz, 1H, ArH), 7.22 (d, $^{4}J_{H,H}$ = 2.2 Hz, 1H, ArH), 7.17 (d, $^{4}J_{H,H}$ = 2.5 Hz, 1H, ArH), 5.71 (s, 2H, NCH_2Ar), 1.49 (s, 9H, $C(CH_3)_3$), 1.47 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 126 MHz): δ = 176.3, 172.9, 167.2, 165.8, 152.7, 143.1, 142.3, 140.6, 138.1, 135.9, 135.3, 134.8, 133.9, 133.1, 130.9, 130.1, 129.7, 129.6, 129.5, 128,9, 119.3, 119.3, 118.4, 113.9, 62.9, 35.7, 35.6, 34.2, 34.1, 31.6, 31.2, 29.9, 29.8. MS (MALDI+, dctb): *m/z* = 694.3 $(M–Br)^+$ (calcd. 694.3). Anal. calcd. for $C_{42}H_{52}BrN_3O_2Zn{\cdot}½H_2O$: C 64.25, H 6.80, N 5.35; found: C 64.26 H 7.02, N 5.31.

2.2.5 Alkylated Ni(salpyr) complex (9): To a brown solution of Ni(salpyr) complex **8** (0.13 g, 0.22 mmol) in THF

(10 mL) was added MeI (1.5 mL, 23.9 mol). The resulting mixture was stirred at r.t. and turned dark in time. After 3 days the solvent was evaporated under vacuum, and the crude was triturated with ether and filtered. The resulting brown to almost black powder was washed with ether and dried in vacuum to give **9**. Yield: 0.14 g (0.19 mmol, 88%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 9.78 (s, 1H, pyr-H), 9.49 (s, 1H, CH=N), 9.38 (s, 1H, CH=N), 8.79 (d, $^3J_{H,H}$ = 6.6 Hz, 1H, pyr-H), 8.66 (d, $^3J_{H,H}$ = 6.6 Hz, 1H, pyr-H), 7.59 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, ArH), 7.49 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, ArH), 7.46 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, ArH), 7.36 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, ArH), 4.41 (s, 3H, pyr-NMe), 1.41 (s, 18H, C(CH$_3$)$_3$), 1.31 (s, 18H, C(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ = 168.4, 165.6, 160.5, 159.1, 153.9, 141.8, 141.6, 141.3, 140.2, 138.7, 137.9, 135.4, 133.7, 132.3, 128.1, 127.6, 120.7, 120.0, 113.3, 47.8, 35.9, 34.3, 34.2, 31.3, 31.1, 29.9; MS (MALDI+, dctb): *m/z* = 612.4 (M–I)$^+$ (calcd. 612.3); Anal. calcd. for $C_{36}H_{48}IN_3NiO_2{\cdot}4½H_2O$: C 52.64, H 6.99, N 5.12; found: C 52.44 H 6.41, N 4.96.

2.3 Crystallographic studies

The measured crystals were stable under atmospheric conditions; nevertheless they were treated under inert conditions and were immersed in perfluoropoly-ether as protecting oil for manipulation. Data collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, an FR591 rotating anode with MoKα radiation, Montel mirrors and a Kryoflex low temperature device (T = −173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008–1 (2008). Structure solution: SHELXTL version 6.10 (Sheldrick, 2000)[37] was used. Structure refinement: SHELXTL-97-UNIX VERSION.

