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Cooperativity in Shape-Persistent Bis-(Zn-salphen) Catalysts for Efficient Cyclic Carbonate Synthesis under Mild Conditions

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Abstract

A series of conformationally rigid (Zn-salphen)₂ complexes with a planar bridging component (xanthene or dibenzofuran) are described. Conformational changes for these assemblies are essentially limited to axial rotation of the Zn-salphen moieties; however, such geometric constraints crucially permit subtle tuning of the intermetallic separation and geometry to potentially enhance catalytic activity (and cooperative effects). The complexes have been investigated as catalysts in conjunction with ⁿBu₄NI for the coupling of CO₂ with epoxides. Selected dibenzofuran derivatives are significantly more active for the production of cyclic carbonate than their mononuclear analogues under identical conditions and concentration of Zn sites. High initial turnover frequencies (up to 29000 h⁻¹; 14500 h⁻¹ per Zn, using 10 bar of CO₂ at 95 °C) and excellent efficiencies under mild conditions (1 bar of CO₂ at 55 °C) have been achieved. Kinetic studies using in-situ (React-IR) spectroscopy and density functional theory calculations have been performed, which reveal the existence of an intramolecular rate component, and a preference for the cooperative pathway as well as transition states that depict the Zn sites operating in tandem, respectively. Taken together, these results provide strong evidence of cooperative reactivity in these Zn₂ catalysts.

Introduction

The development of cooperative reactivity and catalysis between proximal metal centers in multinuclear assemblies has been inspired by the structures found in metalloenzymes.¹ In multimetallic systems, adjacent active sites can react synergistically and cooperatively to afford enhanced efficiency and improved or unusual selectivity, when compared with their mononuclear congeners.² Design strategies for bimetallic frameworks traditionally employ metals held together by judiciously chosen polydentate ligands. Such multi-ligand structures can be flexible and offer a diverse range of metal-metal distances, thus permitting the adoption of optimal conformations and minimizing rigidity-related activation energies, but this inherently leads to unfavorable entropic terms. An alternative approach is to introduce direct bonding between the two metals, but this may reduce their capacity to support (cooperative) reactivity.

Carbon dioxide is a highly appealing C₁ feedstock because it is abundant, inexpensive, non-toxic and sustainable, and its valorization can reduce waste.³ The development of catalysts for CO₂ activation and transformation has received intense scrutiny,⁴ and at the forefront has been the metal-mediated coupling of CO₂ with epoxides to produce synthetically valuable and bio-based cyclic organic carbonates⁵ and biodegradable polycarbonates.^{6,7} Bis-Zn(II) catalysts⁸ bearing *N,N'*-phenylene-1,2-bis(salicylideneimine) auxiliaries (salphen),⁹ as well as oxo-bridged [(Al-salen)₂(μ-O)] relatives,¹⁰ can function efficiently for cyclic carbonate formation, while mono-Al(III) catalysts supported by amino-tris(phenolate)¹¹ and porphyrin¹² may be considered as literature benchmarks for high activity. The employment of β-diiminate,¹³ anilido-alimine,¹⁴ and tetraamine-bis(phenolate)¹⁵ ligands in bimetallic Zn(II) catalysts resulted in the production of polycarbonates, while Zn₃,¹⁶ Zn₄ (such as [Zn₄(OCOCF₃)₆(μ-O)])¹⁷ and MOF¹⁸ derivatives exhibited elevated catalytic efficiencies for the synthesis of cyclic carbonates. The applications

of binuclear Co(III) catalysts for the copolymerization of CO₂ and epoxides were extensively studied.^{19,20} Novel heterometallic [Co, Mg]²¹ and [Co₃, Ln]²² catalysts for polycarbonate synthesis were recently described. Notably, although many multinuclear catalysts exhibiting enhanced efficiency have been reported, experimental evidence in support of cooperative bi- or multimetallic mechanisms is scarce.^{21–23}

Instigated by our ability to adjust and manipulate the intramolecular interactions between bis-(M-salphen) moieties in luminescent host cavities,^{24,25} we proceeded to tailor this approach towards the development of catalytic frameworks. By applying this modular *shape-persistent bimetallic* design strategy, we targeted M₂ systems tethered by an inert, rigid ‘anchor’ component that feature the following important attributes: (1) M–M interactions or “quenching” would be precluded, and coordinative unsaturation conserved, by the inflexible backbone and the incorporation of bulky substituents, and (2) variations in molecular conformations are essentially limited to *axial rotation* of the M-salphen units, yet such rotations can crucially enable subtle adjustment of the intermetallic distance and geometry. Our objective is to modify and control the spatial arrangement and mutual orientation of the cofacial M-salphen moieties, by changing the nature and dimensions of the anchor component, so that the capacity of the resultant frameworks for the binding and activation of small molecules can be probed and adapted. Hence, the creation of a tunable, convergent reaction space, capable of supporting enhanced reactivity and bimetallic cooperativity, was envisaged.

