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Zirconocene Complexes as Catalysts for the Cycloaddition of CO_2 to Propylene Oxide

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Dedicated to Professor Youngkyu Do on the occasion of his honorable retirement from KAIST

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Six zirconocene derivatives were systematically designed; one of the cyclopentadienyl (Cp) ligands of zirconocene dichloride $[Cp_2ZrCl_2]$ was silylated and this group was then incrementally increased in size; furthermore, one derivative with a 4,4'-disilylbiphenyl bridge between the two zirconocene fragments was prepared. One zirconium complex was characterized by single-crystal X-ray analysis. All zirconium complexes were effective catalysts for the cycloaddition

Introduction

Cyclic carbonates, valuable intermediates that can be prepared from the cycloaddition of CO₂ with epoxides, can be prepared through one of the most promising reactions for CO₂ consumption.^[1–4] They are widely used in a variety of applications, including as polar aprotic solvents,^[5] electrolytes for Li-ion batteries,^[6] and synthetic precursors for producing fine chemicals^[7] and polymers.^[8] Numerous homogeneous organometallic catalytic systems, including those with Zn,^[9] Al,^[10] Cr,^[11] Co,^[12] Ni,^[13] and Cu,^[14] have

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of CO_2 to propylene oxide. Two complexes containing a biphenyl group attached to a $SiMe_2$ group showed higher activity than the other complexes. In addition, the dinuclear complex containing the biphenylenebis(dimethylsilyl) bridge showed the highest activity among all the zirconium complexes reported. Furthermore, these complexes are the first examples of zirconocene catalytic systems for the cycloaddition reaction of CO_2 to propylene oxide.

been reported for the synthesis of cyclic carbonates through cycloaddition reactions of various epoxides with CO_2 .^[1–4] Although various metal complexes with salen-type ligands are known to be efficient catalysts for the cycloaddition of CO_2 to epoxides, homogeneous and heterogeneous catalytic systems based on group 4 metal complexes have been rarely investigated.^[15]

Our group previously reported a novel Ti catalytic system containing tetrazoyl ligands with a high catalytic activity (turnover frequency, TOF = 422 h⁻¹) at 75 °C.^[16] In an effort to develop group 4 metal catalytic systems, we focused on Zr complexes for the cycloaddition of CO₂ to epoxides. To the best of our knowledge, zirconocene complexes have never been used as catalysts for cyclic carbonates, though zirconium phosphate^[17] has been used with an ionic liquid and zirconium BINOL (1,1'-bi-2-naphthol) complexes^[18] have been used enantioselectively with other epoxides.

In this regard, we chose $[Cp_2ZrCl_2]$ (Cp = cyclopentadienyl) as a parent compound for the cycloaddition reaction. Generally, silyl-substituted zirconocene complexes can produce polyethylene with a high molecular weight,^[19a] and biphenylene-bridged dinuclear zirconocene compounds have displayed higher catalytic activity for olefin polymerization than their mononuclear counterparts.^[19b,19c] Despite their synergistically enhanced activities, low solubilities of dinuclear complexes in organic solvents and low yields for the final ligands such as biphenylene-bridged bis(cyclopen-

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tadienyl) ligands have been reported. In this regard, we developed new biphenylenebis(dimethylsilyl)-bridged dinuclear complex **6** in high yield with good solubility. As shown in Scheme 1, five other compounds, including [Cp₂ZrCl₂] (1), [Cp(CpSiMe₃)ZrCl₂] (2), [Cp(CpSiMe₂tBu)ZrCl₂] (3), [Cp(CpSiMe₂Ph)ZrCl₂] (4), and [Cp(CpSiMe₂C₆H₄C₆H₅)-ZrCl₂] (5), were systematically prepared through controlled syntheses; all of these compounds resemble complex **6** in part. Herein, we report the synthesis and characterization of these zirconium complexes and their use as catalysts for producing cyclic carbonates.



Scheme 1.