Crystallographic details for complex **3**·2CHCl$_3$·H$_2$O: $C_{46}H_{64}Cl_6N_6O_7Zn$, M_r = 1091.10, triclinic, *P*-1, *a* = 11.5808(7) Å, *b* = 12.8843(8) Å, *c* = 18.9944(11) Å, α = 78.363(2)º, β = 87.683(2)°, γ = 87.378(2)º, *V* = 2771.6(3) Å^3, *Z* = 2, ρ = 1.307 mg·M^{-3}, μ = 0.782 mm^{-1}, λ = 0.71073 Å, *T* = 100(2) K, *F*(000) = 1140, crystal size = 0.20 × 0.15 × 0.07 mm, θ(min) = 1.61°, θ(max) = 27.69°, 20273 reflections collected, 12599 reflections unique (R_{int} = 0.0224), GoF = 1.044, R_1 = 0.0572 and wR_2 = 0.1473 [I > 2σ(I)], R_1 = 0.0839 and wR_2 = 0.1674 (all indices), min/max residual density = −1.119/1.075 [e·Å^{-3}]. Completeness to θ(27.69°) = 97.1%. The structure has been deposited at the CCDC with reference number 974987 and is a solvate; it contains two co-crystallized, disordered $CHCl_3$ molecules and one water molecule.

Crystallographic details for complex **4**·2DMSO: $C_{31}H_{39}N_5O_8S_2Zn$, M_r = 739.16, monoclinic, *P*2(1)/c, *a* = 21.5392(8) Å, *b* = 14.9764(6) Å, *c* = 11.0367(4) Å, β = 102.0060(10)°, *V* = 3482.3(2) Å^3, *Z* = 4, ρ = 1.410 mg·M^{-3}, μ = 0.880 mm^{-1}, λ = 0.71073 Å, *T* = 100(2) K, *F*(000) = 1544, crystal size = 0.35 × 0.20 × 0.05 mm, θ(min) = 0.97°, θ(max) = 30.43°, 38914 reflections collected, 10356 reflections unique (R_{int} = 0.0466), GoF = 1.042, R_1 = 0.0410 and wR_2 = 0.1014 [I > 2σ(I)], R_1 = 0.0669 and wR_2 = 0.1171 (all indices), min/max residual density = −0.638/0.661 [e·Å^{-3}]. Completeness to θ(30.43°) = 98.1%. The structure has been deposited at the CCDC with reference number 972707 and is a bis-solvate; it contains two co-crystallized DMSO molecules.

Crystallographic details for complex [**7**·MeOH]·MeOH: $C_{30}H_{40}IN_3O_4Zn$, M_r = 698.92, monoclinic, *P*2(1)/c, *a* = 20.7881(8) Å, *b* = 19.8405(8) Å, *c* = 7.4304(3) Å, β = 97.6650(10)°, *V* = 3037.3(2) Å^3, *Z* = 4, ρ = 1.528 mg·M^{-3}, μ = 1.863 mm^{-1}, λ = 0.71073 Å, *T* = 100(2) K, *F*(000) = 1424, crystal size = 0.04 × 0.01 × 0.01 mm, θ(min) = 0.99°, θ(max) = 28.33°, 20892 reflections collected, 7337 reflections unique (R_{int} = 0.0336), GoF = 1.159, R_1 = 0.0313 and wR_2 = 0.0800 [I > 2σ(I)], R_1 = 0.0458 and wR_2 = 0.0914 (all indices), min/max residual density = −0.637/0.602 [e·Å^{-3}]. Completeness to θ(28.33°) = 96.9%. The structure has been deposited at the CCDC with reference number 972708 and is a bis-solvate; it contains one co-crystallized MeOH molecule alongside one coordinating one.

2.4 Catalysis experiments

Typical conditions: A solution of the respective catalyst (0.5, 0.25 or 0.1 % mol) in 10 mmol of epoxide was added to a stainless steel reactor. Three cycles of pressurisation and depressurisation of the reactor with carbon dioxide (0.5 MPa) were applied. The final pressure was then adjusted to 1.0 MPa and the reaction was left stirring at the required temperature for 18 h. After this time, the conversion was calculated using ^{1}H NMR spectroscopy ($CDCl_3$) of an aliquot of the reaction mixture. Isolated yields were obtained upon purification of products by filtration through silica gel of the reaction mixture using DCM as eluent. The solvent was evaporated and the epoxide/cyclic carbonate mixture was further dried under reduced pressure for 3 h. All the carbonate products have been previously described and their identification was straightforward by comparison with previously reported data. All cyclic carbonates were analysed by ^{1}H and IR spectroscopy and NMR spectra and assignments are provided in the ESI‡. Cyclic carbonate **10f** was also analysed by ^{13}C NMR and HR-MS analysis (see below).

