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Unexpected Macrocyclic Multinuclear Zinc and Nickel Complexes Function as Multitask Catalysts for CO_2 Fixations

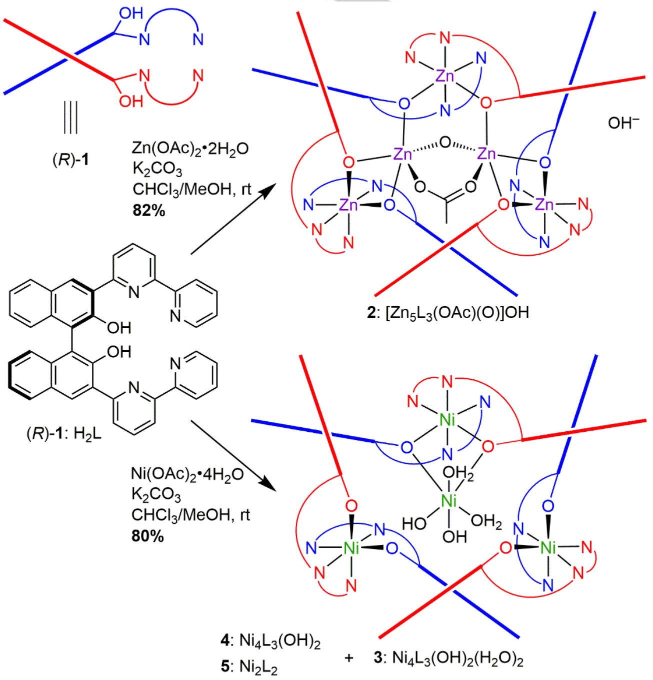
Kazuto Takaishi, Bikash Dev Nath, Yuya Yamada, Hiroyasu Kosugi, and Tadashi Ema**

Abstract: Unique self-assembled macrocyclic multinuclear Zn(II) and Ni(II) complexes with binaphthyl–bipyridyl ligands (L) were synthesized. X-ray analysis revealed that these complexes consisted of an outer ring (Zn_3L_3 or Ni_3L_3) and an inner core (Zn_2 or Ni). In the Zn(II) complex, the inner Zn_2 part rotated rapidly inside the outer ring in solution on an NMR time scale. These complexes exhibited dual catalytic activities for CO_2 fixations: synthesis of cyclic carbonates from epoxides and CO_2 and temperature-switched *N*-formylation/*N*-methylation of amines with CO_2 and hydrosilane.

Artificial metallosupramolecular architectures have been actively investigated, and various macrocycles,[1] cages,[2] and helicates[3] have been synthesized from simple ligands and metal ion sources. Large but ordered multinuclear metal complexes can be constructed by self-assembly. Recently, several metallosupramolecules with catalytic activities have been reported.[4]

CO_2 is a promising C1-building block as an alternative to petroleum-based chemicals, and catalysts for CO_2 fixations have been developed extensively.[5] For example, synthesis of cyclic carbonates from epoxides and CO_2[6] and *N*-functionalization of amines with CO_2 and hydrosilane[7,8] have been actively studied. Cyclic carbonates are raw materials of polycarbonates and polyurethanes, and *N*-functionalized amines are intermediates of various chemicals such as drugs. A multitask catalyst for these CO_2 fixations have not been reported, and its development presents a significant challenge.

Here, we report a new type of macrocyclic multinuclear Zn(II) and Ni(II) complexes **2** and **3**, respectively, prepared by self-assembly of a binaphthyl–bipyridyl ligand (H_2L; (*R*)-**1**) and metal acetate hydrates (Scheme 1). These structures were surprising because we originally expected the formation of simple acyclic dinuclear complexes such as $M_2L(OAc)_2$. The complexes **2** and **3** comprise an outer ring (M_3L_3) and an inner core (M_2 or M). In other words, they are "complex@complex" structures. This type of structure is unprecedented, although many multinuclear metal complexes with binaphthyl-based ligands have been reported.[9] Furthermore, the complexes exhibited high catalytic activities for distinct CO_2 fixations: (1) synthesis of cyclic carbonates from epoxides and CO_2 and (2) *N*-formylation/*N*-methylation of amines with CO_2 and hydrosilane. This is the first example of multitask catalysts for the CO_2 fixations.