Results and Discussion

Synthesis and Characterization

The ligands $ClSiMe_2C_{12}H_9$ (5L) and $[ClSiMe_2C_6H_4]_2$ (6L) were prepared from the reaction of the lithium salt of 4-bromobiphenyl with Me₂SiCl₂ (3 equiv.) in Et₂O and the reaction of the dilithium salt of 4,4'-dibromobiphenyl with Me₂SiCl₂ (6.2 equiv.) in THF, respectively. Ligands 5L and 6L were readily converted into the corresponding CpSiMe₂C₁₂H₉ and [CpSiMe₂C₆H₄]₂ derivatives by treatment with 1.1 equiv. and 2.2 equiv. of NaCp, respectively, in THF. Zirconium compounds 5 and 6 were obtained in good yields (77% for 5 and 61% for 6) in THF, as shown in Scheme 2. Compounds 5 and 6 were synthesized by the reaction of the lithium salt derived from CpSiMe₂C₁₂H₉ with [CpZrCl₃] (0.95 equiv.) and the reaction of the dilithium salt derived from [CpSiMe2C6H4]2 with [CpZrCl3] (1.9 equiv.), respectively, in THF. Compounds 5 and 6 were not stable in air and were insoluble in hexanes, but they were soluble in toluene and polar organic solvents.

The ¹H NMR and ¹³C{¹H} NMR spectra of **5** and **6** were in accord with the suggested structures, and all chemical shifts of the protons and carbon atoms were in the expected range. The spectra of ligands **5L** and **6L** and zirconium compounds **5** and **6** were measured in CDCl₃. The ¹H NMR spectra of **5L** and **6L** exhibit singlets at $\delta = 0.74$ and 0.72 ppm, which correspond to the Si(*Me*)₂ group; multiple peaks at $\delta = 7.36-7.74$ ppm; and doublets at $\delta = 7.65$



Scheme 2. Synthetic route for compounds 5 and 6.

and 7.73 ppm, which correspond to the aryl moieties. In contrast to **5L**, zirconium compound **5** exhibits patterns containing a singlet corresponding to the Zr*Cp* protons at $\delta = 6.28$ ppm and two triplets corresponding to the Si*Cp* protons at $\delta = 6.55$ (J = 2.52 Hz) and 6.75 ppm (J = 2.52 Hz). Moreover, the singlet corresponding to the CpSi(Me)₂ methyl protons is shifted upfield relative to that of **5L**. These features are also evident for compound **6**.

The molecular structure of **5** was determined by singlecrystal X-ray diffraction analysis. Single crystals suitable for X-ray structural analysis were obtained by cooling a solution of saturated CH_2Cl_2/Et_2O to -20 °C. The structural parameters around the zirconium center, including selected bond lengths and bond angles, are listed in the caption of Figure 1.



Figure 1. The crystal structure of **5** and atom labeling. All H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr–Cl1 2.4385(8), Zr–Cl2 2.4384(9), Zr–Cp_{cent} 2.1985(12), Zr–Cp'_{cent} 2.2029(19), Zr–C1 2.519(3), Zr–C2 2.523(2), Zr–C3 2.510(3), Zr–C4 2.472(3), Zr–C5 2.486(3), Zr–C6 2.471(3), Zr–C7 2.484(3), Zr–C8 2.505(3), Zr–C9 2.513(3), Zr–C10 2.505(4), Cl1–Zr–Cl2 95.92(4), Cp_{cent}–Zr–Cp'_{cent} 130.82(8), Cp_{cent}–Zr–Cl1 105.86(4), Cp_{cent}–Zr–Cl2 106.40(4), Cp'_{cent}–Zr–Cl1 107.74(7), Cp'_{cent}–Zr–Cl2 104.69(8), C1–Si–C11 111.96(12), C1–Si–C23 109.87(14), C1–Si–C24 104.71(14).

