

Unprecedented NNC-Scorpionate Zirconium-based Bicomponent System for the Very 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 $[\text{Zr}(\text{NMe}_2)_4]$ for the preparation of the first 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 highly tensioned four-membered heterometallacycles. These κ^3 -NNC-scorpionate zirconium amides were investigated as catalysts in combination with tetra-*n*-butylammonium bromide for CO_2 fixation into five-membered cyclic carbonate products. The study has led to the development of the first zirconium-based bicomponent systems for the efficient and selective cycloaddition reaction of CO_2 with epoxides, which display very broad substrate scope, including mono-, di- and challenging bio-renewable tri-substituted terpene derived substrates, such as limonene oxide, under mild and solvent-free conditions.

INTRODUCTION

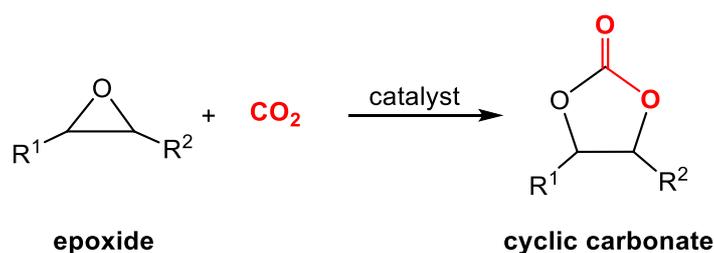
Over the last two decades, our research group has pioneered the modification of the bis(pyrazol-1-yl)methane (bpzm) molecule through the bridging carbon atom,^{1b,c} by adding organic functional groups to form heteroscorpionate ligands.¹ This procedure has allowed us to design a wide variety of novel achiral, chiral and enantiopure NNO,² NNS,³ NNN⁴ and NNCp⁵ κ^3 -scorpionate ligands to prepare very efficient catalysts⁶ for the synthesis of poly(lactide)s,^{4a,7} cyclic carbonates⁸ and polycarbonates.⁹ However, the κ^3 -NNC(*sp*³) 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.¹⁰ Additionally, tungsten-based compounds bearing a bpzm in this coordination fashion, obtained by migration of a SnAr₃ fragment to the metal, were also communicated.¹¹ More recently, an amide-derivative calcium compound containing the bpzm in this tridentate mode has been also reported.¹²

On the other hand, over the last few years our research group has been intensively working on the valorisation of CO₂ as an attractive C–1 renewable building block¹³ since this unsaturated molecule presents a wide spread availability in nature, low cost, non-hazardous features, lack of colour 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)¹⁴ or polycarbonates (PC's)¹⁵ by cycloaddition or ring opening copolymerization (ROCOP) of CO₂ 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.¹⁶

In this context, very active metal-based catalysts have been reported, with chromium,¹⁷ cobalt,¹⁸ iron,¹⁹ magnesium,²⁰ zinc,²¹ or aluminum,^{8,22} as leading metals in this field. However, a few examples of efficient group 4-based systems²³ 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 explored²⁴ in this process, focused exclusively on propylene^{24a,c,d} and styrene^{24a,c} oxide conversions at relatively demanding reaction conditions (40-75 °C at 35-10 bar of CO₂ pressure, and 80 °C at 35 bar of CO₂ pressure, respectively). Alternatively, efficient metal–coordination frameworks containing this metal are currently appearing,^{24e,f} however, these species present very limited channel accessibility to bulkier epoxides, decreasing the range of applicability.

Chart 1. Synthesis of cyclic carbonates.



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 behaviour in the coupling reaction of CO₂ and epoxides, with a much wider substrate scope.

We report hereby the preparation of the first zirconium complexes supported by a highly tensioned organosilyl-derived bis(3,5-dimethylpyrazol-1-yl)methanide in a κ^3 -NNC coordination fashion as the unique zirconium-based catalysts for the cycloaddition of CO₂ to epoxides, which display very broad substrate scope, including terminal, internal and very challenging bio-based derivatives under mild and solvent-free conditions.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Starting Materials and Complexes.