Scheme 1. Synthesis of multinuclear Zn(II) and Ni(II) complexes.

We synthesized (*R*)-**1** via the Suzuki–Miyaura reaction of 3,3'-B(pin)-substituted (*R*)-1,1'-binaphthyl[10] with 6-bromo-2,2'-bipyridyl (Scheme S1). (*R*)-**1** and each metal acetate hydrates were self-assembled to give the Zn(II) or Ni(II) complexes in 80–82% yields (Scheme 1).

The crystal structures of the Zn(II) and Ni(II) complexes were determined by X-ray analyses. The Zn(II) complex was found to have a unique macrocyclic pentanuclear structure, $[Zn_5L_3(OAc)(O)]OH$ (**2**) (Figure 1a). Complex **2** contained a trinuclear macrocyclic part, a dinuclear inner part, and a hydroxide as a counter anion, which can be represented by $[Zn_2(OAc)(O)]@[Zn_3L_3]OH$. MALDI-TOF-MS analysis also clearly demonstrated the formation of **2** (Figure S8). The peripheral macrocyclic part consisted of three hexacoordinate octahedral Zn ions (Zn^{1-3}) and three ligands (L), which were connected via two sets of NNO coordinations of the adjacent ligands. All three Zn^{1-3} centers had Δ-chirality induced by the (*R*)-binaphthyl moieties. The inner part consisted of two distorted square pyramidal pentacoordinate Zn ions (Zn^4 and Zn^5) and bridging AcO^- and O^{2-}, forming a six-membered ring (Zn^4–O–C–O–Zn^5–O) to fill the cavity. This inner core is similar to the active site of a peptidase[11] and a phosphotriesterase[12]. The Zn^{1-3} ions were arranged to form a nearly isosceles triangle, and the dihedral angles of the naphthalene rings of each binaphthyl differed: 68°, 72°, and 88°, because the inner part was horizontally long.

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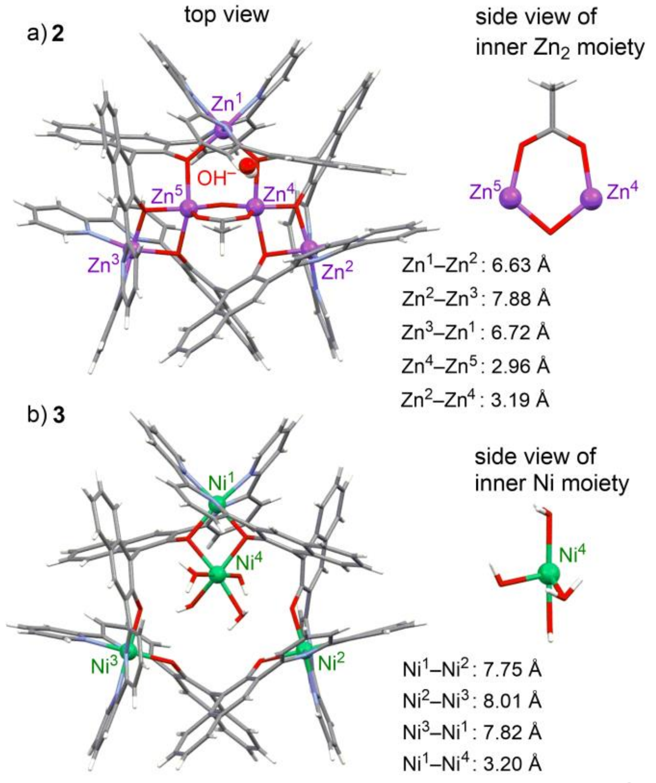


Figure 1. X-ray crystal structures of **2** and **3**. Solvent molecules are omitted for clarity.

