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NNC-Scorpionate Zirconium-Based Bicomponent Systems for the Efficient CO₂ Fixation into a Variety of Cyclic Carbonates

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ABSTRACT: Two new derivatives of the bis(3,5-dimethylpyrazol-1-yl)methane modified by introduction of organosilyl groups on the central carbon atom, one of which bearing a chiral fragment, have been easily prepared. We verified the potential utility of these compounds through the reaction with $[Zr(NMe_2)_4]$ for the preparation of novel zirconium complexes in which an ancillary bis(pyrazol-1-yl)methanide acts as a robust monoanionic tridentate scorpionate in a κ^3 -NNC chelating mode, forming strained four-membered heterometallacycles. These κ^3 -NNC-scorpionate zirconium amides were investigated as catalysts in combination with tetra-*n*-butylammonium bromide as cocatalyst for CO₂ fixation into five-membered cyclic carbonate products. The study has led to the development of an efficient zirconium-based bicomponent system for the selective cycloaddition reaction of CO₂ with epoxides. Kinetics investigations confirmed apparent first-order dependence on the catalyst and cocatalyst concentrations. In addition, this system displays very broad substrate scope, including mono- and disubstituted substrates, as



well as the challenging biorenewable terpene derived limonene oxide, under mild and solvent-free conditions.

INTRODUCTION

Over the past two decades, our research group has pioneered the modification of the bis(pyrazol-1-yl)methane (bpzm) molecule through the bridging carbon atom, by adding organic functional groups to form heteroscorpionate ligands.¹ This procedure has allowed us to design a wide variety of novel achiral, chiral, and enantiopure NNO,^{2a} NNS,^{2b} NNN,^{2c} and NNCp^{2d} κ^3 -scorpionate ligands to prepare very efficient catalysts for different processes including cyclic carbonates.³ However, the κ^3 -NNC(sp³) coordination mode based on the bis(pyrazol-1-yl)methane platform is little known, and only three examples have been reported in the literature. For instance, our research group communicated a bimetallic acetamide neodymium complex that contains a bridging dianionic bpzm-based heteroscorpionate in this coordination mode, which was produced through deprotonation of the RN-H moiety and C-H activation of the bridging methylene group.⁴ Additionally, tungsten-based compounds bearing a bpzm in this coordination fashion, obtained by migration of a SnAr₃ fragment to the metal, were also communicated.⁵ More recently, an amide-derivative calcium compound containing the bpzm in this tridentate mode has been also reported.⁶

On the other hand, over the past few years our research group has been intensively working on the valorization of CO_2 as an attractive C-1 renewable building block⁷ since this unsaturated molecule presents a widespread availability in nature, low cost, nonhazardous features, lack of color, and redox activity. In this sense, several chemical applications are

possible for this low reactive molecule, such as the production of cyclic carbonates $(CC's)^8$ or polycarbonates $(PC's)^9$ by cycloaddition or ring-opening copolymerization (ROCOP) of CO_2 with epoxides, respectively. Of particular interest is the 100% atom-economical synthesis of cyclic carbonates (see Chart 1), as these organic molecules find numerous application in industry such as polar aprotic solvents, high boiling solvents, intermediates in organic synthesis, electrolytes, fuel additives, and as sustainable reagents.¹⁰



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2⊕ ,2 I[⊝] $R = O(CH_2)_6 N^+ Bu_3 Br$ II-Co(TCA) III-Fe(CNN) IV-Mg(porphyrin) I-Cr(salophen) Br, Et₂HN NHEt_{2,} Br OⁱPr ⁱPi OPr . OⁱPr HC 'nн НÓ V-Zn(salen) VI-Al₂ C₂-symmetric VII-Zr(salen) Time Conv TOF [Cat]:[Co-cat] Temp. Press. Cat Ref [mol%] [°C] [bar] [%] [h⁻¹] [h] I-Cr 2.5:2.5 25 3 37 5.9 11b 1 0.1:0.1^(TBAC) II-Co 8 100 120 1 125 12a 5 III-Fe 25 24 10.9 0.3:3.0 76 13c IV-Mg 0.005 120 9 93 2.067 14c 15 0.5(DMF as solvent) V-Zn 90 75 120 1 12 15b 25 24 VI-Al 1.0:1.0 1 99 4.1 16a 91 VII-Zr 0.1:0.1 80 35 8 114 18a

Chart 2. Representative Bicomponent Complex/TBAB Systems Very Active for the Synthesis of Styrene Carbonate under Solvent-Free Conditions