Zirconium complex 5 crystallizes in the $P2_1/c$ space group. The molecular structure of 5 confirms that the zirco-



nium center is η^5 bonded to both Cp rings, symmetric with the Cp ring and asymmetric with respect to the C5H4Si-Me₂C₁₂H₉ ring (Cp'). In addition, the Cl atoms and the centroids of the Cp ring form a considerably distorted pseudotetrahedral coordination geometry around the zirconium center with angles ranging from 95.92 (Cl1-Zr-Cl2) to 130.82° (Cp_{cent}-Zr-Cp'_{cent}). The biphenyl group is significantly bent with a bond angle of 111.96° (C1-Si-C11) with respect to the Cp' ring, which is somewhat larger than that observed in similar zirconium complexes, for example, $[(C_5H_4SiMe_2Ph)CpZrMe_2], 108.65^{\circ};^{[20]} [(C_5H_4CMe_2tol) CpZrMe_2$], 106.50°;^[21] and [($C_5H_4SiMePh_2$)CpZrCl₂], 104.1, 104.5, 107.4, and 110.0°.[22] The biphenyl group is nearly planar and shows no apparent distortion between the two phenylene planes, despite the possible presence of nonbonded repulsion between the ortho hydrogen atoms. The overall molecular symmetry of 5 approaches a C_1 point group. The bond length data show that the Cp rings form with largely uniform $Zr-C_{Cp}$ distances that average 2.499 Å with a small standard deviation of 0.003 Å; this indicates that both the Cp and Cp' rings were bonded to the Zr atom in the usual η^5 fashion. The bond lengths of Zr–Cp_{cent} and Zr-Cp'_{cent} are 2.1985 and 2.2029 Å, respectively. The Cp_{cent}-Zr-Cp'_{cent} (130.82°) and Cl1-Zr-Cl2 angles (95.92°) are in good agreement with those of other zirconocene complexes.[20]

Cycloaddition of CO₂

The cycloaddition reaction of CO_2 with propylene oxide (PO) was performed at 75 °C for 7 h without solvent by using zirconium compounds 1-6 as catalysts. The cycloaddition results are summarized in Table 1. Under our conditions of 75 °C for 7 h, additives such as tetrabutylphosphonium bromide (*n*Bu₄PBr), tetrabutylammonium chloride (nBu₄NCl), tetrabutylammonium bromide (nBu₄NBr), tetrabutylammonium iodide (nBu₄NI), bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), and 4-dimethylaminopyridine (DMAP) did not show any catalytic activity (Table 1, entries 1-6). Catalysts 1-6 in the absence of any cocatalyst also did not show any activity (Table 1, entry 7). However, in the presence of nBu_4PBr as a cocatalyst, zirconium compounds 1–6 behaved as catalysts for the cycloaddition of CO_2 to PO, and the cyclic carbonates were produced with high selectivity (>99%; Table 1, entries 8-13). Compounds 1–6 produced cyclic carbonates efficiently with conversion yields of 64-92% and with high selectivities of >99% without any polymerized products. Interestingly, the overall catalytic activity gradually increased upon going from catalyst 1 to catalyst 6. Consequently, the catalytic activities of 1-6 increase as the substituents on the Cp ring increase in steric bulkiness. Thus, catalyst 6 showed the highest activity among the reported Zr compounds (Table 1, entry 13; TON = 462), though there seems to be no notable difference in the activity of monomeric 5 relative to that of dimeric 6. These similar catalytic activities of these two catalysts were also shown in the polymerization

of ethylene by using zirconocene containing a biphenyl group,^[18] despite different reaction mechanistic pathways,^[19b] More interestingly, these zirconium complexes are more efficient catalysts than the reported titanium systems with respect to conversion.^[16]

Table 1. Cycloaddition of CO₂ to PO by using complexes 1-6.^[a]