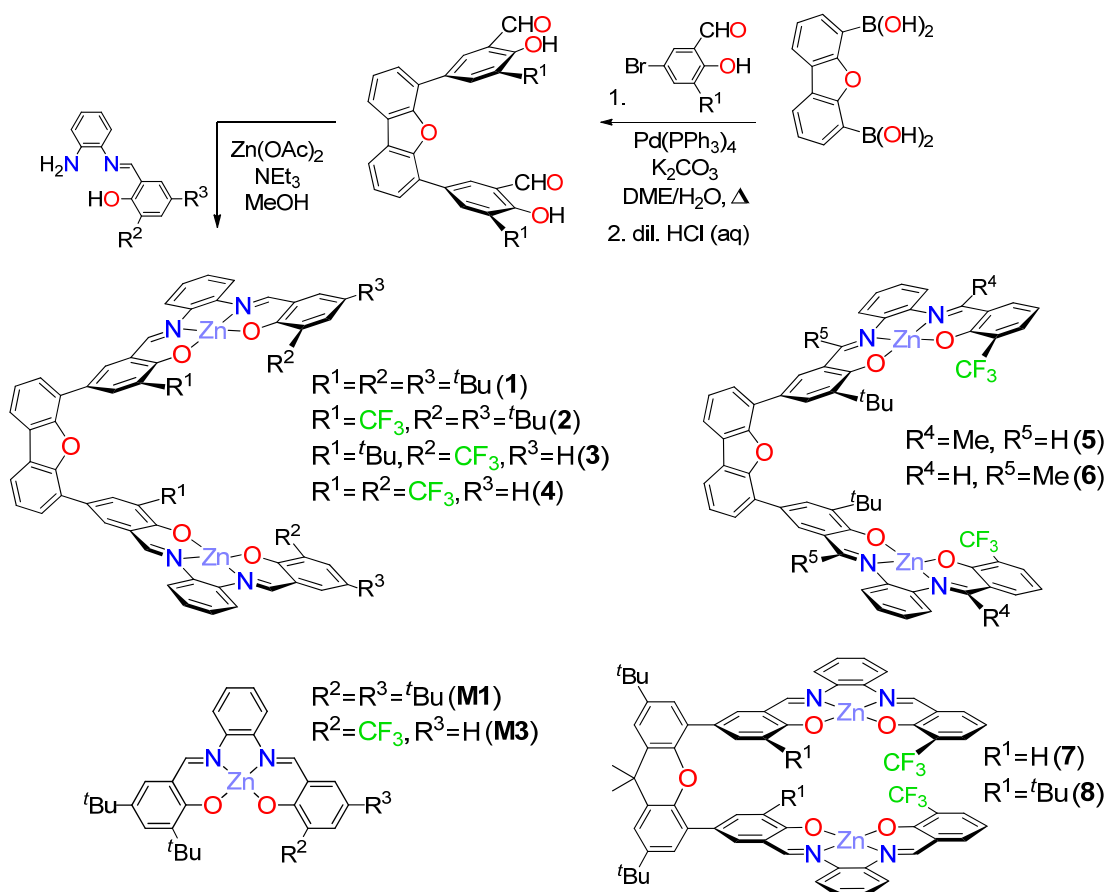
We initially reported bis-(Zn-salphen) complexes bearing *t*-butyl substituents *ortho* to the O(phenolate) atoms, which function as efficient catalysts for cyclic carbonate formation from CO₂ and epoxides under mild conditions.⁸ Structurally diverse Zn₂ catalysts featuring different “anchoring” positions (*para* or *meta* to the O(phenolate) atoms) at the salphen moiety were developed, improved efficiencies were detected for salphen (vs. salcy) derivatives using ⁿBu₄NI

(vs. other halides), and high initial turnover frequencies (TOFs, up to 7400 h⁻¹ per Zn; 95 °C, 10 bar *p*CO₂) were observed. The aims of the present study are 1) to evaluate the effects of the xanthene and dibenzofuran bridges, which afford parallel and acutely angled cofacial systems, respectively (critically, intermetallic distances can vary upon axial rotation because the Zn sites do not reside on the rotational axes), and 2) to study substituent effects in order to improve catalytic activity and stability. Enhanced electrophilicity at the metal center can promote substrate binding, and the incorporation of fluorinated moieties as electron-withdrawing substituents is an effective strategy.^{17,26} Hence, high efficiencies and elevated TOFs have been developed for the Zn₂ catalysts in this work, which have been rationally designed to mediate cooperative reactivity. Saliently, kinetic studies using in-situ (React-IR) spectroscopic analysis and density functional theory (DFT) calculations have been employed to investigate the reaction mechanism, which reveal the existence of an intramolecular rate component, and a preference for the intramolecular pathway as well as transition states involving cooperating Zn centers, respectively, thus providing clear evidence of bimetallic cooperativity.

Results and Discussion

Synthesis and Characterization. A series of bis-(Zn-salphen) complexes have been designed and successfully prepared, and various functionalities have been introduced to investigate substituent effects (**1–8**). The modular, stepwise synthetic method employed in this study connects two Zn-bound salphen moieties (which are robust and easily derivatized) with a bridging anchor group, and allows the incorporation of different substituents at the “inner” and “outer” phenolate and imine groups (see Supporting Information for details). In general, these structures afford minimal lateral displacement but varying extents and propensity for axial

rotation of the cofacial Zn-salphen units (e.g. by changing the intermetallic distance and orientation between the Zn-salphen units in **3** vs. **8**).



Scheme 1. Synthesis of complexes **1–4**, and structures of **5–8** and mono-Zn controls **M1** and **M3**.

As illustrative examples (Scheme 1), starting from the bis-boronic acid of dibenzofuran, complexes **1–4** were prepared by Pd-catalyzed coupling with substituted 5-bromosalicylaldehydes at elevated temperature, followed by a one-pot templated condensation reaction in MeOH using $\text{Zn}(\text{OAc})_2$ and the corresponding “semi-Schiff base” substrate in the presence of NEt_3 . For complexes **2–6** bearing CF_3 substituents, precipitation from the reaction mixture using CH_2Cl_2 /hexane yielded triethylamine- and acetic acid-containing products (observable by ^1H NMR spectroscopy), reflecting the highly Lewis acidic nature of the Zn centers. Sequential removal of the base (by dissolving in dry THF, followed by removal of volatiles) and acid (by

stirring in CaCl₂/CH₂Cl₂ for 30 minutes) were accomplished to afford analytically pure products. The Zn₂ complexes exhibit different solubilities in organic solvents depending on the salphen substituents; the presence of multiple *t*-butyl substituents in complex **1** contributes to its high solubility compared with trifluoromethyl-substituted derivatives **2** and **3**, while **4** without *t*-butyl groups displays the lowest solubility. Complexes **5** and **6** exhibit good solubility in organic solvents, including CH₂Cl₂ and 2-butanone (MEK). The increased solubility of complexes bearing *t*-butyl groups can be ascribed to reduced intermolecular π -stacking and aggregation processes.