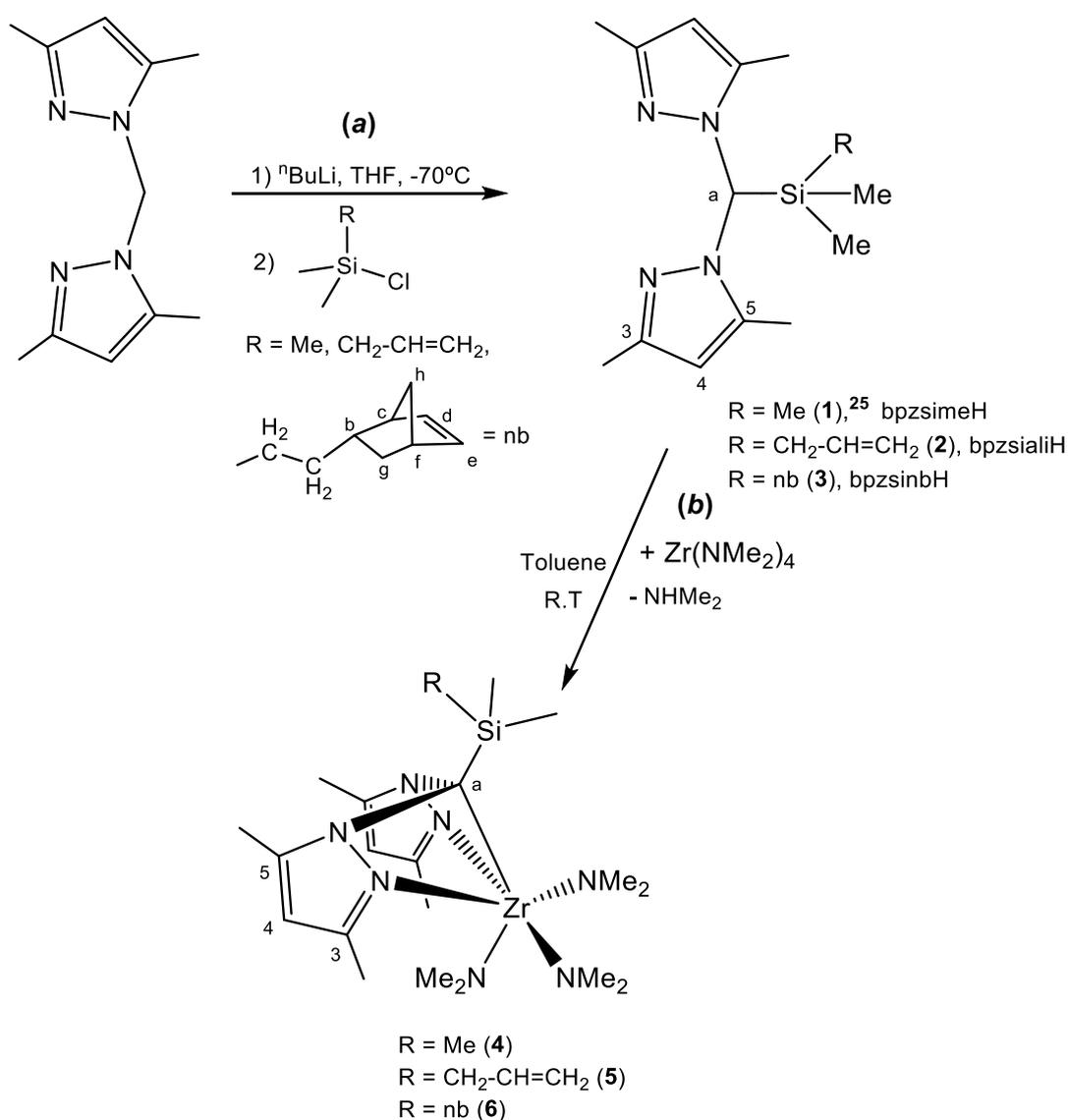
The modification of the bis(3,5-dimethylpyrazol-1-yl)methane molecule by organosilyl groups on the central carbon atom was carried out by reaction of lithium bis(3,5-dimethylpyrazol-1-yl)methanide, prepared *in situ* from ⁿBuLi and bis(3,5-dimethylpyrazol-1-yl)methane at -70 °C, with the corresponding organosilyl chloride to afford the starting materials bpzsimeH (**1**), bpzsialiH (**2**) and bpzsinbH (**3**) (see Scheme 1a). It should be noted that the use of 5-norbornen-2-yl(ethyl)chlorodimethylsilane allowed us to introduce an organosilyl chiral group in the bridging carbon atom in the case of **3**. The soft treatment of the ligands **1–3** with Zr(NMe₂)₄ in a 1:1 molar ratio in toluene gave the complexes [Zr(NMe₂)₃(κ³-NNC)] (**4–6**), through the C–H activation of the bridging methane group in the ligand, as a consequence of the silyl group placed in α-position to the carbon atom C^a. These complexes were isolated as yellow solids in good yield (*ca.* 90%) after the appropriate work-up (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). 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{¹H} 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(sp³)^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).