Entry	Catalyst	Cocatalyst ^[b]	TON ^[c]	Conv. [%] ^[d]	Selectivity [%] ^[d]
1	none	<i>n</i> Bu₄PBr	0	0	_
2	none	nBu ₄ NCl	0	0	_
3	none	<i>n</i> Bu ₄ NBr	0	0	_
4	none	<i>n</i> Bu ₄ NI	0	0	_
5	none	PPNC1	0	0	_
6	none	DMAP	0	0	_
7	1–6	none	0	0	_
8	1	<i>n</i> Bu ₄ PBr	319	64	>99
9	2	<i>n</i> Bu ₄ PBr	357	71	>99
10	3	nBu ₄ PBr	371	74	>99
11	4	<i>n</i> Bu ₄ PBr	408	82	>99
12	5	<i>n</i> Bu ₄ PBr	449	90	>99
13	6	<i>n</i> Bu ₄ PBr	462	92	>99
14	1	<i>n</i> Bu ₄ NCl	220	44	>99
15	1	<i>n</i> Bu ₄ NBr	264	53	>99
16	1	<i>n</i> Bu ₄ NI	253	51	>99
17	1	<i>n</i> Bu ₄ PBr	319	64	>99
18	1	PPNC1	176	35	>99
19	1	DMAP	60	12	>99
20	5	<i>n</i> Bu ₄ NCl	318	64	>99
21	5	<i>n</i> Bu ₄ NBr	392	78	>99
22	5	<i>n</i> Bu ₄ NI	364	73	>99
23	5	<i>n</i> Bu ₄ PBr	449	90	>99
24	5	PPNC1	439	88	>99
25	5	DMAP	120	24	>99
26	6	<i>n</i> Bu ₄ NCl	330	66	>99
27	6	<i>n</i> Bu ₄ NBr	402	81	>99
28	6	nBu_4NI	370	74	>99
29	6	<i>n</i> Bu ₄ PBr	462	92	>99
30	6	PPNC1	452	90	>99
31	6	DMAP	126	25	>99

[a] Cycloaddition conditions: [PO] = 0.7 mL (10 mmol), [Zr] = 20 μ mol, [cocatalyst] = 20 μ mol, [PO]/[Zr] = 500, CO₂ = 1.0 MPa, $T_{\rm p} = 75$ °C, time = 7 h. [b] PPNCl = bis(triphenylphosphoranylidene)ammonium chloride, DMAP = 4-dimethylaminopyridine. [c] Turnover number (TON) = (mol of PO consumed)/(mol of Zr center). [d] Calculated by ¹H NMR spectral integration.

Further studies to determine the effect of the cocatalyst on the catalytic activity were performed by using catalysts 1, 5, and 6 in the cycloaddition reaction (Table 1, entries 14–31). Six different kinds of cocatalysts including *n*Bu₄PBr, *n*Bu₄NCl, *n*Bu₄NBr, *n*Bu₄NI, PPNCl, and DMAP were used. As shown in Table 1 (entries 17, 23, and 29), nBu_4PBr showed superior activity to the five other catalysts. Moreover, catalysts 1, 5, and 6 with the non-salttype cocatalyst DMAP showed lower activity than the other cocatalysts (Table 1, entries 19, 25, and 31) because of a strong interaction of neutral DMAP with the Lewis acidic metal center.^[11,23] These features are very similar to those of the aluminum complexes previously reported.^[24] Although they usually show different catalytic activities in cycloaddition reactions of CO₂ to epoxides according to the catalysts and cocatalysts,^[25] our zirconocene catalytic systems showed the highest activities in the presence of

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Figure 2. A plausible mechanism for the cycloaddition of CO_2 to epoxides by using a zirconocene catalyst.

 nBu_4PBr as a cocatalyst. More interestingly, nBu_4PBr is the cheapest among the six commercially available cocatalysts tested. All zirconium complexes showed the highest activity in the presence of nBu_4PBr . In addition, complexes **5** and **6**, which contain a biphenyl group attached to the SiMe₂ group, exhibited higher catalytic activities than the other complexes.

As shown in Figure 2, a plausible mechanism for the cycloaddition of CO_2 to epoxides by using zirconocene complexes involves attachment of the epoxide to the zirconium atom of the zirconocene compound; resulting complex I is activated toward nucleophilic attack by halide ions such as CI^- , Br^- , and I^- . It is possible that coordination of an epoxide to a Lewis acid center promotes nucleophilic ring opening of the epoxide. Carbonato species II is converted by insertion of CO_2 into coordinated zirconocene complex III. Finally, the cyclic carbonate product is formed by ring-closing of III. The proposed mechanism is similar to the cycloaddition reaction of CO_2 with epoxides with other catalyst systems.^[26]

Conclusions

Zirconium catalysts bearing silyl-substituted Cp ligands were easily prepared and their catalytic behavior in the cycloaddition of CO_2 to propylene oxide was investigated. Zirconium complex **6** showed the highest activity among the reported Zr catalysts. To the best of our knowledge, this is the first example of the zirconocene-catalyzed synthesis of cyclic carbonates through cycloaddition of CO_2 to propylene oxide.