In this context, very active metal-based catalysts have been reported, with chromium,¹¹ cobalt,¹² iron,¹³ magnesium,¹⁴ zinc,^{14a,15} or aluminum,^{3,16} as leading metals in this field (see Chart 2). However, a few examples of efficient group 4 based systems¹⁷ have been successfully developed for the selective cycloaddition of CO₂ to epoxides for cyclic carbonates production, and particularly, the employment of zirconium-based catalysts still remains poorly explored¹⁸ in this process, focused exclusively on propylene^{18a,c,d} and styrene^{18a,c} oxide conversions at relatively demanding reaction conditions (see Chart 2). Alternatively, efficient metal–coordination frameworks containing this metal are currently appearing,^{18e,f} however, these species present very limited channel accessibility to bulkier epoxides, decreasing the range of applicability.

Now, we take the stimulating challenge of designing more efficient and selective zirconium-based catalysts containing κ^3 -NNC(*sp*³) scorpionates built on the bis(pyrazol-1-yl)methane ancillary platform, and explore their catalytic behavior in the coupling reaction of CO₂ and epoxides, with a much wider substrate scope.

We report hereby the preparation of novel zirconium complexes supported by a strained organosilyl-derived bis(3,5-dimethylpyrazol-1-yl)methanide in a κ^3 -NNC coordination fashion as the first zirconium-based catalysts for the cyclo-

addition of $\rm CO_2$ to epoxides, which display very broad substrate scope, including terminal, internal, biobased, and a very challenging biorenewable derivative under mild and solvent-free conditions.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Starting Materials and Complexes. The modification of the bis(3,5-dimethylpyrazol-1-yl)methane molecule by organosilyl groups on the central carbon atom was carried out by reaction of lithium bis(3,5-dimethylpyrazol-1-yl)methanide, prepared in situ from "BuLi and bis(3,5-dimethylpyrazol-1-yl)methane at -70 °C, with the corresponding organosilyl chloride to afford the starting materials bpzsimeH (1),¹⁹ bpzsialiH (2), and bpzsinbH (3) (see Scheme 1a). It should be noted that the use of 2-(5-norbornen-2-yl)ethylchlorodimethylsilane allowed us to introduce an organosilyl chiral group in the bridging carbon atom in the case of 3. The soft treatment of the ligands 1-3with $Zr(NMe_2)_4$ in a 1:1 molar ratio in toluene gave the complexes $[Zr(NMe_2)_3(\kappa^3-NNC)]$ (4–6), through the C–H activation of the bridging methane group in the ligand, as a consequence of the silvl group placed in α -position to the carbon atom C^a. These complexes were isolated as yellow pubs.acs.org/IC

Scheme 1. Synthesis of the Modified Bis(3,5dimethylpyrazol-1-yl)methane with Organosilyl Groups 1– 3, and Complexes $[Zr(NMe_2)_3(\kappa^3-NNC)]$ (4–6)



solids in very good yields after the appropriate workup (see Scheme 1b).

The different compounds were characterized spectroscopically. The ¹H NMR spectra of **1**–**3** show one singlet for each of the H⁴, Me³, Me⁵ pyrazole protons and for the bridging CH^a (e.g., Figure S1 in the Supporting Information (SI)). Furthermore, the spectra show signals corresponding to the R moieties of the scorpionate ligands. The ¹H NOESY-1D experiments enabled the unequivocal assignment of all ¹H resonances, and the assignment of the ¹³C{H} NMR signals was carried out on the basis of ¹H–¹³C heteronuclear correlation (g-HSQC) experiments.

The ¹H and ¹³C {¹H} NMR spectra of the zirconium amide complexes 4 and 5 show a singlet for the pyrazole signals H⁴, Me³, and Me⁵, two singlets corresponding to the amides (a double integral signal for two amides and a single for another amide), and finally, a singlet corresponding to the silane methyls, and the corresponding for R substituent. It should be noted that the signal of the bridging CH^a for compounds 4–6 has disappeared, as a result of the C–H activation bond, and subsequent coordination of the carbanion $C(sp^3)^a$ to the zirconium atom (e.g., Figure S2 in the SI).

On the other hand, it should be mentioned that complex **6** shows different signals for the pyrazole protons H⁴, Me³, and Me⁵, indicating that the pyrazole rings are not equivalent, as a result of the restricted rotation between the C^a carbon and the silicon atoms. In addition, **6** shows three different singlets for the amides, which means that these groups are not exchanged, and therefore, there is no equivalence between them. The results are consistent with an octahedral structure resulting from the κ^3 -NNC coordination mode of the ligand to the metal center (see Scheme 1b).