Binuclear complexes **1–8** were characterized by ¹H, ¹³C and ¹⁹F (except for **1**) NMR spectroscopy, ESI-MS, and elemental analysis. In their ESI mass spectra, parent peak clusters with *m/z* values corresponding closely to the respective calculated isotopic patterns were obtained (Supporting Information). The molecular structure of the xanthene-bridged CF₃-substituted complex **7** bearing coordinated DMSO and H₂O molecules was determined by X-ray crystallography (Figure 1). The intramolecular interplanar distance (defined as the average separation between Zn(II) and adjacent [N₂O₂] plane) is 3.66 Å, although the two [N₂O₂] planes are not parallel and show a dihedral angle of 6.3°. Dihedral angles (aryl-to-aryl) of 40.4 and 39.0° are apparent between the xanthene backbone and the respective salphen moieties, and the overlap between the Zn-salphen moieties is therefore offset and the CF₃ groups do not experience repulsion. Consequently, in the absence of substituents at R¹, the two Zn-salphen units exist in a *syn* (head-to-head) cofacial conformation, and a relatively short intramolecular Zn···Zn distance of 4.914(1) Å is observed. This is in contrast to the *anti* (head-to-tail) conformation reported previously for a close relative of the dibenzofuran-bridged **1**, which exhibits a noticeably longer Zn···Zn distance of 6.433(1) Å.⁸ It is apparent, from DFT

calculations, that the *anti* conformation can mediate lower-energy processes (see below; Zn \cdots Zn distances of up to 6.5 Å have been determined for cooperative Zn₂ sites).

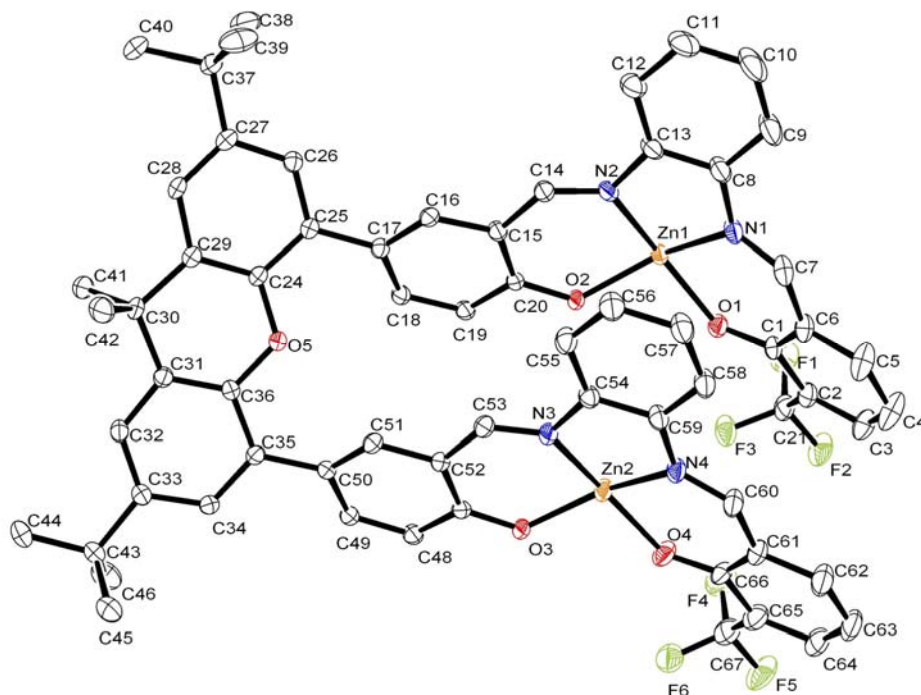
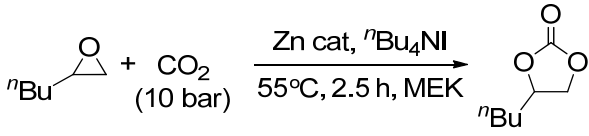


Figure 1. Perspective view of 7·DMSO·H₂O (30% probability ellipsoids; Zn-coordinated solvent molecules omitted).

Coupling of CO₂ with Epoxides Catalyzed by Zn₂ Complexes: High Efficiencies and Mild Conditions. Initial evaluation of the catalytic efficiency of the bimetallic complexes (using ⁿBu₄NI cocatalyst) for cyclic carbonate formation, from CO₂ and 1,2-epoxyhexane in 2-butanone (MEK), was undertaken (Table 1). The highest conversions are observed for catalysts **2**, **5** and especially **3**. It became clear that i) the presence of substituents *ortho* to the “inner” O(phenolate) groups can suppress typically facile dimerization processes (via intermolecular Zn \cdots O(salphen) interactions),^{24,27} while inhibiting the aggregation and obstruction of active sites, and ii) the CF₃/*t*-butyl combination of substituents is beneficial. Compared with *t*-butyl (**1**), the CF₃ substituents in **2** and **3** would enhance the Lewis acidity of the Zn centers. However, the superior

activity of **3** (run 3), and the lower conversion rate observed for **4** (run 4), apparently emphasize the need for bulkier “inner” *t*Bu groups at R¹ to promote repulsion and thereby ensure the preferred *anti* conformation. The ketimine moiety is not advantageous, and is clearly detrimental at the inner position for **6** (run 6). Lower conversions are evident for xanthene-based **7** (revealed as the *syn* form in the crystal structure) and **8**; it may be inferred that the Zn₂ centers in these parallel, cofacial Zn-salphen units are insufficiently separated to support bimetallic cooperativity.