Scheme 1. Synthesis of the modified bis(3,5-dimethylpyrazol-1-yl)methane with organosilyl groups **1–3**, and complexes [Zr(NMe₂)₃(κ^3 -NNC)] (**4–6**).



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 1 (Crystallographic

details are included in Table S1 in the SI). The structure consists on a scorpionate ligand bonded to the 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,¹⁰ tungsten¹¹ and calcium.¹²

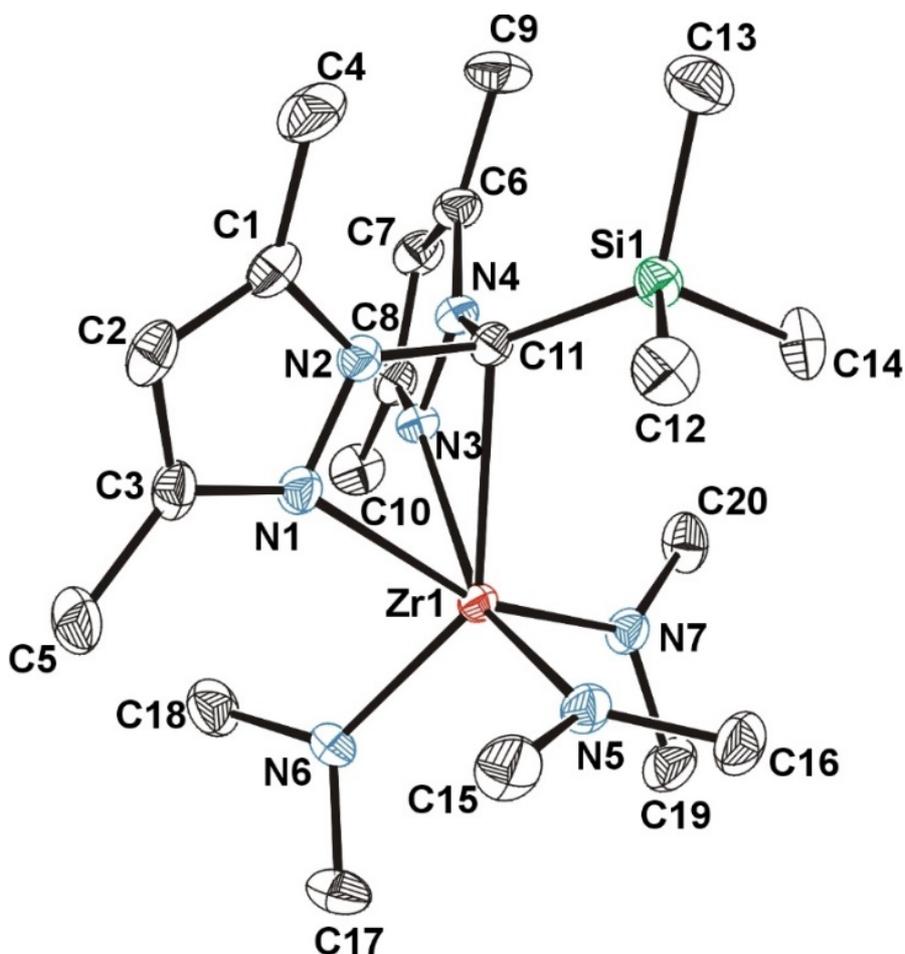


Figure 1. ORTEP view of $[\text{Zr}(\text{NMe}_2)_3(\text{bpzsime})]$ (**4**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability.

However, as far as we aware, 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)°, 56.50(5)° and 56.65(5)°, respectively, are very far to 90°. The Zr-amide 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.^{4b}

Table 1. Selected bond lengths [Å] and angles [°] for **4**.