The geometry found in solution was also confirmed in the solid state by X-ray diffraction analysis of complex 4 (see Figure 1). Selected bond lengths and angles are listed in Table



Figure 1. ORTEP view of $[Zr(NMe_2)_3(bpzsime)]$ (4). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability.

1 (crystallographic details are included in Table S1 in the SI). The structure consists of a scorpionate ligand bonded to the

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 4

Distances [Å]		Angles [deg]			
Zr(1) - N(1)	2.386(1)	N(1)-Zr(1)-N(3)	79.20(5)		
Zr(1) - N(3)	2.391(1)	N(1)-Zr(1)-C(11)	56.50(5)		
Zr(1) - N(5)	2.071(2)	N(2)-C(11)-N(4)	109.53(14)		
Zr(1) - N(6)	2.069(2)	N(2)-C(11)-Si(1)	119.11(12)		
Zr(1) - N(7)	2.079(1)	N(2)-C(11)-Zr(1)	89.32(10)		
Zr(1) - C(11)	2.594(2)	N(3)-Zr(1)-C(11)	56.65(5)		
N(2)-C(11)	1.459(2)	N(4) - C(11) - Si(1)	124.08(12)		
N(4) - C(11)	1.467(2)	N(4)-C(11)-Zr(1)	88.77(10)		
Si(1) - C(11)	1.857(2)	N(5)-Zr(1)-N(7)	94.28(6)		
		N(6)-Zr(1)-N(5)	100.65(7)		
		N(6)-Zr(1)-N(7)	104.20(7)		
		Si(1)-C(11)-Zr(1)	116.39(8)		

zirconium atom through the two nitrogen atoms of the pyrazole rings and the bridging carbon atom C^a in a κ^3 -NNC coordination mode. In addition, the zirconium center is coordinated to three amide ligands. The most interesting structural feature of 4 is the highly constrained coordination mode of the scorpionate ligand resulting in the formation of two novel four-membered heterometallacycles. This coordination feature is known in metals such as neodymium,⁴ tungsten,⁵ and calcium.⁶

However, to our knowledge, complex 4 represents the first example of a κ^3 -NNC coordination mode of a bpzm-based scorpionate ligand in zirconium. The formation of these metallacycles causes the metal center to have a very distorted octahedral environment, with very small angles in the tripod that the scorpionate forms with the metal. Thus, the N(1)–Zr(1)-N(3), N(1)–Zr(1)-C(11), and N(3)–Zr(1)-C(11)

angles, which have values of $79.20(5)^{\circ}$, $56.50(5)^{\circ}$, and $56.65(5)^{\circ}$, respectively, are very far toward 90° . The Zramide distances, Zr(1)-N(6), Zr(1)-N(5), and Zr(1)-N(7)of 2.069(2) Å, 2.071(2) Å, and 2.079(1) Å, respectively, are in agreement with other zirconium amide complexes previously described in our group.²⁰

Catalytic Studies for the Cycloaddition of CO_2 to Epoxides for Cyclic Carbonates. Initially, the mononuclear zirconium complexes 4–6 were tested as catalysts for the formation of styrene carbonate 8a by the coupling reaction of CO_2 with styrene oxide 7a as a benchmark reaction (see Scheme 2). The process was assessed at 20 °C and 1 bar of

Scheme 2. Cyclic Carbonate Synthesis Catalyzed by Complexes $[Zr(NMe_2)_3(\kappa^3-NNC)]$ (4–6)



 CO_2 pressure and under solvent free conditions for 3, 6, and 24 h in a 1:1 molar ratio for all complexes, using a catalyst loading of 5% in the presence of tetrabutylammonium bromide (TBAB), which was selected as an efficient cocatalyst on the basis of our previous work with analogous scorpionate complexes, given the optimal balance between nucleophilicity, coordination ability to the metal, and leaving ability from the carbonate intermediate species of bromide ion in these experiments.^{3,21}

The results are presented in Table 2. Styrene oxide conversion into the styrene carbonate was determined by ¹H NMR at the established time intervals without any further purification (see Figure S3 in the SI). Expectedly, formation of

Table 2. Conversion of Epoxide 7a into Styrene Carbonate 8a Using Catalysts $4-6^a$

				Conversion [%]		
Entry	Catalyst	[Cat.]/ [cocat.] [mol %]	Temp [°C]	$\frac{3 h^b}{(\text{TOF } h^{-1})^c}$	6 h ^b	24 h ^b
1	4	5.0:5.0	25	22 (1.5)	34	67
2	5	5.0:5.0	25	17 (1.1)	31	61
3	6	5.0:5.0	25	15 (1.0)	28	57
4	4	5.0:0	25	0	0	0
5	TBAB	0:5.0	25	0	0	5
6	TBAB	0:5.0	60	3	8	13
7	bpzsimeH	5.0:5.0	25	0	0	4
8	4 ^{<i>d</i>}	0.5:0.5	60	42 (28.0)	71	100
9	TBAB ^d	0:0.5	60	5	11	16
10	4 ^{<i>d</i>}	0.25:0.25	80	72 (96.0)	98	-