Table 1. Coupling of CO₂ with epoxyhexane in MEK: substituent effects ^{a,b}

			
run	cat. (mol%)	co-cat. (mol%)	conv. ^c (%)
1	1 , 1	1.3	50
2	2 , 1	1.3	66
3	3 , 1	1.3	78
4	4 , 1	1.3	40
5	5 , 1	1.3	63
6	6 , 1	1.3	34
7	7 , 1	1.3	31
8	8 , 1	1.3	36

^aConditions: 2 mmol epoxyhexane, 0.667 mmol mesitylene (internal standard) in MEK (5 mL), 10 bar CO₂ initial pressure, 55 °C, 2.5 h. ^bCatalyst and *n*Bu₄NI (co-catalyst) concentrations are calculated on per-metal atom basis and relative to epoxide. ^cAverage conversions from repeated runs; determined by ¹H NMR analysis of reaction mixture (selectivity >99%).

The performance of catalyst **3** under mild conditions was investigated, and comparisons with **2** and **5** were made (Table 2). At 10 bar *p*CO₂, good conversion is observed at 35 °C after 12 hours (run 1), and increasing the temperature to 55 °C yielded 92% conversion after only 3

hours (run 2; high conversions are also detected for **2** and **5**). Catalyst **3** is found to give good efficiencies at decreasing CO₂ pressures, with excellent conversions achieved at 1 bar *p*CO₂ and 55 °C for different epoxides after 8 hours (runs 6–8), and especially at elevated temperatures (runs 9, 10). The high conversion rates have been achieved at relatively low *p*CO₂ and temperatures, signifying that these catalysts are stable over several hours.

Table 2. Coupling of CO₂ with epoxides in MEK under various conditions ^{a,b}

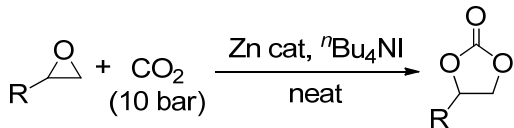
run	R	cat.	<i>p</i> CO ₂ (bar)	temp (°C)	<i>t</i> (h)	conv. ^c (%)
1	<i>n</i> Bu	3	10	35	12	80
2	<i>n</i> Bu	3	10	55	3	92
3	<i>n</i> Bu	2	10	55	3	79
4	<i>n</i> Bu	5	10	55	3	78
5	<i>n</i> Bu	3	5	55	3.5	89
6	<i>n</i> Bu	3	1	55	8	93
7	Et	3	1	55	8	92
8	Me	3	1	55	8	89
9	<i>n</i> Bu	3	1	65	4	94
10	<i>n</i> Bu	3	1	95	1.5	95
11	<i>n</i> Bu	2	1	95	1.5	73
12	<i>n</i> Bu	5	1	95	1.5	74

^a Conditions: 2 mmol epoxide, 0.667 mmol mesitylene (internal standard) in MEK (5 mL). ^b Catalyst concentration (1.0 mol%; 1.3 mol% *n*Bu₄NI co-catalyst) is calculated on per-metal atom basis and relative to epoxide. ^c Average conversions from repeated runs; determined by ¹H NMR analysis of reaction mixture (selectivity >99%).

For the coupling of CO₂ with epoxybutane (neat; Table S1), evaluation of the catalytic performance confirmed that **3** is the most active, followed by **2** and **5**. The reactions of CO₂ (10 bar) with various epoxides (neat) at different catalyst loadings and temperatures were examined (Table 3). In epoxypropane, catalyst **3** displays significant activity at low concentrations, and a higher TOF per Zn center is obtained using a larger excess of the co-catalyst. Thus, a TOF of 750 h⁻¹Zn⁻¹ is observed using **3** (0.01 mol%; 0.1 mol% of ⁿBu₄NI) at 45 °C, which increases to 1100 h⁻¹Zn⁻¹ with 0.5 mol% of ⁿBu₄NI (runs 1, 2; N.B. run 3 confirms minimal conversion in the absence of **3**, even at 85 °C). In epoxybutane, elevated temperatures and lower catalyst loading produce improved TOFs (runs 4, 5).

In epoxyhexane (Table 3), the stability of catalyst **3** at 95 °C is indicated by comparable TOFs after 1 and 2 hours (runs 6, 7). Enhanced TOFs are generally observed at 95 °C and low catalyst loading. For **5**, the ketimine moiety is detrimental, and its impact is more pronounced at the inner position for **6** (runs 13 and 14 respectively, vs. run 8). DFT calculations (see below) regarding the reaction mechanism revealed transition states that feature considerable twisting and distortion of the Zn-salphen moieties, which would be impeded more by the inner methyl group (i.e. for **6**), leading to increased barriers. At 95 °C, catalysts **3** and **2** display exceptionally high TOFs for epoxyhexane (runs 8, 11: 13750 and 11000 [vs. 6000 for **1**, run 10] h⁻¹ per metal, respectively; conditions: 10 bar *p*CO₂, 2 h, 0.002 mol% cat. (per-M basis), 0.1 mol% ⁿBu₄NI), and the highest initial molecular TOF of 29000 h⁻¹, equivalent to 14500 h⁻¹ per metal, was observed for styrene oxide using **3** (run 9). Significantly, these TOFs for catalyst **3** approach the values for benchmark examples in the literature under mild conditions (at or below 10 bar *p*CO₂ and below 100 °C) for cyclic organic carbonate synthesis.^{5,28}