4-*tert*-Butoxymethyl-1,3-dioxolan-2-one (10f): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.83 – 4.72 (m, 1H), 4.48 (dd, $^2J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H), 4.39 (dd, $^2J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.1 Hz, 1H), 3.63 (dd, $^2J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 4.6 Hz, 1H), 1.30 (dd, $^2J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 3.7 Hz, 4H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ = 155.3, 75.4, 73.7, 66.4, 61.2, 27.2; IR (neat, cm^{-1}): 2974, 2934, 2874, 1786 (C=O), 1477, 1390, 1365, 1163, 1102, 1053, 1013, 883, 770, 713. HR-MS (ESI+): calcd. *m/z* = 175.0965; found: 175.0962.

3. Results and discussion

3.1 Synthesis and characterisation of complexes

We previously reported on the synthesis of Zn(salpyr) complexes **1**[34] and **2**.[35] These complexes having a heteroaryl bridging group (cf., pyridyl) can be constructed in a one-pot two step procedure via condensation/metalation of a suitable salicylaldehyde (cf., compounds **A-C**, Scheme 1), commercially available 3,4-diaminopyridine and $Zn(OAc)_2{\cdot}2H_2O$ in MeOH reminiscent of the synthetic approach for a series of Zn(salphen) [salphen = *N,N´*-bis(salicylidene)-1,2-phenylenediamine] complexes.[38] When preparing these compounds on a smaller scale, isolated yields are typically >90%; however, we attempted to prepare Zn(salpyr) complex **1** on a larger scale (see experimental section) using a stoichiometric rather an excess amount of the Zn reagent. Although this procedure indeed afforded the targeted Zn(salpyr) complex, a much lower yield was obtained (24%). Interestingly, from the reaction mixture in addition a secondary product could be isolated (cf., compound **3**, Scheme 1) that was analysed as $Zn(OAc)_2$ associated to two monoimine molecules based on the 3,4-diaminopyridine reagent (yield: 44%), i.e. an intermediate structure with respect to the targeted Zn(salpyr) **1**. In theory, two possible isomeric monoimine structures may be formed differing in the position of the bridgehead nitrogen atom but ^{1}H NMR analysis only displayed one set of signals (see ESI‡). Therefore we believe that the monoimine connectivity in solution and the solid state (vide infra) are the same and only one isomeric form of **3** is isolated. Crystals of complex **3** suitable for X-ray diffraction studies were obtained from $CDCl_3$ and the structure is reported in Figure 1.

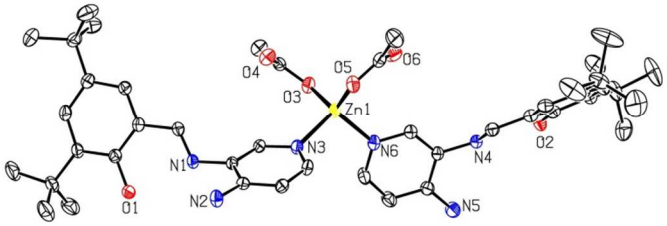


Fig. 1 X-ray molecular structure (ball and stick representation) for complex **3**, co-crystallized solvent molecules and H-atoms are omitted for clarity. Only one molecule of the asymmetric unit is shown here. Selected bond distances (Å) and angles (º) with esd´s in parentheses: Zn(1)-O(3) = 1.950(2), Zn(1)-O(5) = 1.963(2), Zn(1)-N(3) = 2.044(3), Zn(1)-N(6) = 2.018(3); N(6)-Zn(1)-N(3) = 106.02(11), O(5)-Zn(1)-O(3) = 123.88(10), N(6)-Zn(1)-O(5) = 114.84(11), N(3)-Zn(1)-O(3) = 107.37(10).