^{*a*}Reactions carried out at 20 °C and 1 bar of CO₂ pressure using 5 mol % of complexes 4-6/5 mol % of TBAB as cocatalyst unless specified otherwise. ^{*b*}Determined by ¹H NMR spectroscopy of the crude reaction mixture. ^{*c*}TOF (Turnover frequency) = number of moles of styrene oxide consumed/(moles of catalyst × time of polymerization). ^{*d*}Reactions carried out at 10 bar of CO₂ pressure.

polycarbonate was not detected under the aforementioned conditions (selectivity >99%).²¹

The trimethylsilyl derivative 4 displayed slightly higher catalytic activity than the counterparts 5 and 6 (Table 2, entries 1-3) for the synthesis of 8a. This is probably due to the analogous nature of the three complexes; however, the norbornene derivative 6 showed the lowest activity as a result of the highest sterically hindered organosilyl fragment.

Moreover, a control experiment for 4 revealed no catalytic activity without the presence of TBAB, whereas the employment of TBAB in the absence of 4 produced minimal conversion at 20 °C (5%) and very low conversion at 60 °C (13%) after 24 h. Additionally, the performance of the corresponding ancillary protoiligand bpzsimeH (1) in complex 4 in the presence of TBAB was also inspected, displaying no significant conversion (4%) under these conditions (Table 2, entries 4–7). In addition, we explored the effect of temperature and pressure for the synthesis of 8a from 7a employing complex 4/TBAB as the catalytic system, by working at 60 °C and 10 bar of CO₂ pressure. Remarkably, under these conditions, catalyst and cocatalyst loadings can be reduced at 0.5 mol % to reach very good conversion in 6 h (Table 2, entries 8–9).

More interestingly, thermal stability was also successfully proven for catalyst 4 by increasing the reaction temperature up to 80 °C, reaching almost complete conversion even at lower catalyst loadings (0.25 mol %) in 6 h (Table 2, entry 10), reaching a TOF value of 96 h⁻¹ and proving no thermal degradation of both the highly constrained κ^3 -NNC-scorpionate complex 4 and the auxiliary ligand coordinated to the zirconium center (see Figure 1). Therefore, according to the results presented in Table 2, complex 4 was selected as the most efficient catalyst for further investigations under these experimental conditions.

Considering the good results attained by 4/TBAB, a variety of terminal substrates were additionally explored to test the efficiency of this bicomponent system (see Scheme 2), including alkyl, aryl, and functionalized terminal epoxides 7b-7e at 60 °C and 10 bar of CO₂ pressure, with a 10-fold reduction in catalyst/cocatalyst loading (0.5 mol %) under solvent-free conditions (see Figures S4–S7 in the SI). Remarkably, under these conditions excellent conversions were achieved in only 16 h, including those substrates bearing alcohol or ether functionalities with phenyl or alkyl chains (see Figure 2).

In view of the high activity displayed by the bicomponent system 4/TBAB, we additionally extended the substrate scope for catalyst 4 and assessed the conversion of internal and disubstituted epoxides 9a-9d, as well as biobased derived substrates 11a-11d, into the corresponding cyclic carbonates 10a-10d and 12a-12d, respectively. Although these transformations have received less attention than their monosubstituted analogous, intensive progress has been reported in the very recent years employing iron(II)-, calcium(II)-, and aluminum(III)-based catalyst systems.²² However, to our knowledge, no examples employing zirconium-based complexes or zirconium-coordination frameworks as catalyst have been reported until now.¹⁸ Interestingly, the synthesis of cyclic carbonates 10a-10b from the corresponding internal epoxides can be conducted using very low loadings (0.5 mol %) of the binary system 4/TBAB, in 1:1 proportion under mild and solvent-free conditions (60 °C, 10 bar CO₂ pressure) in 16 h (see Figure 3 and Figures S8–S9 in the SI), reaching high



Figure 2. Synthesis of cyclic carbonates **8a–8e** from epoxides 7**a**–7**e** using 0.5 mol % of the system complex 4/TBAB at 60 °C and 10 bar of CO_2 pressure for 16 h. (a) Conversion and selectivity were determined by ¹H NMR. (b) Isolated yield after column chromatography.