Experimental Section

General Considerations: All reactions of air- and moisture-sensitive materials were performed under an atmosphere of dinitrogen by using standard Schlenk-type glassware with a dual manifold Schlenk line in a glove box.^[27] Dinitrogen was deoxygenated by using an activated Cu catalyst and was dried with drierite.^[28] [CpZrCl₃] was purchased from Strem, and all other chemicals were obtained from Aldrich and were used without further purification. All solvents, toluene, diethyl ether, THF, and *n*-hexane, were dried by distillation from sodium diphenylketyl under an atmosphere of nitrogen and were stored over 3 Å activated molecular sieves. CDCl₃ was dried with activated molecular sieves (4 Å) and was used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

Measurements: ¹H NMR and ¹³C{¹H} NMR spectra were recorded at ambient temperature with a 300 or 400 MHz NMR spectrometer by using standard parameters. All chemical shifts are reported in δ units with reference to the signals of residual CDCl₃ (δ = 7.24 ppm, ¹H NMR; δ = 77.0 ppm, ¹³C{¹H} NMR). Elemental analyses were performed by using an EA 1110-FISONS analyzer (CE Instruments).

Synthesis of 2–4: Complexes **2–4** were prepared according to previously published procedures.^[22]

CISiMe₂C₁₂H₉ (5L): *n*BuLi (2.5 M in hexane, 8.8 mL, 22 mmol) was slowly added by syringe to a solution of 4-bromobiphenyl (2.3 g, 10 mmol) in Et₂O (30 mL) at -78 °C. The mixture was warmed to room temperature. After stirring for 3 h, Me₂SiCl₂ (3.6 mL, 30 mmol) was slowly added by syringe at -78 °C. The mixture was then warmed to room temperature and stirred for 15 h. All of the volatiles were evaporated under vacuum, which left a colorless sticky powder to which *n*-hexane (30 mL) was added. The solution was filtered, and the solvent was evaporated to afford product **5L** as a colorless powder (99%, 2.5 g). ¹H NMR (400.13 MHz, CDCl₃): δ = 7.74 (d, *J* = 1.72 Hz, 2 H, Ar*H*), 7.60 (m, 4 H, Ar*H*),



7.45 (m, 2 H, Ar*H*), 7.36 (m, 1 H, Ar*H*), 0.74 [s, 6 H, Si(C*H*₃)₂] ppm. ¹³C{¹H} NMR (100.63 MHz, CDCl₃): δ = 143.14, 140.67, 134.84, 133.61, 128.83, 127.68, 127.19, 126.82 (Ar), 2.13 [Si-(CH₃)₂] ppm.