Compound **3** offers the possibility to form nonsymmetrical Zn(salpyr) derivatives upon reaction with suitable salicyladehyde precursors. Upon introduction of electron-withdrawing substituents in the latter, the Lewis acidity of the metal center may be increased. Thus, we set out to prepare Zn(salpyr) **4** (Scheme 1) and the bis-monoimine salt **3** could be selectively converted into **4** after treatment with salicylaldehyde **C** (72% yield). The molecular structure determined for **4** is presented in Figure 2. The structure determined for **4** shows that the pyridyl-*N* atom mediates self-assembly of the complex into a coordination polymer (see ESI‡) via Zn-N_{pyr} motifs despite the presence of an excess of a potentially strongly coordinating ligand such as DMSO during the crystallization process.

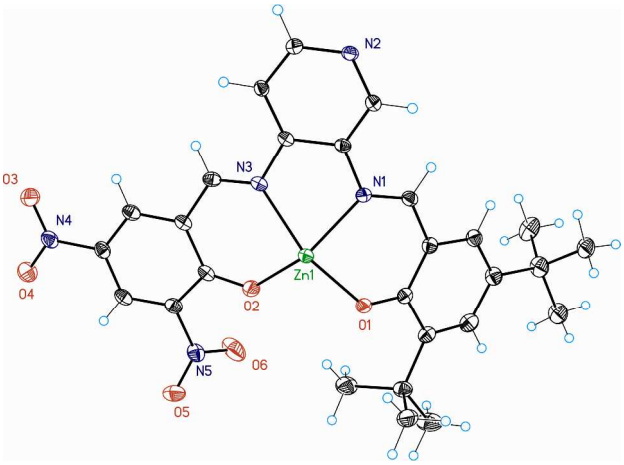


Fig. 2 X-ray molecular structure determined for **4**, co-crystallized solvent molecules and H-atoms are omitted for clarity. Note that only one molecule from the unit cell is shown. Selected bond distances (Å) and angles (º) with esd´s in parentheses: Zn(1)-O(1) = 1.9431(13), Zn(1)-O(2) = 2.0124(15), Zn(1)-N(1) = 2.0738(16), Zn(1)-N(2#) = 2.0837(16) with N(2#) being the nitrogen atom from another Zn(salpyr) unit, Zn(1)-N(3) = 2.1410(16); O(1)-Zn(1)-O(2) = 99.03(6), N(1)-Zn(1)-N(3) = 76.92(6), N(3)-Zn(1)-O(1) = 159.72(6), N(1)-Zn(1)-O(2) = 145.13(6), N(3)-Zn(1)-O(2) = 86.34(6), N(1)-Zn(1)-O(1) = 87.99(6).

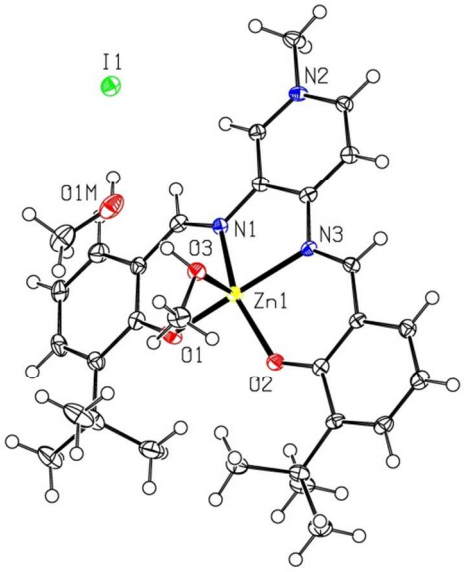


Fig. 3 X-ray molecular structure for **7**. Note that only one molecule is shown from the unit cell. Selected bond distances (Å) and angles (º) with esd´s in parentheses: Zn(1)-O(1) = 1.943(2), Zn(1)-O(2) = 1.962(2), Zn(1)-N(1) = 2.057(2), Zn(1)-N(3) = 2.086(2), Zn(1)-O(3) = 2.091(2); N(1)-Zn(1)-N(3) = 79.46(9), O(1)-Zn(1)-O(2) = 95.83(9), N(1)-Zn(1)-O(2) = 154.15(9), N(1)-Zn(1)-O(1) = 90.37(9), N(3)-Zn(1)-O(1) = 163.44(9), N(3)-Zn(1)-O(2) = 88.12(9), N(3)-Zn(1)-O(3) = 96.24(9), O(1)-Zn(1)-O(3) = 98.96(9).