Figure 3. Synthesis of cyclic carbonates 10a–10d, 12a–12d, and 14 from epoxides 9a–9d, 11a–11d, and 13, respectively, using equimolecular amounts of the system 4/TBAB at 60 °C and 10 bar CO_2 pressure for 16 h, unless specified otherwise. (a) Conversion and selectivity were determined by ¹H NMR. (b) Isolated yield after column chromatography.

conversion values, thus showing the efficiency of this system. In addition, the reaction proceeds with retention of the epoxide stereochemistry through a double inversion process,²³ which led to the exclusive formation of the cis-isomer for the cyclohexene oxide, with a selectivity higher than 99%. In the case of cyclopentene oxide, only the cis-isomer is thermodynamically allowed.²⁴ Very good conversions were also observed for the disubstituted cyclic carbonates 10c-10d; however, an increase in catalyst loading (0.75-2.5 mol %) and reaction conditions (70-80 °C, respectively, 20 bar CO₂ pressure) was necessary (see Figure 3 and Figures S10-S11 in the SI), in agreement with the higher steric hinderance of the substituents in these substrates. Moreover, we turned our attention to the synthesis of biobased cyclic carbonates 12a-12d, given their potential use as a nontoxic feedstock to produce nonisocyanate poly(hydroxy)urethanes (NIPUs).²⁵ To our delight, excellent conversion was obtained in the synthesis of the biobased furanderived cyclic carbonate 12a after 16 h at 60 °C and 10 bar of CO₂ pressure, employing identical equimolecular catalyst/ cocatalyst loading (0.5 mol %) to that used for the terminal epoxides 8a-8e. As a result, we were encouraged to extend this study to transform other biobased diepoxide derivatives based on the fumaryl, succinil, and glutaryl building blocks, 11b-11d. We were also delighted to find that cyclic carbonates 12b-12d were obtained in quantitative yields under identical conditions to those for 12a, also using only 0.5 mol % of the bicomponent system 4/TBAB (see Figure 3 and Figures S12-S15 in the SI).

More interestingly, we finally endeavored the production of another biorenewable cyclic carbonate obtained from limonene, a highly substituted monocyclic unsaturated terpene derived from biomass.²⁶ Thus, the commercially available (*R*)-(+)-limonene oxide **13** (a mixture of *cis/trans* isomers 43:57) was efficiently transformed (56%), into the trisubstituted bicyclic terpene limonene carbonate **14** by a combination of 2.5 mol % of complex 4 and 2.5 mol % of TBAB at 80 °C and 20 bar of CO₂ pressure for 24 h, with high stereoselectivity to the *trans*-limonene carbonate (*cis/trans* = 6/94) (see Figure 3 and Figure S16 in the SI).

Interestingly, the employment of the norbornene derivative complex 6 resulted in a slight increase in stereoselectivity to the *trans*-carbonate (>99%) under otherwise identical conditions, but an expected reduction in conversion was also observed (48%), as a consequence of the sterically hindered chiral fragment in the scorpionate ligand (see Figure 3 and Figure S17 in the SI). To our knowledge, the combination of 4 and TBAB constitutes the first zirconium-based bicomponent system for the efficient cycloaddition of CO_2 to a wide variety of epoxides, as described above.

Finally, considering that the system 4/TBAB resulted in being very active in the synthesis of cyclic carbonates 8a-8e, 10a-10d, 12a-12d, and 14 with retention of the epoxide stereochemistry, a plausible mechanism for cyclic carbonate production catalyzed by this bicomponent zirconium-based system is presented in Figure 4. This mechanism follows a monometallic binary pathway considering that the kinetic investigations employing complex 4 and Bu_4NBr revealed an apparent first-order dependence on the catalyst and cocatalyst concentrations (see full study in Figures S18–S19 and Tables S2–S3 in the SI), which also agrees with those previously proposed for analog mononuclear scorpionate-based complexes²⁷ used for coupling CO₂ and epoxides into cyclic carbonates. Unfortunately, all attempts to follow this catalytic





Figure 4. Plausible mechanism for the conversion of epoxides and CO_2 into cyclic carbonates catalyzed by the system 4/TBAB.

process in CDCl₃ or CD₂Cl₂ produced degradation of complex 4 possibly as a consequence of protic traces in solution, whereas the use of thf- d_8 or C₆D₆ did not afford enough solubility to the TBAB. The proposal is consistent with the initial coordination of the epoxide to the zirconium center, with expansion of the coordination sphere, as recently reported in analog octahedral zirconium-based catalysts,²⁸ subsequent nucleophilic attack of the bromide to the less sterically hindered carbon atom of the epoxide, CO₂ insertion into the Zr–O bond, and final ring closing of the cyclic carbonate with stereochemistry retention.