[CpZrCl₂(CpSiMe₂C₁₂H₉)] (5): A solution of NaCp (2.0 M in THF, 1.4 mL, 2.8 mmol) was slowly added by syringe to a solution of 5L (0.63 g, 2.6 mmol) in THF (20 mL) at -78 °C. The mixture was then warmed to room temperature and stirred for 15 h. The reaction was stopped by the addition of water (50 mL), and the organic portion was separated. The aqueous layer was extracted with diethyl ether $(3 \times 20 \text{ mL})$, and the combined organic phase was dried with MgSO₄, filtered, and concentrated. Removal of the volatile compounds under reduced pressure gave CpSiMe₂C₁₂H₉ (99%, 0.70 g) as a light yellow sticky oil. Obtained CpSiMe₂C₁₂H₉ was redissolved in Et₂O (20 mL) and cooled to -78 °C. nBuLi (2.5 M in hexane, 1.1 mL, 2.6 mmol) was slowly added to the reaction vessel. The mixture was warmed to room temperature and stirred for 5 h. Removal of all volatiles under reduced pressure gave a light ivory powder, which was mixed with [CpZrCl₃] (0.22 g, 0.84 mmol) in THF (30 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 15 h. Removal of all the volatiles under reduced pressure and recrystallization (n-hexane and CH₂Cl₂, 5:1 v/v) gave product 5 as a light ivory powder (77%, 0.33 g). 1 H NMR (400.13 MHz, CDCl₃): δ = 7.57 (m, 6 H, ArH), 7.41 (m, 2 H, ArH), 7.34 (m, 1 H, ArH), 6.75 (t, J = 2.52 Hz, 2 H, SiCp), 6.55 (t, J = 2.52 Hz, 2 H, SiCp), 6.28 (s, 5 H, Zr–Cp), 0.63 [s, 6 H, Si(CH₃)₂] ppm. ¹³C{¹H} NMR (100.63 MHz, CDCl₃): δ = 142.23, 140.71, 136.39, 134.55, 128.80, 127.55, 127.10, 126.65, 125.27, 123.83, 118.07, 116.05 (Ar, Cp), -1.75 [Si(CH₃)₂] ppm. C₂₄H₂₄Cl₂SiZr (502.6633): calcd. C 57.35, H 4.81; found C 58.47, H 4.93.

[CISiMe₂C₆H₄]₂ (6L): *n*BuLi (2.5 M in hexane, 28 mL, 70 mmol) was slowly added by syringe to a solution of 4,4'-dibromobiphenyl (5.0 g, 16 mmol) in Et₂O (50 mL) at 0 °C. The mixture was warmed to room temperature. After stirring for 5 h, all volatiles were removed under vacuum, and then THF (50 mL) was added. Me₂SiCl₂ (12 mL, 99 mmol) was slowly added by syringe to the solution containing the dilithium salt at -78 °C. The mixture was warmed to room temperature and stirred for 15 h. Removal of all the volatiles under vacuum and recrystallization (*n*-hexane, 30 mL) gave product **6L** as a colorless powder (74%, 4.0 g). ¹H NMR (300.13 MHz, CDCl₃): δ = 7.73 (d, *J* = 8.12 Hz, 4 H, Ar*H*), 7.65 (d, *J* = 7.55 Hz, 4 H, Ar*H*), 0.72 [s, 12 H, Si(CH₃)₂] ppm. ¹³C{¹H} NMR (75.47 MHz, CDCl₃): δ = 142.6, 135.42, 133.81, 126.87 (Ar), 2.12 [Si(CH₃)₂] ppm.

 $[CpZrCl_{2}{CpSiMe_{2}C_{6}H_{4}}]_{2}$ (6): NaCp (2.0 m in THF, 2.4 mL, 4.8 mmol) was slowly added by syringe to a solution of 6L (0.73 g, 2.2 mmol) in THF (30 mL) at -78 °C. The mixture was then warmed to room temperature and stirred for 15 h. The reaction was stopped by the addition of water (50 mL), and the organic portion was separated. The aqueous layer was extracted with diethyl ether $(3 \times 30 \text{ mL})$, and the combined organic phase was dried with MgSO₄, filtered, and concentrated. All of the volatiles were evaporated under vacuum, which left a yellow sticky oil of [CpSiMe₂C₆H₄]₂ (80%, 0.69 g). Obtained [CpSiMe₂C₆H₄]₂ was dissolved in Et₂O (30 mL), and *n*BuLi (2.5 M in hexane, 1.5 mL, 3.6 mmol, 2.1 equiv.) was slowly added by syringe to a solution of $[CpSiMe_2C_6H_4]_2$ at –78 °C. The mixture was then warmed to room temperature, stirred for 5 h, and washed with *n*-hexane $(3 \times$ 20 mL). All of the volatiles were evaporated under vacuum, which left a colorless powder (0.55 g, 1.4 mmol), to which [CpZrCl₃] (0.67 g, 2.6 mmol, 1.9 equiv.) was added in a dry box. Then, THF