We envisioned that the pyridyl N-atoms could be simply alkylated by alkyl halides and thus lead to pyridinium based Zn complexes displaying bifunctionality, i.e. a combination of a Lewis acidic Zn centre and a nucleophile (halide). Thus, Zn(salpyr) derivatives **1**, **2** and **4** were treated with either MeI or BnBr, and these simple procedures afforded the alkylated systems **6-8** in good yields (81–88%)[32] without affecting the stability of the starting compounds.[39]

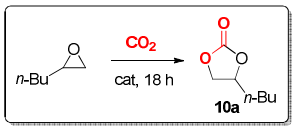
As a control compound (see catalysis section) we also prepared the methylated Ni(salpyr) complex **9** (Scheme 1) in 88% yield as this Ni(II) complex is a non-Lewis acidic analogue of Zn(salpyr) derivative **6**. Upon alkylation, the peaks corresponding to the pyridyl unit significantly shift downfield (typical $\Delta\delta$ up to 0.5 ppm) indicative of the formation of the pyridinium unit (more details in the ESI‡). Mass spectrometric analysis carried out for complexes **6-9** (MALDI-TOF in the positive ion mode) showed support for the cationic part of the structures and in each case fragment ions of type $[M–halide]^+$ were observed as the predominant species. Further to that, crystals suitable for X-ray diffraction were obtained for Zn(salpyr) complex **7** from MeOH and the structure is presented in Figure 3. The complex crystallises as a MeOH solvate (O3 coordinating to the Zn centre) with an additional MeOH molecule hydrogen bonding to the coordinated one via O(1M). One of the MeOH molecules shows an interaction with the iodide anion through H-bonding. These H-bond patterns allow for a crystal lattice (see ESI‡) where the pyridinium rings are involved in pi-pi stacking with one another. The structure of bifunctional Zn(salpyr) complex **7** represents to our knowledge one of the few structurally characterised bifunctional complexes in the context of carbon dioxide catalysis.[26]

3.2 Catalyst screening phase

In order to investigate the use of the alkylated Zn(salpyr) complexes as bifunctional catalysts for cyclic carbonate synthesis from epoxides and CO_2, a benchmark substrate (1,2-epoxyhexane) was chosen and complex **6** was first evaluated under various conditions (Table 1). From Table 1 it is clear that complex **6** is an active catalyst for the formation of the cyclic carbonate derived from 1,2-epoxyhexane and CO_2 with reaction temperatures above 50ºC favoring higher conversion levels. At 80ºC using 0.5 mol% **6** a quantitative conversion into carbonate product could be achieved, and these conditions seem to be ideal for the 1,2-epoxyhexane substrate.

Then, the activity of catalyst **6** (0.25 mol%, 67% conversion) was compared against a series of other bifunctional/binary complexes including **1**, **7-9** and binary systems comprising of Zn(salpyr) **1** and halide nucleophiles (NBu_4I or 4-*tert*-butyl-N-methyl-pyridinium iodide, **BNMPI**) and these results are shown in Table 2. The **BNMPI** was used to mimic the activity of the N-methyl-pyridinium fragment in the bifunctional system **6**. The *tert*-butyl group was needed to assist its solubility in the medium.