<i>Distances [Å]</i>		<i>Angles [°]</i>	
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)

Catalytic Studies for the Cycloaddition of CO₂ 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 CO₂ with styrene oxide **7a** as a benchmark reaction (see Scheme 2). The process was assessed at 20 °C, 1 bar of CO₂ pressure and under solvent free conditions for 3, 6 and 24 hours 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 co-catalyst on the basis of our previous works with analogous scorpionate complexes.⁸

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

complexes, however, the norbornen 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 (5%) after 24 h. Additionally, the performance of the corresponding ancillary protioligand bpzsimeH (**1**) in complex **4** in the presence of TBAB was also inspected, displaying no significant conversion (4%) under these conditions (Table 2, entries 4-6). In addition, we explored the effect of temperature and pressure for the synthesis of **8a** from **7a** employing complex **4** as catalyst, by working at 60 °C and 10 bar CO₂ pressure. Remarkably, under these conditions, catalyst and co-catalyst loadings can be reduced at 0.5 mol% to reach very good conversion in 6 hours (Table 2, entry 7).

More interestingly, thermal stability was also successfully proved 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 hours (Table 2, entry 8), proving the thermodynamic stability of both the highly constrained κ^3 -NNC-scorpionate and the auxiliary ligands 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, more demanding 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/co-catalyst 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 hours, including those substrates bearing alcohol or ether functionalities with phenyl or alkyl chains (see Figure 2).

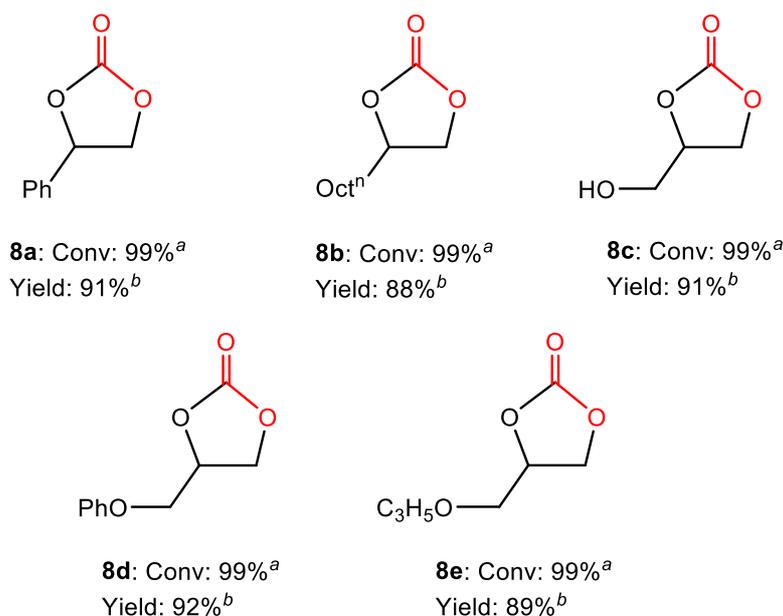


Figure 2. Synthesis of cyclic carbonates **8a–8e** from epoxides **7a–7e** using 0.5 mol% of the system complex **4**/TBAB at 60 °C and 10 bar CO₂ pressure for 16 hours. (a) Conversion and selectivity were determined by ¹H NMR. (b) Isolated yield after column chromatography.

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 di-substituted epoxides **9a–9d**, as well as bio-based derived substrates **11a–11d**, into the corresponding cyclic carbonates **10a–10d** and **12a–12d**, respectively. However, these more challenging transformations have received far less attention than their mono-substituted analogues, and as far as we are aware, no examples employing zirconium-based complexes or metal–coordination frameworks as catalyst have been reported until now.²⁴ The use of more demanding epoxides for their coupling reaction with CO₂, such as internal and di-substituted epoxides **9a–9d** is of particular interest owing to their low reactivity and selectivity towards the synthesis of the corresponding cyclic carbonates. 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 hours (see Figure 3, Figures S8-S9 in the SI), reaching high conversions values, thus showing the efficiency of this system. In addition, the reaction proceeds

with retention of the epoxide stereochemistry through a double inversion process,²⁶ which led to the exclusive formation of the *cis*-isomer for both cyclohexene and cyclopentene oxides, with a selectivity higher than 99%. The di-substituted substrates **10c–10d** also exhibited very good conversions, 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 higher steric hinder of the substituents in these substrates.