On the other hand, the Ni(II) complexes exhibited polymorphism (Schemes 1 and S2), and two types of single crystals of macrocyclic complexes were obtained (Figures 1b and S3). One of them was a cocrystal of tetranuclear complexes $Ni_4L_3(OH)_2(H_2O)_2$ (**3**) and $Ni_4L_3(OH)_2$ (**4**), and the other was a dinuclear complex Ni_2L_2 (**5**). Complex **3** consisted of a macrocyclic part (Ni_3L_3) and an inner part ($Ni(OH)_2(H_2O)_2$). The macrocyclic part was very similar to that of Zn(II) complex **2**. In contrast, the inner part of **3** consisted of a hexacoordinate octahedral Ni^4 ion, two OH$^-$, and two H_2O. The Ni$^{1-3}$ ions of the macrocyclic part have Δ-chirality again. The difference between **3** and **4** was the presence or absence of two H_2O molecules coordinating the inner Ni ion. Complex **5** has two hexacoordinate Ni ions without a cavity. The average Ni–Ni distances in the macrocyclic parts were 7.86 Å for **3** and 6.95 Å for **4**, indicating that the cavity size is somewhat variable.

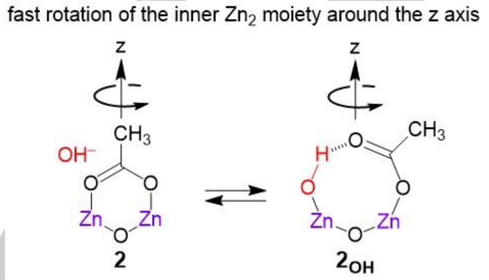
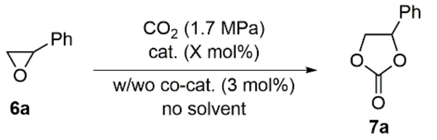


Figure 2. Equilibrium mixture of **2** and **2_{OH}** in solution.

We next analyzed the conformations of Zn(II) complex **2** in solution. ^{1}H NMR, ^{13}C NMR, COSY, and NOESY spectra suggested an averaged C_3-symmetrical structure with the inner core rotating around the z-axis like a molecular motor as shown in Figure 2 (see the Supporting Information for details). The OH$^-$ proton appeared at a high magnetic field (–0.38 ppm in $CDCl_3$), suggesting that the OH$^-$ of **2** was incorporated into the inner part in equilibrium to form **2_{OH}** with a hydrogen-bonded OH ligand surrounded by aromatic rings (Figures 2 and S4). The Ni(II) complexes were NMR-inactive due to paramagnetism, and hence, UV-Vis and CD spectra were analyzed instead. The solution of the cocrystal of **3** and **4** exhibited the same spectra as that of **5** (Figure S10), which suggests a rapid equilibrium between complexes **3**–**5** in solution (Scheme S2).

In view of the quite unique static and dynamic structures of the Zn(II) and Ni(II) complexes **2** and **3**, we decided to investigate the latent catalytic activity of **2** and **3**. In the context of our ongoing research for CO_2 fixations,[13] we tested these metal complexes for the synthesis of cyclic carbonate **7a** from CO_2 and epoxide **6a** (Table 1).[14] We screened combinations of **2** or **3** (2 mol%) and tetrabutylammonium halide (TBAX) at 50 °C under solvent-free conditions (entries 1–6), expecting that the metal ions and halide anions act as a Lewis acid and a nucleophile, respectively. The simultaneous use of complex **2** or **3** and TBAI yielded **7a** in high yield (73–95%, entries 3 and 6). The reaction did not proceed significantly in the presence of either metal complex alone or TBAI alone (entries 7 and 8). The substrate scope of **3** and TBAI was broad; styrene oxides, glycidyl ethers, and hexene oxide **6b**–**i** were efficiently converted into the corresponding cyclic carbonates (Scheme S3).