Table 3. Coupling of CO₂ with epoxides (neat) under various conditions ^{a,b}



run	R	cat. (mol%)	co-cat. (mol%)	temp (°C)	t (h)	conv. ^c (%)	TOF ^d (h ⁻¹ Zn ⁻¹)
1	Me	3 , 0.01	0.1	45	2	15	750
2	Me	3 , 0.01	0.5	45	2	22	1100
3	Me	–	0.5	85	2	2	–
4	Et	3 , 0.01	0.1	85	2	93	4650
5	Et	3 , 0.002	0.1	85	2	35	8750
6	<i>n</i> Bu	3 , 0.0025	0.125	95	1	26	10400
7	<i>n</i> Bu	3 , 0.0025	0.125	95	2	56	11200
8	<i>n</i> Bu	3 , 0.002	0.1	95	2	55	13750
9	Ph	3 , 0.002	0.1	95	2	58	14500
10	<i>n</i> Bu	1 , 0.002	0.1	95	2	24	6000
11	<i>n</i> Bu	2 , 0.002	0.1	95	2	44	11000
12	<i>n</i> Bu	4 , 0.002	0.1	95	2	28	7000
13	<i>n</i> Bu	5 , 0.002	0.1	95	2	39	9750
14	<i>n</i> Bu	6 , 0.002	0.1	95	2	23	5750
15	<i>n</i> Bu	7 , 0.002	0.1	95	2	22	5500
16	<i>n</i> Bu	8 , 0.002	0.1	95	2	25	6250

^aConditions: 3 mL epoxide, 1 mol% mesitylene (internal standard), 10 bar CO₂ initial pressure. ^bCatalyst and co-catalyst (*n*Bu₄NI) concentrations are calculated on per-metal atom basis and relative to epoxide.

^cReproducible within 2% in three independent runs for selected experiments; determined by ¹H NMR analysis of reaction mixture (selectivity >99%). ^d Average turnover frequency (= mol_(substrate converted)/mol_{cat}/h/metal).

Probing Cooperative Reactivity Using In-Situ (React-IR) Spectroscopy and DFT

Calculations. At relatively low catalyst concentrations, complex **3** displays conversion rates that exceed those for the mono-Zn reference **M3** (Table 4). The substantially higher TOFs for **3** under identical conditions and concentration of Zn sites (runs 1, 3) are noteworthy, and point to the possibility of cooperative effects between the Zn centers. Hence, kinetic studies using in-situ (React-IR) spectroscopy have been employed to probe the reaction mechanism and provide evidence of bimetallic cooperativity.

Table 4. Coupling of CO₂ with epoxides (neat and in MEK): comparing **3** and **M3**^a

run	R	cat. (mol%)	co-cat. (mol%)	pCO ₂ (bar)	temp (°C)	t (h)	conv. ^d (%)	TOF ^e (h ⁻¹ Zn ⁻¹)
1	Et ^b	3 , 0.00125	0.0625	15	65	4	22	4400
2	Et ^b	M3 , 0.00125	0.0625	15	65	4	12	2400
3	Ph ^c	3 , 0.5	0.65	10	65	3	80	53
4	Ph ^c	M3 , 0.5	0.65	10	65	3	43	29

^aCatalyst and co-catalyst (ⁿBu₄NI) concentrations are calculated on per-metal atom basis and relative to epoxide. ^b Conditions: 3 mL epoxide, 1 mol% mesitylene (internal standard). ^c Conditions: 2 mmol epoxide, 0.667 mmol mesitylene (internal standard) in MEK (5 mL). ^dAverage conversions from repeated runs; determined by ¹H NMR analysis of reaction mixture (selectivity >99%). ^e Average turnover frequency (= mol_(substrate converted)/mol_{cat}/h/metal).

For a bimetallic catalyst, the rate equation can be considered as a function of [M] (concentration of metal centers) and a sum of both first- and second-order contributions:²⁹

$$\text{rate} = k_{\text{intra}}[\text{M}] + k_{\text{inter}}[\text{M}]^2 \quad (1)$$

For a plot of rate/[M] versus [M], the y intercept and slope correspond to the intramolecular (k_{intra}) and intermolecular (k_{inter}) rate coefficients, respectively. While the y intercept should be zero for mononuclear species that lack intramolecular reactions, a non-zero y intercept for binuclear catalysts would substantiate the existence of an intramolecular reaction (i.e. cooperativity). Using Zn₂ catalysts **1** and **3** and their respective mono-Zn references **M1** and **M3**, the initial reaction rates were determined for the coupling of CO₂ with 1,2-epoxybutane at different [Zn] (0.005–0.025 mol%) by calculating the tangent ($t = 0$) for the conversion plots obtained by React-IR spectroscopy (Figure 2 and Supporting Information).³⁰ The plots of rate/[Zn] versus [Zn] (Figure 3) for the mononuclear controls **M1** and **M3** are linear ($k_{\text{inter}} = 0.46$ and $0.50 \text{ M}^{-1} \text{ min}^{-1} \times 10^3$, respectively) and pass through the origin, thus confirming the expected absence of an intramolecular component. Saliiently, for binuclear catalysts **1** and **3** ($k_{\text{inter}} = 0.09$ and $0.17 \text{ M}^{-1} \text{ min}^{-1} \times 10^3$, $k_{\text{intra}} = 0.63$ and 0.50 min^{-1} , respectively), non-zero y intercepts are observed for the linear correlations, thereby verifying the existence of the k_{intra} term and thus cooperative reactivity for the Zn centers.

Interestingly, the k_{inter} slopes signify that the second-order, intermolecular contribution is operative for the catalysts studied. The smaller k_{inter} terms for **1** and **3** can be ascribed to the reduction in the total catalyst concentration (by half) due to the non-randomization of metal sites in the binuclear structure. Overall, these results show that the intramolecular, cooperative pathway plays a prominent role in determining the overall catalytic efficiencies and conversion

rates at low Zn concentrations (below 0.013 mol%, under conditions of the described experiment), which is pertinent with regard to practical applications.