(50 mL) was added by cannula at -78 °C. The mixture was then warmed to room temperature and stirred for 15 h. All volatiles were evaporated under vacuum, which left a light brown powder. Recrystallization (*n*-hexane and CH₂Cl₂, 5:1 v/v) gave product **6** as a light brown powder (0.72 g, 61%). ¹H NMR (300.13 MHz, CDCl₃): $\delta = 7.59$ (s, 8 H, Ar*H*), 6.75 (t, J = 2.47 Hz, 5 H, Si*Cp*), 6.56 (t, J = 2.42 Hz, 5 H, Si*Cp*), 6.28 (s, 8 H, Zr–*Cp*), 0.62 [s, 12 H, Si(CH₃)₂] ppm. ¹³C{¹H} NMR (75.47 MHz, CDCl₃): $\delta = 134.58$, 134.04, 126.61, 125.27, 119.97, 118.06, 116.06, 115.98 (Ar, Cp), -1.74 [Si(CH₃)₂] ppm. C₃₆H₃₈Cl₄Si₂Zr₂ (851.1179): calcd. C 50.80, H 4.50; found C 50.97, H 4.71.

X-ray Structural Determination for 5: Crystallographic measurements of complex **5** were performed at 296(2) K by using a Bruker APEX II diffractometer with Mo- K_{α} ($\lambda = 0.71073$ Å) radiation. Specimens of suitable quality and size ($0.1 \times 0.1 \times 0.1 \text{ mm}^3$) were selected, mounted, and centered in the X-ray beam by using a video camera. The structure was solved by direct methods and refined by full-matrix least-squares methods by using the SHELXTL^[29] program package with anisotropic thermal parameters for all non-hydrogen atoms. Final refinement based on the reflections [$I > 2 \cdot \sigma(I)$] converged at $R_1 = 0.0464$, $wR_2 = 0.1126$, and GOF = 1.008 for **5**.

CCDC-1013633 (for 5) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cycloaddition of CO₂ to Propylene Oxide: The cycloaddition reaction of CO₂ to propylene oxide (10 mmol) was performed in a 15 mL stainless-steel autoclave equipped with a stirring bar, propylene oxide, zirconium catalyst (20 μ mol), and cocatalyst (20 μ mol) in a glove box. The autoclave was sealed prior to removal from the glove box. The autoclave was initially operated at a pressure of 1.0 MPa CO₂ and then heated to 75 °C for 7 h. After the reactor was cooled and vented, a small sample of the mixture was taken for analysis by ¹H NMR spectroscopy.

Supporting Information (see footnote on the first page of this article): ¹H NMR and ¹³C NMR spectra for **2–6** and details of the X-ray structure of **5**.

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- A. Decortes, A. M. Castilla, A. W. Kleij, Angew. Chem. Int. Ed. 2010, 49, 9822–9837; Angew. Chem. 2010, 122, 10016–10032.
- [2] M. North, R. Pasquale, C. Young, Green Chem. 2010, 12, 1514–1539.
- [3] T. Sakakura, J.-C. Choi, H. Yasuda, Chem. Rev. 2007, 107, 2365–2387.
- [4] S. Kumar, S. L. Jain, B. Sain, Chem. Lett. 2012, 142, 615-618.
- [5] a) B. Schäffner, F. Schäffner, S. P. Verevkin, A. Börner, *Chem. Rev.* 2010, *110*, 4554–4581; b) M. North, P. Villuendas, *Org. Lett.* 2010, *12*, 2378–2381; c) W. Clegg, R. W. Harrington, M. North, F. Pizzato, P. Villuendas, *Tetrahedron: Asymmetry* 2010, *21*, 1262–1271; d) M. North, F. Pizzato, P. Villuendas, *Chem-SusChem* 2009, *2*, 862–865.
- [6] a) V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* 2011, 4, 3243–3262; b) K. Xu, *Chem. Rev.* 2004, 104, 4303–4418.