Table 1: Synthesis of cyclic carbonate **7a** from styrene oxide (**6a**) and CO_2[a]



6a **7a**

Entry	Cat.	X [mol%]	co-cat.[b]	Temp [°C]	Time [h]	Yield [%][c]
1	**2**	2	TBAC	50	12	15
2	**2**	2	TBAB	50	12	59
3	**2**	2	TBAI	50	12	73
4	**3**[d]	2	TBAC	50	12	31
5	**3**[d]	2	TBAB	50	12	68
6	**3**[d]	2	TBAI	50	12	95
7	**3**[d]	2	–	50	12	16
8	–	2	TBAI	50	12	11
9	**2**	0.1	–	120	24	70
10	**3**[d]	0.1	–	120	24	97
11	$Zn(OAc)_2 \cdot 2H_2O$	2	–	120	24	0
12	$Ni(OAc)_2 \cdot 4H_2O$	2	–	120	24	0
13[e]	**2**	2	–	120	24	99
14[f]	**3**[d]	1	–	120	24	97

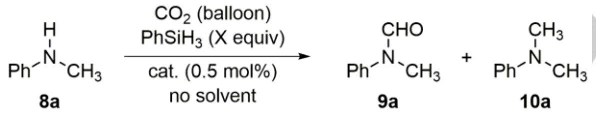
[a] Conditions: **6a** (2.0 mmol), CO_2 (1.7 MPa), cat. (amount indicated above), co-cat. (3 mol%). [b] Tetrabutylammonium chloride (TBAC), bromide (TBAB), and iodide (TBAI). [c] Isolated yield. [d] Equilibrium mixture of **3–5**. The amounts (mol%) are based on **3**. [e] After four-time recycling of the catalyst. [f] After nine-time recycling of the catalyst.

Interestingly, **2** and **3** with only 0.1 mol% loading worked well without a co-catalyst at 120 °C to produce **7a** in high yields (70–97%, entries 9 and 10). By contrast, $Zn(OAc)_2$ and $Ni(OAc)_2$ hydrates showed no catalytic activity (entries 11 and 12). In addition, $ZnCl_2$, $ZnBr_2$, ZnI_2, and $Zn(OCOCF_3)_2{\cdot}H_2O$ also showed no activity (not shown). These results suggest a catalytic mechanism specific to **2** and **3**. The counter anion or ligand such as $OH^–$ and $AcO^–$, or $HCO_3^–$ generated by the reaction of $OH^–$ with CO_2,[15] might act as a nucleophile, and the inner metal ion in **2** and **3** might act as a Lewis acid; the inner Zn ions of **2** are likely to provide a vacant site by the partial dissociation of the AcO bridge, while the inner Ni ion of **3** seems to act as a Lewis acid after loss of a H_2O molecule. In addition, the catalysts were recyclable without lowering catalytic activity at least over five cycles (entries 13 and 14 and Figure S1).

Epoxide **6a** was kinetically resolved in the presence of **3** and TBAI (Scheme S4). The reaction proceeded to give (*S*)-**7a** with 21% ee and (*R*)-**6a** with 16% ee at a 44% conversion ($k_S/k_R = s$ value = 1.8).[16] This result suggests that the macrocyclic structure was retained to some degree during the reactions. We suppose that the low stereoselectivity was due to the active center remote from the chiral axes. We expected that **2** and **3** might show catalytic activities for other CO_2 fixations as well.

We next investigated *N*-formylation and *N*-methylation of amines with CO_2 and hydrosilane (Table 2).[7,8] First, Zn(II) complex **2** (0.5 mol%) was used as a catalyst for the *N*-functionalization of *N*-methylaniline (**8a**) in the presence of CO_2 (1 atm) and phenylsilane under solvent-free conditions. To our delight, *N*-methylformanilide (**9a**) was obtained with complete selectivity at 30 °C (99%, entry 1).

Table 2: *N*-Formylation and *N*-methylation of *N*-methylaniline (**8a**)[a]