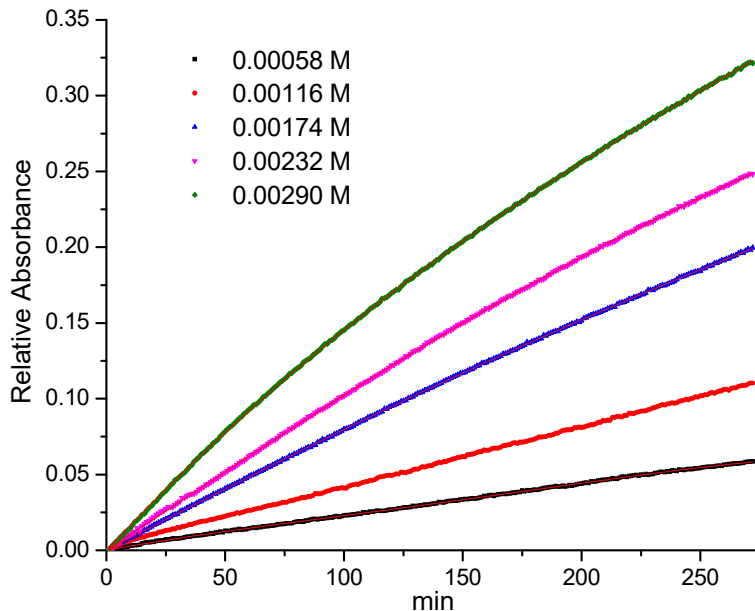


Figure 2. Conversion plots obtained by React-IR for coupling of CO₂ with 1,2-epoxybutane at different Zn concentrations ([Zn]) for catalyst **3** (conditions: 3 mL epoxybutane, 10:1 ratio of ⁿBu₄NI co-cat/cat, 1 bar CO₂ initial pressure, 25 °C; catalyst concentration is calculated on per-Zn atom basis and relative to epoxide).

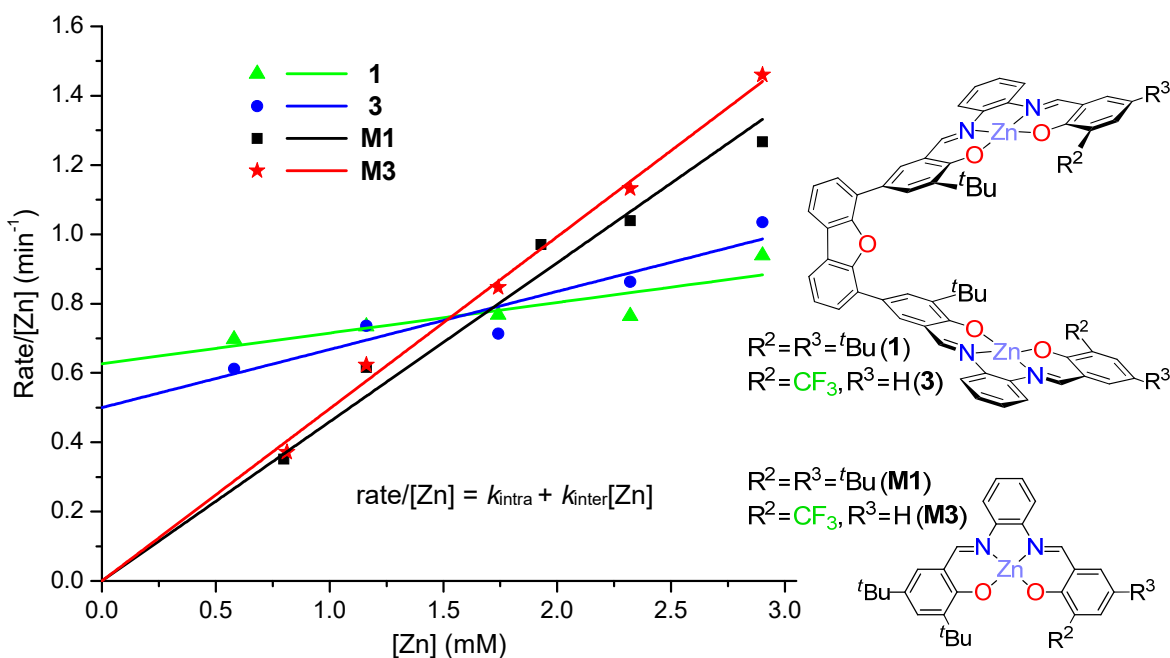


Figure 3. Initial rate plots (25 °C) for coupling of CO₂ (1 bar) with 1,2-epoxybutane (neat) catalyzed by Zn₂ complexes **1** and **3** and their mono-Zn references **M1** and **M3** (conditions: see Figure 2).

Next, DFT calculations (employing the two-layer ONIOM-SMD(DFT:PM6) method³¹) were performed for the coupling of propylene oxide with CO₂ by catalyst **3**, to investigate the cooperative mechanism and probe different reaction pathways (Figures 4 and 5; see Supporting Information for details). Namely, an intramolecular process inside the structure involving cooperating Zn₂ centers (**A**), and a reaction occurring on the exterior of the cavity (**B**), were examined. First, regarding the different possible conformers of the catalyst, the *anti* (head-to-tail) form was found to be the most stable (Figure S10). The initial step in both pathways is the coordination of the O(epoxide) atom at a Zn center, and the resultant complex is more stable in path **A** (**1a**) than path **B** (**1b**). The reaction consists of three major steps: ring-opening³² to give Zn-alkoxide (i), CO₂ addition to give Zn-carbonate (ii); and ring closure/back-biting (v). In the

case of path **A**, the ring-closure step becomes more favorable because of the inclusion of two additional steps, namely, dissociation of the Zn–I bond (iii), and coordination of the O(carbonate) atom to the Zn ion (iv), which occur before the ring-closure process.