- [7] J. H. Clements, Ind. Eng. Chem. Res. 2003, 42, 663–674.
- [8] a) R. Zevenhoven, S. Eloneva, S. Teir, *Catal. Today* 2006, 115, 73–79; b) S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, *Green Chem.* 2003, 5, 497–507.
- [9] H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang, S. O. Kang, Angew. Chem. Int. Ed. 2000, 39, 4096–4098; Angew. Chem. 2000, 112, 4262–4264.
- [10] J. Meléndez, M. North, P. Villuendas, Chem. Commun. 2009, 2577–2579.
- [11] D. J. Darensbourg, Chem. Rev. 2007, 107, 2388-2410.
- [12] X.-B. Lu, D. J. Darensbourg, Chem. Soc. Rev. 2012, 41, 1462– 1484.
- [13] F. Li, C. Xia, L. Xu, W. Sun, G. Chen, Chem. Commun. 2003, 4, 2042–2043.
- [14] M. Ulusoy, O. Şahin, A. Kilic, O. Büyükgüngör, *Catal. Lett.* 2011, 141, 717–725.
- [15] D. Bai, H. Jing, Q. Liu, Q. Zhu, X. Zhao, Catal. Commun. 2009, 11, 155–157.
- [16] M. J. Go, K. M. Lee, C. H. Oh, Y. Y. Kang, S. H. Kim, H. R. Park, Y. Kim, J. Lee, *Organometallics* 2013, 32, 4452–4455.
- [17] H. Hu, J. C. Martin, M. Zhang, C. S. Southworth, M. Xiao, Y. Meng, L. Sun, *RSC Adv.* 2012, *2*, 3810–3815.
- [18] a) M. Brunner, L. Mußmann, D. Vogt, Synlett 1994, 69–70; b)
 M. Brunner, L. Mußmann, D. Vogt, Synlett 1993, 893–894.
- [19] a) H. G. Alt, A. Köppl, *Chem. Rev.* 2000, 100, 1205–1221; b)
 M. H. Lee, S. K. Kim, Y. Do, *Organometallics* 2005, 24, 3618–3620; c) M. Delferro, T. J. Marks, *Chem. Rev.* 2011, 111, 2450–2485.
- [20] J. Sassmannshausen, J. C. Green, F. Stelzer, J. Baumgartner, Organometallics 2006, 25, 2796–2805.

- [21] L. H. Doerrer, M. L. H. Green, D. Häussinger, J. Sassmannshausen, J. Chem. Soc., Dalton Trans. 1999, 2111– 2118.
- [22] P. A. Deck, X. Cheng, E. J. Stoebenau, C. Slebodnick, D. R. Billodeaux, F. R. Fronczek, *Organometallics* 2000, 19, 5404– 5409.
- [23] a) M. A. Fuchs, S. Staudt, C. Altesleben, O. Walter, T. A. Zevaco, E. Dinjus, *Dalton Trans.* 2014, 43, 2344–2347; b) S. Klaus, S. I. Vagin, M. W. Lehenmeier, P. Deglmann, A. K. Brym, B. Rieger, *Macromolecules* 2011, 44, 9508–9516; c) D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers, A. L. Phelps, *Inorg. Chem.* 2004, 43, 1831–1834.
- [24] S. H. Kim, D. Ahn, M. J. Go, M. H. Park, M. Kim, J. Lee, Y. Kim, Organometallics 2014, 33, 2770–2775.
- [25] a) R. L. Paddock, S. Nguyen, *Chem. Commun.* 2004, 1622– 1623; b) Y.-M. Shen, W.-L. Duan, M. Shi, *J. Org. Chem.* 2003, 68, 1559–1562.
- [26] a) Z.-Z. Yang, Y.-N. Zhao, L.-N. He, J. Gao, Z.-S. Yin, *Green Chem.* 2012, 14, 519–527; b) R. L. Paddock, S. T. Nguyen, *Chem. Commun.* 2004, 1622–1623; c) V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* 2002, 4, 2561–2563.
- [27] a) D. F. Shriver, M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley, New York, **1986**; b) G. S. Girolami, T. B. Rauchfuss, R. J. Angelici, *Synthesis and Technique in Inorganic Chemistry*, 3rd ed., University Science Books, Sausalito, CA, **1999**.
- [28] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 6th ed., Elsevier, New York, 2009.
- [29] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112–122. Received: August 16, 2014 Published Online: October 1, 2014