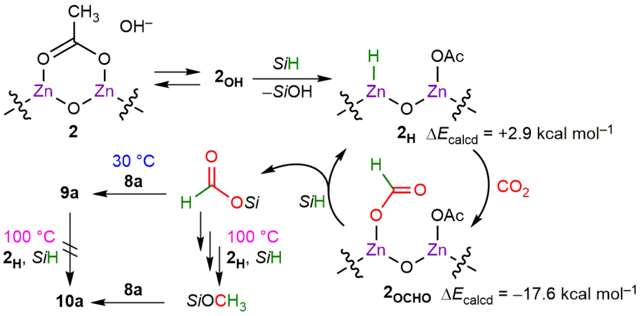
Entry	Cat.	Temp [°C]	X [equiv]	Yield [%][b]	
				9a	**10a**
1	**2**	30	2	**99**	0
2	**2**	30	6	97	0
3	**2**	100	6	9	**60**
4	**3**[c]	30	2	15	0
5	**3**[c]	100	6	0	21
6	$Zn(OAc)_2{\cdot}2H_2O$[d]	30	2	0	0
7	$Zn(OAc)_2{\cdot}2H_2O$[d]	100	6	0	10
8[e]	**2**	100	6	–	0

[a] Conditions: **8a** (0.25 mmol), CO_2 (1 atm, balloon), cat. (0.5 mol% of **8a**), $PhSiH_3$ (amount indicated above), 24 h. [b] Determined by ^1H NMR using mesitylene as an internal standard. [c] Equilibrium mixture of **3–5**. The amounts (mol%) are based on **3**. [d] $Zn(OAc)_2{\cdot}2H_2O$ (2.5 mol%). [e] **9a** was used as a substrate.

In contrast, *N*,*N*-dimethylaniline (**10a**) was obtained preferentially at 100 °C (60%, entry 3). The selectivity for **9a** or **10a** was independent of the amount of phenylsilane (entry 2) and controlled by temperature. Catalyst **2** was applicable to other aromatic and aliphatic amines **8b–e** (Scheme S5). Although several examples of chemoselective *N*-formylation/*N*-methylation were reported,[8] the method using **2** has the following advantages: (1) catalyst loading is low (0.5 mol%), (2) the reaction proceeds in no solvent under the CO_2 pressure of 1 atm, and (3) chemoselectivity is controlled by only temperature.

Ni(II) complex **3** showed much lower catalytic activity than **2** (entries 4 and 5), probably because the Ni(II) ions were reduced to Ni(0) during the reaction. $Zn(OAc)_2{\cdot}2H_2O$ was a poor catalyst (entries 6 and 7). When **9a** was used as a substrate at 100 °C, **10a** was not obtained, but **9a** was recovered (entry 8). This result indicates that **9a** is not an intermediate leading to **10a**.

The reaction pathway for the **2**-catalyzed *N*-functionalization is tentatively proposed in Scheme 2. Initially, the inner Zn_2 moiety of **2** is reduced to give hydride complex $\mathbf{2_H}$.[17] Insertion of a CO_2 molecule gives formate $\mathbf{2_{OCHO}}$. Subsequent reaction with phenylsilane gives silylformate at 30 °C, and further successive reactions with phenylsilane take place at 100 °C to give methoxysilane species. Silylformate and methoxysilane react with **8a** to afford **9a** and **10a**, respectively. DFT calculations support $\mathbf{2_H}$ and $\mathbf{2_{OCHO}}$ as plausible intermediates (Figure S11).[18]



Scheme 2. Proposed pathway for *N*-functionalization of **8a**. ΔE_{calcd} values are relative energies based on $\mathbf{2_{OH}}$ + CO_2 + $PhSiH_3$.

In summary, we demonstrated that binaphthyl–bipyridyl ligands and metal acetates self-assembled to form novel multinuclear Zn(II) and Ni(II) complexes. These complexes acted as multitask catalysts for CO_2 fixations, the synthesis of cyclic carbonates from epoxides and the temperature-switched *N*-formylation/*N*-methylation of amines, under solvent-free conditions. The macrocyclic complexes presented here have great potential in catalysis and other functions, and a further study is underway in our laboratory.

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Conflict of interest

The authors declare no conflict interest.