The initial ring-opening process is determined to be the rate-limiting step, and significantly for path **A**, the lowest barrier is found for the preferred *anti* conformation (Figure S13). The relative energies of the transition states for path **A** are lower than for **B** (Figure 5), thus indicating a kinetic preference for an intramolecular (first-order) cooperative pathway involving the secondary Zn' site.³³ In particular, the transition states on path **A** involve 1) Zn'⋯I⁻ coordination for ring-opening (**2a***), and 2) Zn'⋯O(carbonate) coordination for the ring-closing (back-biting) process (**11a***).

It is important to note that the lower stability of path **B** for catalyst **3** is entirely consistent with the kinetic results obtained for the mononuclear relative **M3**, for which the first-order intramolecular contribution, equivalent to path **B**, was not detected (Figure 3). Considering the range of Zn⋯Zn distances (5.13–6.53 Å) in these transition states (Figure 5), it is apparent that the dibenzofuran-bridged shape-persistent structures can engender suitable distances and geometries between the Zn centers to facilitate bimetallic cooperativity in these catalysts. Taken in tandem, the results from the kinetic studies and DFT calculations provide strong evidence for the existence of cooperative reactivity in these Zn₂ catalysts.

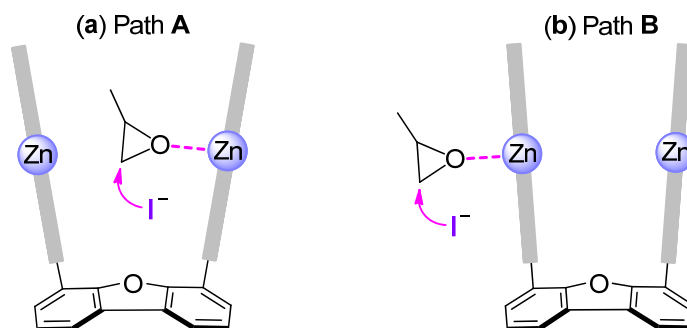


Figure 4. Reaction pathways (inside and outside cavity) examined by DFT calculations.

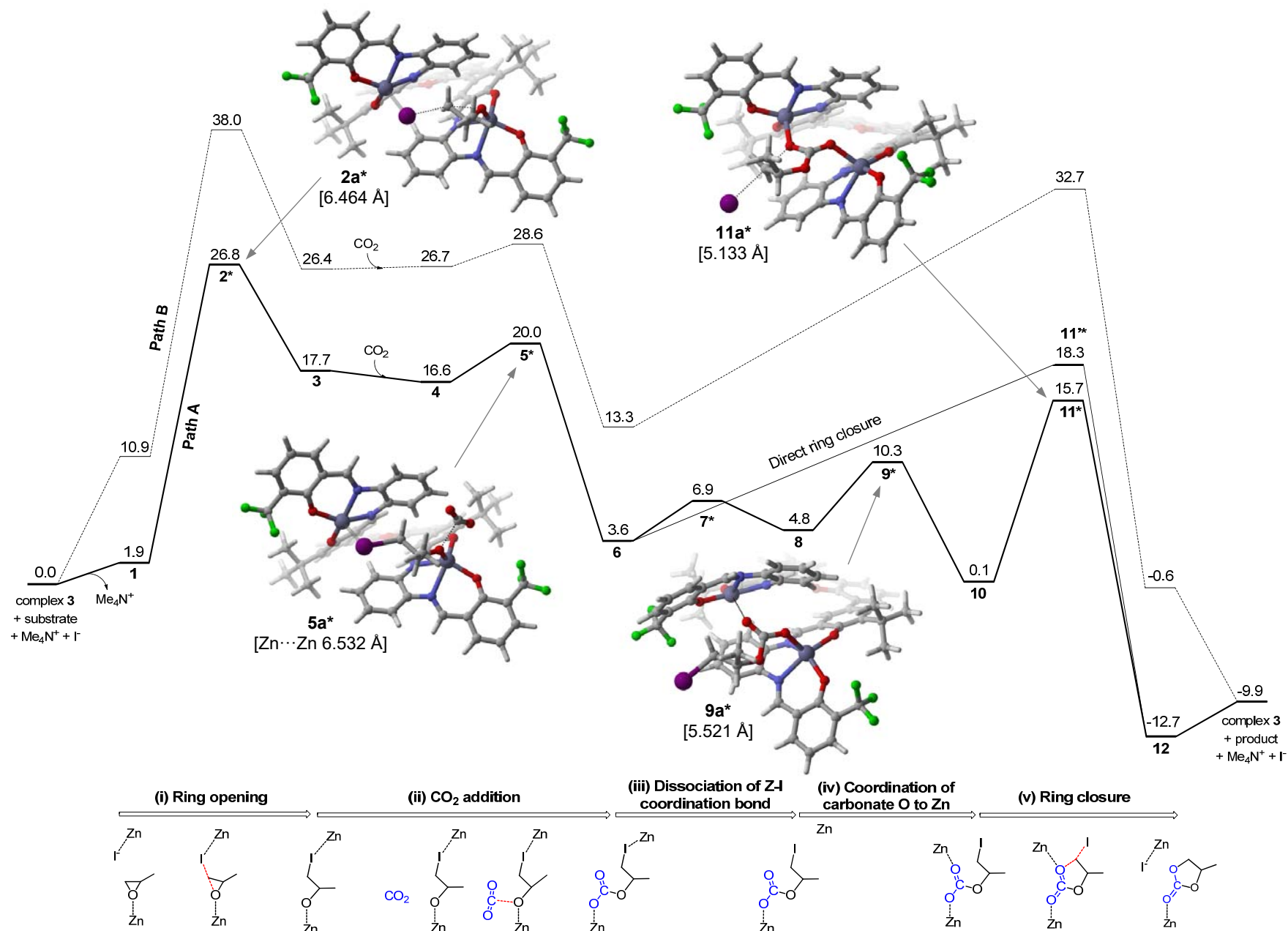


Figure 5. ONIOM-SMD-determined Gibbs free-energy profile (in kcal/mol, at 298.15 K) for coupling reaction inside (A; cooperative) and outside (B) $(\text{Zn-salphen})_2$ cavity of **3** (optimized geometries on path A: Zn, lavender; C, gray; N, blue; O, red; F, green; I, purple; Zn...Zn distances in [parentheses]).