Moreover, we turned our attention to the synthesis of bio-based cyclic carbonates **12a–12d**, given their potential use as a non-toxic feedstock to produce non-isocyanate poly(hydroxy)urethanes (NIPUs).²⁷ To our delight, excellent conversion was obtained in the synthesis of the bio-based furan-derived cyclic carbonate **12a** after 16 hours at 60 °C and 10 bar CO₂ pressure, employing identical equimolecular catalyst/co-catalyst loading (0.5 mol%) than that used for the terminal epoxides **8a–8e**. As a result, we encouraged to extend this study to transform other bio-based diepoxides 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 than 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 bio-renewable cyclic carbonate obtained from limonene, a highly substituted monocyclic unsaturated terpene derived from biomass.²⁸ Thus, the commercially available (*R*)-(+)-limonene oxide **13** (a mixture of *cis/trans* isomers 43:57) was efficiently transformed into the tri-substituted 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 norbornen 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). As far as we are conscious, the combination of **4** and TBAB constitute the first zirconium-based

bicomponent system for the efficient cycloaddition of CO₂ to a wide variety of epoxides, as described above.

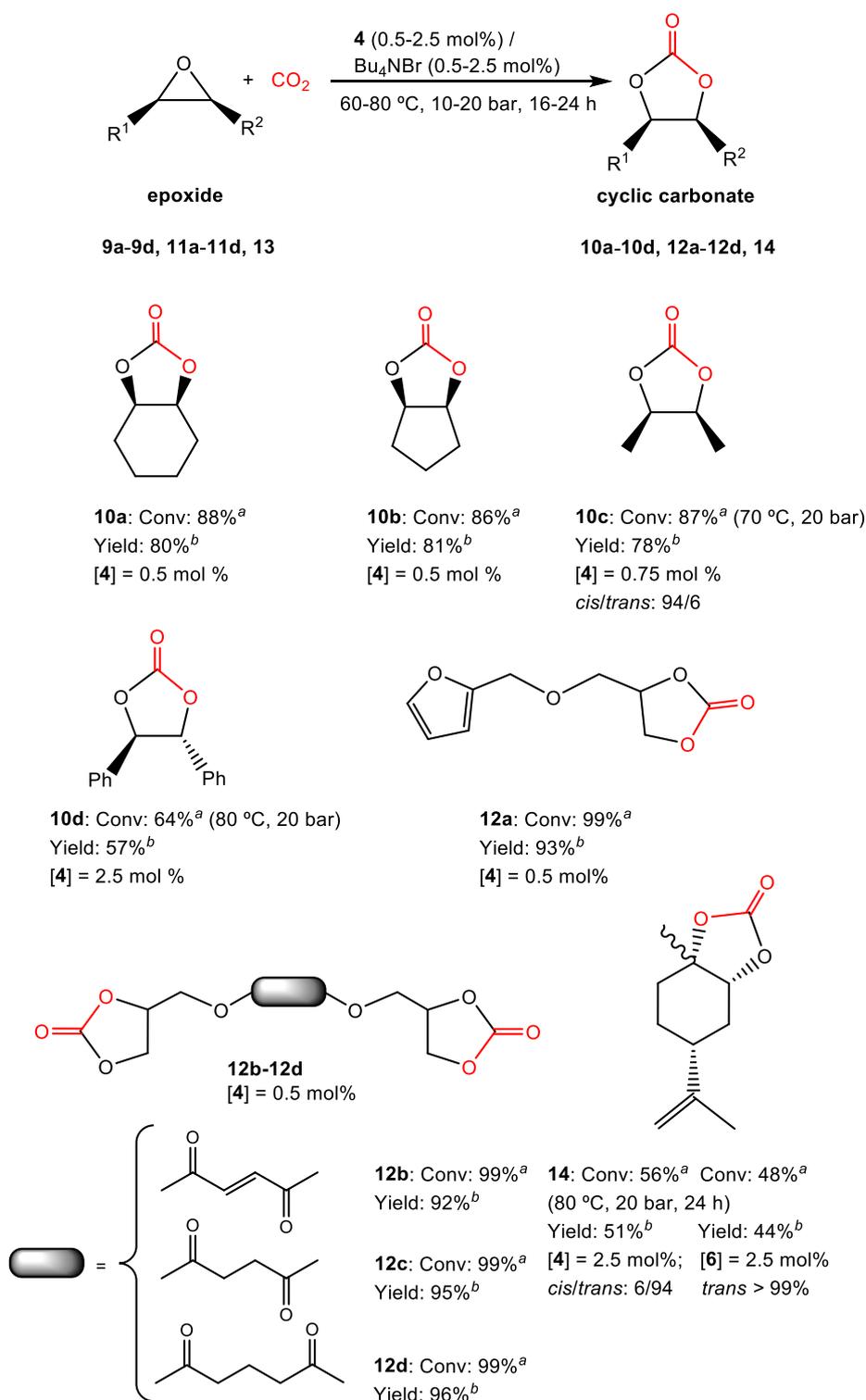


Figure 3. Synthesis of cyclic carbonates **10a–10d**, **12a–12d** and **14** from epoxides **9a–9d**, **11a–11d** and **13**, respectively, using equimolar amounts of the system **4**/TBAB at 60 °C and 10 bar CO₂ pressure for 16 hours, unless specified otherwise. (a) Conversion and selectivity were determined by ¹H NMR. (b) Isolated yield after column chromatography.

CONCLUSIONS

We have designed a simple strategy for the preparation of the first 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 indicates that these species are highly constrained, forming four-membered heterometallacycles in the molecule.

These κ^3 -NNC-scorpionate zirconium amides in the presence of a co-catalyst resulted highly effective catalysts for CO₂ fixation into five-membered cyclic carbonates. The study allowed the development of the first zirconium-based bicomponent system consisting on a combination of the complex **4** and TBAB, which resulted highly efficient and selective for the cycloaddition of CO₂ to epoxides in good to excellent yields, with very broad substrate scope, including terminal, internal, di-substituted and very challenging bio-renewable terpene derived substrates such as 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.