Keywords: multinuclear complexes • self-assembly • carbon dioxide fixation • cyclic carbonates • *N*-functionalization

[1] For recent reviews, see: a) J. Dong, C. Tan, K. Zhang, Y. Liu, P. J. Low, J. Jiang, Y. Cui, *J. Am. Chem. Soc.* **2017**, *139*, 1554; b) L.-J. Chen, H.-B. Yang, M. Shionoya, *Chem. Soc. Rev.* **2017**, *46*, 2555; c) D. A. Roberts, B. S. Pilgrim, J. R. Nitschke, *Chem. Soc. Rev.* **2018**, *47*, 626; d) S. Chakraborty, G. R. Newkome, *Chem. Soc. Rev.* **2018**, *47*, 3991.

[2] For recent examples, see: a) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka, M. Fujita, *Nature* **2016**, *540*, 563; b) W. M. Bloch, Y. Abe, J. J. Holstein, C. M. Wandtke, B. Dittrich, G. H. Clever, *J. Am. Chem. Soc.* **2016**, *138*, 13750; c) S. H. A. M. Leenders, R. Becker, T. Kumpulainen, B. de Bruin, T. Sawada, T. Kato, M. Fujita, J. N. H. Reek, *Chem. Eur. J.* **2016**, *22*, 15468; d) A. J. Musser, P. P. Neelakanden, J. M. Richter, H. Mori, R. H. Friend, J. R. Nitschke, *J. Am. Chem. Soc.* **2017**, *139*, 12050; e) D. Peterson, J. E. M. Lewis, J. D. Crowley, *J. Am. Chem. Soc.* **2017**, *139*, 2379; f) X.-Z. Li, L.-P. Zhau, L. L. Yan, Y.-M. Dong, Z.-L. Bai, X.-Q. Sun, J. Diwu, S. Wang, J.-C. Bünzil, Q.-F. Sun, *Nat. Commun.* **2018**, *9*, 547; g) L. Zhang, D. P. August, J. Zhong, G. F. S. Whitehead, I. Victoria-Yrezabal, D. A. Leigh, *J. Am. Chem. Soc.* **2018**, *140*, 4982; h) D. Samanta, D. Galaktionova, J. Gemen, L. J. W. Shimon, Y. Diskin-Posner, L. Avram, P. Král, R. Klajn, *Nat. Commun.* **2018**, *9*, 641.

[3] For recent examples, see: a) O. Gidron, M. O. Ebert, N. Trapp, F. Diederich, *Angew. Chem. Int. Ed.* **2014**, *53*, 13614; *Angew. Chem.* **2014**, *126*, 13833; b) O. Gidron, M. Jirásek, N. Trapp, M.-O. Ebert, X. Zhang, F. Diederich, *J. Am. Chem. Soc.* **2015**, *137*, 12502; c) M. H.-Y. Chan, M. Ng, S. Y.-L. Leung, W. H. Lam, V. W.-W. Yam, *J. Am. Chem. Soc.* **2017**, *139*, 8639; d) P. Mateus, B. Wicher, Y. Ferrand, I. Huc, *Chem. Commun.* **2018**, *54*, 5078.

[4] For reviews, see: a) C. J. Brown, F. D. Toste, R. G. Bergman, K. N. Raymond, *Chem. Rev.* **2015**, *115*, 3012; b) C. Tan, D. Chu, X. Tang, Y. Liu, W. Xuan, Y. Cui, *Chem. Eur. J.* **2019**, *25*, 662; For recent examples, see: c) C. García-Simón, R. Gramage-Doria, S. Raoufmoghaddam, T. Parella, M. Costas, X. Ribas, J. H. N. Reek, *J. Am. Chem. Soc.* **2015**, *137*, 2680; d) D. M. Kaphen, M. D. Levin, R. G. Bergman, K. N. Raymond, F. D. Toste, *Science* **2015**, *350*, 1235; e) W. Cullen, M. C. Misuraca, C. A. Hunter, N. H. Williams, M. D. Ward, *Nat. Chem.* **2016**, *8*, 231; f) P. Howlader, P. Das, E. Zangrando, P. S. Mukherjee, *J. Am. Chem. Soc.* **2016**, *138*, 1668; g) Y. Ueda, H. Ito, D. Fujita, M. Fujita, *J. Am. Chem. Soc.* **2017**, *139*, 6090; h) L. Zhao, J. Wang, P. Wu, C. He, X. Guo, C. Duan, *Sci. Rep.* **2017**, *7*, 14347; i) J. Jiao, C. Tan, Z. Li, Y. Liu, X. Han, Y. Cui, *J. Am. Chem. Soc.* **2018**, *140*, 2251; j) L. R. Holloway, P. M. Bogie, Y. Lyon, C. Ngai, T. F. Miller, R. R. Julian, R. J. Hooley, *J. Am. Chem. Soc.* **2018**, *140*, 8078.