CONCLUSIONS

We have designed a simple strategy for the preparation of a novel family of zirconium complexes containing organosilyl derived bis(pyrazol-1-yl)methanides that act as robust monoanionic κ^3 -NNC scorpionate ligands. X-ray diffraction analysis indicated that these species are very strained, forming four-membered heterometallacycles in the molecule.

These κ^3 -NNC-scorpionate zirconium amides in the presence of a cocatalyst showed to be effective catalysts for CO₂ fixation into five-membered cyclic carbonates. The study allowed the development of a new zirconium-based system consisting of a combination of the complex 4 and TBAB, which resulted in being efficient and selective for the cycloaddition of CO₂ to epoxides in good to excellent yields. Kinetic studies revealed apparent first-order dependence on the catalyst and cocatalyst concentrations. Furthermore, this bicomponent system displayed very broad substrate scope, including terminal, internal, and disubstituted substrates, as well as the challenging biorenewable terpene derived limonene oxide, under mild and solvent-free conditions. The presence of a chiral fragment in complex 6 exerted a slight stereoselective *trans*-influence for limonene oxide.

EXPERIMENTAL SECTION

General Procedures. Reactions for the synthesis of complexes were performed using Schlenk techniques or a glovebox under an atmosphere of dry nitrogen. Solvents were predried over sodium wire and distilled under nitrogen from sodium (toluene and *n*-hexane) sodium-benzophenone (THF). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze—thaw cycles. The starting materials allyl(chloro)dimethylsilane and 2-(5-norbornen-2-yl)ethylchlorodimethylsilane, $Zr(NMe_2)_{4^{j}}$ and "BuLi were used as purchased (Aldrich). The compounds bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane]²⁹ and bpzsimeH (1)¹⁹ were prepared as previously reported. (*R*)-(+)-Limonene oxide (*cis and trans* mixture) was distilled from calcium hydride under vacuum. The remaining epoxide substrates were used as received unless specified otherwise (Aldrich, Across). CO₂ (99,99%) was commercially obtained and used without further purification.

Instruments and Measurements. NMR spectra were recorded on a Bruker Advance Neo 500 (¹H NMR 500 MHz and ¹³C NMR 125 MHz) spectrometer and were referenced to the residual deuterated solvent signal. The NOESY-1D spectra were recorded with the following acquisition parameters: irradiation time 2 s and number of scans 256 using standard VARIAN-FT software. 2D NMR spectra were acquired using the same software and processed using an IPC-Sun computer. Microanalyses were performed with a PerkinElmer 2400 CHN analyzer.

Preparation of Compounds 2-6. Synthesis of bpzsialiH (2). In a 250 mL Schlenk tube, bdmpzm (2.00 g, 9.79 mmol) was dissolved in dry THF (70 mL) and cooled to -70 °C. A 1.6 M solution of "BuLi (6.12 mL, 9.79 mmol) in hexane was added, and the suspension was stirred for 1 h. The reaction mixture was warmed to -20 °C, and the resulting yellow suspension was treated with a solution of allyl(chloro)dimethylsilane (1.48 mL, 9.79 mmol) in dry THF (20 mL), after which the solution was stirred for 30 min. The reaction mixture was warmed to room temperature and was stirred for an additional hour. The solvent was removed under reduced pressure, and the residual solid was extracted in hexane (70 mL) to give a yellow solid of 2. Yield: (2.72 g, 92%). Anal. Calcd for C₁₆H₂₆N₄Si: C, 63.53; H, 8.66; N, 18.52. Found: C, 63.49; H, 8.63; N, 18.50. ¹H NMR (C_6D_6 , 297 K), δ 6.02 (s, 1H, CH^a), 5.78 (m, 1H, -CH₂-<u>CH</u>=CH₂), 5.63 (s, 2H, H⁴), 4.88 (m, 2H, -CH₂-CH=<u>CH₂</u>), 2.14 (s, 6H, Me³), 1.87 (m, 1H, $-\underline{CH}_2-CH=CH_2$), 1.81 (s, 6H, Me⁵), 0.35 (s, 6H, SiMe₂). ¹³C {¹H} NMR (C₆D₆, 297 K), δ 146.5 (C³), 139.3 (C⁵), 134.3 (-CH₂-<u>CH</u>=CH₂), 113.5 (-CH₂-CH=<u>CH₂</u>), 106.1 (C⁴), 66.9 (C^a), 22.7 (-<u>CH</u>₂-CH=CH₂), 13.3 (Me³), 10.4 (Me^5) , -3.2 (SiMe₂).