First of all, the Zn(salpyr) complex **1** was found to be inactive in the absence of a halide source. Further to that, Zn(salpyr) **1** when combined with NBu_4I or **BNMPI** show activities higher than that of the bifunctional catalyst **6**. The electronic nature of **BNMPI** compared to the pyridinium unit in **6** is not similar and probably the **BNMPI** system represents a weaker ion pair. The additive (or: nucleophile) **BNMPI** itself shows lower activity than that noted for the binary system **1**/**BNMPI** demonstrating that the Lewis acidic complex **1** does indeed play an important role in the catalytic process. In order to investigate the role of the Zn centre in **6** in the activation process we then used the methylated Ni(salpyr) complex **9** and compared its activity with that of the methylated Zn(salpyr) **6**. Ni(II) based salen complexes usually form square planar, coordinatively saturated complexes that do not show any axial coordination ability.[34,40]



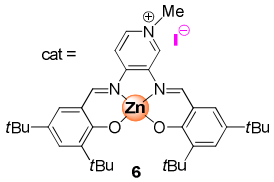


Table 1 Catalytic results for complex **6** using 1,2-epoxyhexane as substrate yielding carbonate **10a**.[a]

Cat. **6** (mol%)	$p(CO_2)$ (MPa)	T (ºC)	Conv. (%)[b]
0.5	1.0	40	7
0.5	1.0	50	32
0.5	1.0	60	67
0.5	1.0	80	>99
0.25	1.0	80	63
0.10	1.0	80	7

[a] General conditions: 1,2-epoxyhexane (10 mmol), 18 h, neat. [b] Conversion determined by ^{1}H NMR ($CDCl_3$), selectivity for the cyclic carbonate >99%.

Therefore, any activity measured for this Ni-based system would provide a value that would be closely associated to the activity of the pyridinium unit within Zn(salpyr) **6** as these systems should be electronically similar. As the conversion in the presence of bifunctional Ni(salpyr) complex **9** was only 14% (cf., 67% in the case of the Zn analogue **6**) it can be concluded that the Zn centre indeed shows a synergistic effect upon combination with the pyridinium unit within the same structure providing improved catalytic properties.

Having established that complex **6** is able to display bifunctional catalysis behaviour, its activity was then compared against the two other bifunctional Zn(salpyr) catalyst (**7** and **8**, Table 2) and significantly lower conversion levels were noted for the latter, making Zn(salpyr) **6** the preferred bifunctional catalyst system within the series **6-9**. Zn(salpyr) complex **6** was subsequently used for the conversion of a series of other substrates under the most preferred conditions (0.5 mol% **6**, 80ºC, pCO_2 = 1.0 MPa; see Figure 4) leading to the isolation of a variety of cyclic carbonates **10a-10l**. Most terminal epoxides could be cleanly converted into their cyclic carbonates in

moderate to high isolated yield depending on the substrate functionality.

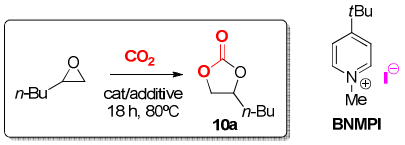


Table 2 Comparison between **6** and various binary/bifunctional catalyst systems in the conversion of 1,2-epoxyhexane.[a]

Catalyst	Additive	Conv. (%)
1	-	0
1	NBu_4I	92
1	BNMPI	>99
-	BNMPI	45
6	-	67
7	-	39
8	-	31
9	-	14

[a] General conditions: 1,2-epoxyhexane (10 mmol), catalyst (0.25 mol%), additive (0.25 mol), 18 h, $p(CO_2)$ = 1.0 MPa, 80ºC, neat. [b] Conversion determined by ^1H NMR ($CDCl_3$), selectivity for the cyclic carbonate >99%.