[5] For recent reviews, see: a) C. Maeda, Y. Miyazaki, T. Ema, *Catal. Sci. Technol.* **2014**, *4*, 1482; b) Q.-W. Song, Z.-H. Zhou, L.-N. He, *Green Chem.* **2017**, *19*, 3707; c) Y.-Y. Gui, W.-J. Zhou, J.-H. Ye, D.-G. Yu, *ChemSusChem* **2017**, *10*, 1337; d) T. Janes, Y. Yang, D. Song, *Chem. Commun.* **2017**, *53*, 11390.

[6] For recent reviews, see: a) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353; b) X.-D. Lang, L.-N. He, *Chem. Rec.* **2016**, *16*, 1337; c) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembler, *Catal. Sci. Technol.* **2017**, *7*, 2651; d) R. R. Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal.* **2018**, *8*, 419.

[7] a) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem. Int. Ed.* **2012**, *51*, 187; *Angew. Chem.* **2012**, *124*, 191; b) O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, T. Cantat, *J. Am. Chem. Soc.* **2012**, *134*, 2934; c) O. Jacquet, X. Frogneux, C. Das Neves Gomes, T. Cantat, *Chem. Sci.* **2013**, *4*, 2127; d) Y. Li, X. Fang, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 9568; *Angew. Chem.* **2013**, *125*, 9747; e) S. Itagaki, K. Yamaguchi, N. Mizuno, *J. Mol. Catal. A: Chem.* **2013**, *366*, 347; f) K. Motokura, M. Naijo, S. Yamaguchi, A. Miyaji, T. Baba, *Chem. Lett.* **2015**, *44*, 1217.

[8] a) X. Frogneux, O. Jacquet, T. Cantat, *Catal. Sci. Technol.* **2014**, *4*, 1529; b) S. Das, F. D. Bobbink, S. Bulut, M. Soudani, P. J. Dyson, *Chem. Commun.* **2016**, *52*, 2497; c) C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu, B.-L. Lin, *ACS Catal.* **2016**, *6*, 7876; d) X.-F. Liu, R. Ma, C. Qiao, H. Cao, L.-N. He, *Chem. Eur. J.* **2016**, *22*, 16489; e) M.-Y. Wang, N. Wang, X.-F. Liu, C. Qiao, L.-N. He, *Green Chem.* **2018**, *20*, 1564; f) R. H. Lam, C. M. A. McQueen, I. Pernik, R. T. McBurney, A. F. Hill, B. A. Messerle, *Green Chem.* **2019**, *21*, 538.

[9] a) E. C. Escudero-Adán, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2010**, *12*, 4592; b) K. Endo, M. Ogawa, T. Shibata, *Angew. Chem. Int. Ed.* **2010**, *49*, 2410; *Angew. Chem.* **2010**, *122*, 2460; c) S. Akine, T. Shimada, H. Nagumo, T. Nabeshima, *Dalton Trans.* **2011**, *40*, 8507; d) L. Ma, R. Jin, Z. Bian, C. Kang, Y. Chen, J. Xu, L. Gao, *Chem. Eur. J.* **2012**, *18*, 13168; e) B. Wu, J. C. Gallucci, J. R. Parquette, T. V. RajanBabu, *Chem. Sci.* **2014**, *5*, 1102; f) Y. Deng, C. V. Karunaratne, E. Csatary, D. L. Tienrney, K. Wheeler, H. Wang, *J. Org. Chem.* **2015**, *80*, 7984; g) N. Kumagai, M. Kanai, H. Sasai, *ACS Catal.* **2016**, *6*, 4699. h) J. T. Fleming, P. G. Waddell, M. R. Probert, W. Clegg, L. J. Higham, *Eur. J. Inorg. Chem.* **2017**, 2837; i) K.-Y. Cheng, S.-C. Wang, Y.-S. Chen, Y.-T. Chan, *Inorg. Chem.* **2018**, *57*, 3559; j) T. Arai, K. Sato, A. Nakamura, H. Makino, H. Masu, *Sci. Rep.* **2018**, *8*, 837.