Synthesis of bpzsinbH (3). The synthesis of 3 was carried out in an identical manner to 2, using bdmpzm (2.00 g, 9.79 mmol), 1.6 M solution of "BuLi (6.12 mL, 9.79 mmol) in hexane and 2-(5-norbornen-2-yl)ethylchlorodimethylsilane (2.12 mL, 9.79 mmol), to give 3 as a yellow solid. Yield: (3.33 g, 89%). Anal. Calcd for $C_{22}H_{34}N_4Si: C, 69.06; H, 8.96; N, 14.64.$ Found: C, 69.01; H, 8.82; N, 14.69. ¹H NMR (C_6D_6 , 297 K), δ 6.07 (dd, ${}^3J_{H-H} = 10.9$ Hz, ${}^3J_{H-H} = 6.2$ Hz, 1H, H^d), 6.06 (s, 1H, CH^a), 5.92 (dd, ${}^3J_{H-H} = 10.9$ Hz, ${}^3J_{H-H} = 6.2$ Hz, 1H, H^e), 5.65 (s, 2H, H⁴), 2.76 (s, 1H, H^f), 2.66 (s, 1H, H^c), 2.19 (s, 6H, Me³), 1.89 (m, 1H, H^b), 1.84 (s, 6H, Me⁵), 1.50, 0.52 (m, 2H, H^h), 1.15 (m, 2H, Si-CH₂-CH₂-), 0.90 (m, 2H, H^g), 0.39, 0.37 (s, 6H, SiMe₂), 0.22 (t, 2H, ${}^3J_{H-H} = 7.1$ Hz, Si-CH₂-CH₂-). ${}^{13}C$ {¹H} NMR (C_6D_6 , 297 K), δ 146.3 (C³), 139.3 (C⁵), 136.7 (C^d), 132.2 (C^e), 106.1 (C⁴), 67.6 (C^a), 49.5 (C^f), 45.0 (C^c), 42.6 (C^b), 32.3 (C^h), 28.5 (Si-CH₂-CH₂-), 13.9 (C^g), 13.4 (Me³), 10.5 (Me⁵), -2.7 (Si-<u>CH₂</u>-CH₂-), -2.8 (SiMe₂).

Synthesis of $[Zr(NMe_2)_3(bpzsime)]$ (4). In a 250 mL Schlenk tube, bpzsimeH (1.0 g, 3.62 mmol) was dissolved in dry toluene (60 mL). A solution of $Zr(NMe_2)_4$ (0.97 g, 3.62 mmol) in toluene (30 mL) was added, and the mixture was stirred during 12 h at room temperature. The solvent was evaporated to dryness under reduced pressure to yield a yellow product. The product was washed with *n*-hexane (1 × 25 mL) to give compound 4 as a yellow solid. Crystals suitable for Xray diffraction were obtained by recrystallization from toluene at -26 °C. Yield: (1.62 g, 90%). Anal. Calcd for $C_{20}H_{41}N_7SiZr: C$, 48.15; H, 8.28; N, 19.65. Found: C, 48.19; H, 8.35; N, 19.75. ¹H NMR (C_6D_6 , 297 K), δ 5.49 (s, 2H, H⁴), 3.29 [s, 12H, $Zr(NMe_2)_3$], 3.13 [s, 6H, $Zr(NMe_2)_3$], 2.11 (s, 6H, Me³), 2.00 (s, 6H, Me⁵), 0.26 (s, 9H, SiMe_3). ¹³C {¹H} NMR (C_6D_6 , 297 K), δ 146.2 (C³), 140.9 (C⁵), 105.6 (C⁴), 65.1 (C^a), 44.4, 42.9 [$Zr(NMe_2)_3$], 12.3 (Me³), 11.3 (Me⁵), 1.2 (SiMe_3).

Synthesis of $[Zr(NMe_2)_3(bpzsiali)]$ (5). The synthesis of 5 was carried out in an identical manner to 4, using bpzsialiH (1.0 g, 3.31 mmol) and $Zr(NMe_2)_4$ (0.88 g, 3.31 mmol), obtained 5 as a yellow solid. Yield: (1.58 g, 91%). Anal. Calcd for $C_{22}H_{43}N_7SiZr$: C, 50.34; H, 8.26; N, 18.68. Found: C, 50.35; H, 8.41; N, 18.61. ¹H NMR (C_6D_6 , 297 K), δ 5.78 (m, 1H, $-CH_2-C\underline{H}=CH_2$), 5.46 (s, 2H, H⁴), 4.94 (m, 2H, $-CH_2-CH=C\underline{H}_2$), 3.27 [s, 12H, $Zr(NMe_2)_3$], 3.12 [s, 6H, $Zr(NMe_2)_3$], 2.15 (m, 1H, $-C\underline{H}_2-CH=CH_2$), 2.09 (s, 6H, Me³), 1.99 (s, 6H, Me⁵), 0.31 (s, 6H, SiMe_2). ¹³C {¹H} NMR (C_6D_6 , 297 K), δ 146.3 (C³), 140.9 (C⁵), 136.1 ($-CH_2-C\underline{H}=CH_2$), 112.6 ($-CH_2-CH=\underline{CH}_2$), 105.7 (C⁴), 65.5 (C^a), 44.6, 43.7 [$Zr(NMe_2)_3$], 24.9 ($-\underline{CH}_2-CH=CH_2$), 12.2 (Me³), 11.9 (Me⁵), -0.6 (SiMe_2).