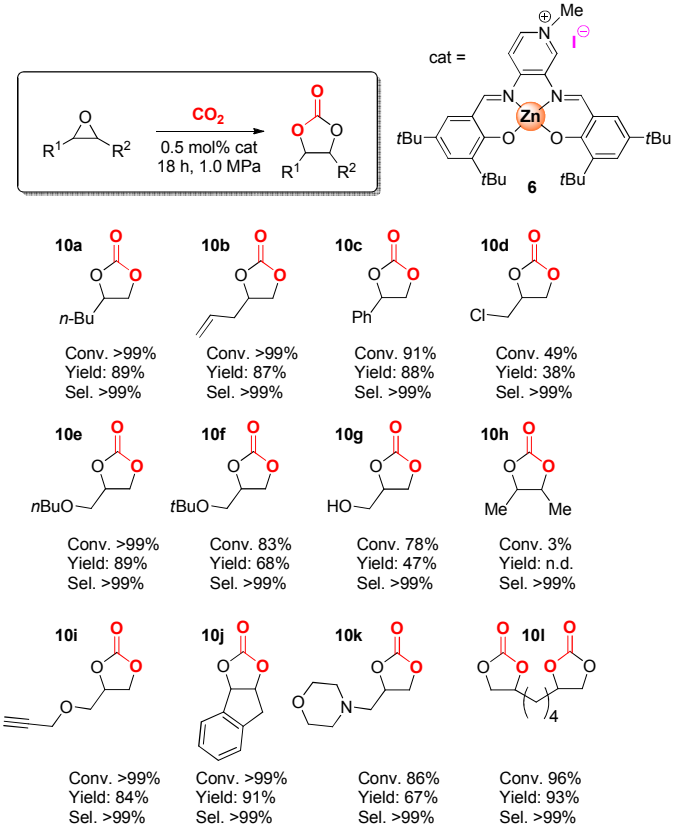


Fig. 4 Substrate scope with Zn(salpyr) complex **6**. General conditions: 10 mmol substrate, 0.5 mol% **6**, pCO_2 = 1.0 MPa, 18 h, 80ºC, neat. N.d. stands for not determined. The reported yields represent isolated yields after chromatographic purification.

An exception to this is represented by the formation of cyclic carbonate **10d**: in this case the use of epichlorohydrin may lead to halide exchange in the catalyst structure **6** and it is known that chloride is a poorer nucleophile/leaving group than iodide. Thus, during the catalysis halide exchange would lead to lower activities and consequently lower isolated yields.

The internal epoxide 2,3-epoxybutane (3% conversion) turned out to be a challenging substrate, most likely due to the much higher kinetic barriers associated to the key steps involved in the mechanism of formation for product **10h** as reported recently for the binary Zn(salphen)/NBu_4I catalyst.[41] Of particular note is the formation of carbonate products **10i-10l** which have not been often reported. The synthesis of the indene-based carbonate **10j** shows that epoxides based on fused ring systems can also be conveniently converted in high selectivity and yield.[36] We also tried to convert cyclohexene oxide (CHO) with our bifunctional catalyst **6**; however, under the conditions reported in Figure 4 only 2% conversion was noted after 18 h (selectivity towards the cyclic carbonate). This result may be expected since the *binary* version of **6** (i.e., a Zn(salphen) complex combined with NBu_4I) previously proved to be ineffective for CHO conversion even at elevated reaction temperatures (105ºC),[31] and conversion of CHO (an internal epoxide such as 2,3-dimethyloxirane in the synthesis of **10h**; Figure 4) required a condensed CO_2 phase for better mixing of the reactants.[33] In the case of the binary catalyst no previous copolymerization activity was observed in line with the features of the present, bifunctional Zn-based catalyst **6**.

Conclusions

We have detailed the simple formation of bifunctional catalyst systems for the synthesis of cyclic carbonates. These catalysts comprise of a Zn(salpyr) framework that can be alkylated at the pyridyl-N atom, providing a complex with a built-in nucleophile (either I or Br). The catalysis data are supportive of a synergistic effect between the Lewis acidic site and the halide nucleophile showing markedly improved catalysis behaviour compared with a system that lacks a Lewis acid activator (cf., **9**). The bifunctional catalyst **6** was applied as an efficient system for a variety of substrates, and our current focus is now on the design of other types of bifunctional catalysts for CO_2 conversion in the presence of suitable substrates such as epoxides and similar structures.

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Notes and references

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Electronic Supplementary Information (ESI‡) available: Copies of relevant NMR/MS spectra and further experimental details, crystallographic details in cif format. See DOI: 10.1039/b000000x/

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