Conclusion

A family of shape-persistent (Zn-salphen)₂ complexes with a rigid bridging moiety (xanthene or dibenzofuran) has been developed. The strategy of modifying the structure and connectivity of these frameworks has been explored, in order to create Zn₂ cavities as well as tune and improve their attendant catalytic reactivity. Excellent catalytic performance for the coupling of CO₂ with epoxide, in terms of enhanced TOFs (per metal center) and high conversion rates under mild conditions (low *p*CO₂ and temperature), have been achieved. In particular, the CF₃/*t*-butyl-substituted dibenzofuran-based catalyst **3** displayed elevated initial TOFs (up to 29000 h⁻¹; 14500 h⁻¹ per Zn, using 10 bar *p*CO₂ at 95 °C) and excellent efficiencies under mild conditions (1 bar *p*CO₂ at 55 °C).

Kinetic studies using in-situ (React-IR) spectroscopy revealed the existence of an intramolecular rate component, and thus, cooperative reactivity for the Zn₂ catalysts. This intramolecular, cooperative process plays a dominant role in conferring high catalytic efficiency at low Zn concentrations, which is attractive from a practical viewpoint because reduced loading and consumption of catalysts are desirable. DFT calculations showed a kinetic preference for an intramolecular pathway inside (rather than outside) the cavity involving cooperating Zn₂ sites. Hence, the combined kinetics/DFT results provide strong evidence of bimetallic cooperativity in these catalysts.

These proof-of-concept results emphasize the importance of the relative orientation of active sites, and intermetallic separation and geometry, for attaining synergistic effects and high activity. It should be noted that the utilization of abundant, non-toxic Zn is appealing, and further functionalization of salphen ligands (e.g. with ammonium/piperidinium pendants) is well-established. This shape-persistent bimetallic design approach may be applicable to catalyst

systems that operate through or invoke a cooperative, bimetallic mechanism. This work paves the way for the further creation and development of shape-persistent multinuclear frameworks that can mediate important catalytic reactions with enhanced efficiency and cooperativity.

Supporting Information Available: Experimental details, procedures for catalyst screening, and characterization data for ligands and complexes; in-situ (React-IR) spectroscopic analysis and determination of rate constants; DFT calculations.

Notes. The authors declare no competing financial interests.

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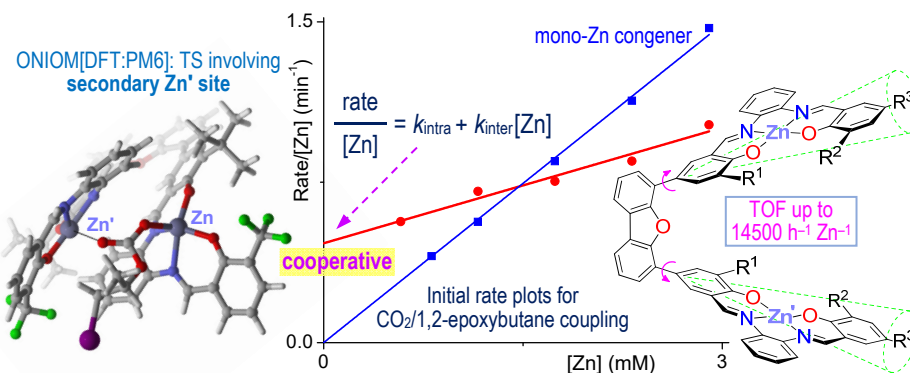
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- (30) Curve fittings were performed using the ORIGIN software, and the tangent ($t = 0$) corresponding to k_{obs} (absorbance/min) was obtained. A calibration curve was then used to determine the relationship between relative absorbance and product concentration (in M), so that k_{obs} can be converted into the initial reaction rate (M min^{-1}), which allows the

determination of the rate constants (see Supporting Information for details).

- (31) For the two-layer ONIOM (DFT:PM6) method, the entire system was treated as a “low layer”, while all of the atoms of the Zn-salphen moiety (except *t*-butyl groups) and substrates were defined as a “high layer” to which M06-2X DFT was applied. For geometry optimization, the Lanl2dz effective core basis set was used for Zn and iodine, and the 6-31G* basis set was used for all other atoms. The def2-TZVP basis set and SMD solvent model were used for energy calculations.
- (32) For the ring-opening step, nucleophilic attack by iodide at the secondary C atom of the epoxide is preferred as expected, because the tertiary C site is less electrophilic and more crowded.
- (33) The kinetic analysis of the reaction catalyzed by **3** indicates that the second-order intermolecular contribution (Eq. 1) is also operative. This presumably involves a reaction between two Zn centers on different molecules, but DFT calculations of such processes are challenging because of the large size of the catalytic system.

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High initial turnover frequencies (up to 29000 h⁻¹) for CO₂-epoxide coupling have been achieved for rigidly-linked catalysts featuring cofacial Zn-salphen units. Kinetic studies using in-situ (React-IR) spectroscopic analysis have been employed to probe the reaction mechanism, which revealed the existence of an intramolecular rate component (that is absent for mono-Zn congeners). Taken in tandem with DFT calculations, these results provide strong evidence of cooperative reactivity for these bimetallic catalysts.