Synthesis of $[Zr(NMe_2)_3(bpzsinb)]$ (6). The synthesis of 6 was carried out in an identical manner to 4, using bpzsinbH (1.0 g, 2.61 mmol) and Zr(NMe₂)₄ (0.70 g, 2.61 mmol), obtained 6 as a yellow solid. Yield: (1.43 g, 91%). Anal. Calcd for C₂₈H₅₁N₇SiZr: C, 55.58; H, 8.50; N, 16.20. Found: C, 55.35; H, 8.62; N, 16.11. ¹H NMR $(C_6 D_6, 297 \text{ K}), \delta 6.11 \text{ (dd, } {}^3J_{H-H} = 10.9 \text{ Hz}, {}^3J_{H-H} = 6.2 \text{ Hz}, 1\text{H}, \text{H}^{d}),$ 5.99 (dd, ${}^{3}J_{H-H} = 10.9$ Hz, ${}^{3}J_{H-H} = 6.2$ Hz, 1H, H^e), 5.50, 5.49 (s, 2H, H^{4,4'}), 3.29 [s, 6 H, Zr(NMe₂)₃], 3.17 [s, 6 H, Zr(NMe₂)₃], 3.16 [s, 6 H, $Zr(NMe_2)_3$], 2.88 (s, 1H, H^t), 2.68 (s, 1H, H^t), 2.13, 2.12 (s, 6H, Me^{3,3'}), 2.05 (m, 1H, H^b), 2.04 (s, 6H, Me^{5,5'}), 1.50, 0.59 (m, 2H, H^h), 1.17 (m, 2H, Si-CH₂- CH_2 -), 0.90 (m, 2H, H^g), 0.27, 0.26 (s, 6H, SiMe₂), 0.14 (t, ${}^{3}J_{H-H} = 7.1$ Hz, 2H, Si $-C\underline{H}_{2}-CH_{2}-$). ${}^{13}C$ {¹H} NMR (C₆D₆, 297 K), δ 146.3 (C³), 141.2 (C⁵), 136.9 (C^d), 132.6 (C^e), 105.8, 105,6 (C^{4,4}), 66.3 (C^a), 49.6 (C^f), 45.3 (C^c), 44.8, 44.6, 43.8 [Zr(NMe₂)₃], 42.8 (C^b), 32.6 (C^h), 29.6 (Si-CH₂-<u>C</u>H₂-), 13.4 $(C^{g}), 12.2, 12,1 (Me^{3,3'}), 11.4, 11.2 (Me^{5,5'}), -2.7 (Si-<u>C</u>H₂-CH₂-),$ -0.2, -0.4 (SiMe₂).

Crystallographic Refinement and Structure Solution. Suitable crystals of 4 were grown from toluene. Intensity data were collected at 230 K on a Bruker X8 APEX II CCD-based diffractometer, equipped with a graphite monochromatic Mo K α radiation source ($\lambda = 0.71073$ Å). Data were integrated using SAINT,³⁰ and an absorption correction was performed with the program SADABS.³¹ The structures were solved by direct methods using the WINGX package³² and refined by full-matrix least-squares methods based on F^2 .

Final R(F), $wR(F^2)$, and goodness-of-fit agreement factors, details on the data collection, and analysis can be found in Table S1. CCDC 2002543 contains the supplementary crystallographic data for this paper.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01532.

Spectroscopic details of compound 1 and complex 4; details of crystal data and structure refinement for 4; experimental details for the synthesis of cyclic carbonates, including ¹H and ¹³C NMR spectroscopic data and spectra of cyclic carbonates 8a-8e, 10a-10e, 12a-12e, and 14; and kinetic studies to determine the reaction order with respect to catalyst and cocatalyst (PDF)

Accession Codes

CCDC 2002543 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cam-

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Notes

The authors declare no competing financial interest.

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