[10] a) H.-B. Yu, Q.-S. Hu, L. Pu, *J. Am. Chem. Soc.* **2000**, *122*, 6500; b) L. Ma, R.-Z. Jin, G.-H. Lü, Z. Bian, M.-X. Ding, L.-X. Gao, *Synthesis* **2007**, 2461.

[11] D. Jozic, G. Bourenkow, H. Bartunik, H. Scholze, V. Dive, B. Henrich, R. Huber, W. Bode, K. Maskos, *Structure* **2002**, *10*, 1097.

[12] G. Gotthard, J. Hiblot, D. Gonzalez, M. Elias, E. Chabriere, *PLoS One* **2013**, *8*, e77995.

[13] For selected papers, see: a) T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda, J. Hasegawa, *J. Am. Chen. Soc.* **2014**, *136*, 15270; b) C. Maeda, T. Taniguchi, K. Ogawa, T. Ema, *Angew. Chem. Int. Ed.* **2015**, *54*, 134; *Angew. Chem.* **2015**, *127*, 136; c) C. Maeda, J. Shimonishi, R. Miyazaki, J. Hasegawa, T. Ema, *Chem. Eur. J.* **2016**, *22*, 6556; d) T. Ema, M. Yokoyama, S. Watanabe, S. Sasaki, H. Ota, K. Takaishi, *Org. Lett.* **2017**, *19*, 4070; e) K. Takaishi, T. Okuyama, S. Kadosaki, M. Uchiyama, T. Ema, *Org. Lett.* **2019**, *21*, 1397.

[14] For macrocyclic multinuclear Zn complexes as epoxide/CO_2 copolymerization catalysts, see: a) H. Nagae, R. Aoki, S. Akutagawa, J. Kleemann, R. Tagawa, T. Schindler, G. Choi, T. P. Spaniol, H. Tsurugi, J. Okuda, K. Mashima, *Angew. Chem. Int. Ed.* **2018**, *57*, 2492; *Angew. Chem.* **2018**, *130*, 2518; b) J. A. Garden, P. K. Saini, C. K. Williams, *J. Am. Chem. Soc.* **2015**, *137*, 15078.

[15] T. Ema, K. Fukuhara, T. Sakai, M. Ohbo, F.-Q. Bai, J. Hasegawa, *Catal. Sci. Technol.* **2015**, *5*, 2314.

[16] Zn complex **2** did not promote the kinetic resolution (*s* value = 1.0).

[17] For the hydrosilylation of CO_2 with zinc hydride complexes, see: a) A. Rit, A. Zanardi, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2014**, *53*, 13273; *Angew. Chem.* **2014**, *126*, 13489; b) M. Rauch, G. Parkin, *J. Am. Chem. Soc.* **2017**, *139*, 18162; c) M. Tüchler, L. Gärtner, S. Fischer, A. D. Boese, F. Belaj, N. C. Mösch-Zanetti, *Angew. Chem. Int. Ed.* **2018**, *57*, 6906; *Angew. Chem.* **2018**, *130*, 7022.

[18] DFT calculations were performed using Gaussian16, revision A.03. Frisch, M. J. et al., Gaussian, Inc., Wallingford, CT, 2016.

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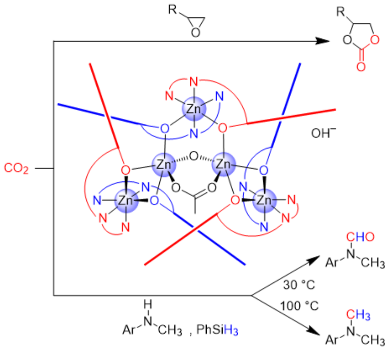

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