We consider these results represent a significant further step forward in the development of more efficient and selective catalysts for CO₂ fixation into cyclic carbonates.

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 5-norbornen-2-yl(ethyl)chlorodimethylsilane], Zr(NMe₂)₄ and ⁿBuLi were used as purchased (Aldrich). The compounds bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane]²⁹ and (bpzsimeH (**1**)²⁵ were prepared as previously reported. (*R*)-(+)-limonene oxide (*cis* and *trans* mixture) was distilled from calcium hydride under vacuum. The rest of the 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 Perkin-Elmer 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 ⁿBuLi (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 a

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 (C₆D₆, 297 K), δ 6.02 (s, 1H, CH^a), 5.78 (m, 1H, -CH₂-CH=CH₂), 5.63 (s, 2H, H^d), 4.88 (m, 2H, -CH₂-CH=CH₂), 2.14 (s, 6H, Me³), 1.87 (m, 1H, -CH₂-CH=CH₂), 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-CH=CH₂), 113.5 (-CH₂-CH=CH₂), 106.1 (C⁴), 66.9 (C^a), 22.7 (-CH₂-CH=CH₂), 13.3 (Me³), 10.4 (Me⁵), -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 ⁿBuLi (6.12 mL, 9.79 mmol) in hexane and 5-norbornen-2-yl(ethyl)chlorodimethylsilane (2.12 mL, 9.79 mmol), to give **3** as a yellow solid. Yield: (3.33 g, 89%). Anal. Calcd. For C₂₂H₃₄N₄Si: C, 69.06; H, 8.96; N, 14.64. Found: C, 69.01; H, 8.82; N, 14.69. ¹H NMR (C₆D₆, 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-). ¹³C {¹H} NMR (C₆D₆, 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-CH₂-CH₂-), -2.8 (SiMe₂).

Synthesis of [Zr(NMe₂)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(NMe₂)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 yellow solid. Crystals suitable for X-ray diffraction were obtained by recrystallization from toluene at -26 °C. Yield: (1.62 g, 90%). Anal. Calcd. For C₂₀H₄₁N₇SiZr: C, 48.15; H, 8.28; N, 19.65. Found: C, 48.19; H, 8.35; N, 19.75. ¹H NMR (C₆D₆, 297 K), δ 5.49 (s, 2H, H⁴), 3.29 [s, 12H, Zr(NMe₂)₃], 3.13 [s, 6H, Zr(NMe₂)₃], 2.11 (s, 6H, Me³), 2.00 (s, 6H, Me⁵), 0.26 (s,

9H, SiMe₃). ¹³C {¹H} NMR (C₆D₆, 297 K), δ 146.2 (C³), 140.9 (C⁵), 105.6 (C⁴), 65.1 (C^a), 44.4, 42.9 [Zr(NMe₂)₃], 12.3 (Me³), 11.3 (Me⁵), 1.2 (SiMe₃).

Synthesis of [Zr(NMe₂)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(NMe₂)₄ (0.88 g, 3.31 mmol), obtained **5** as a yellow solid. Yield: (1.58 g, 91%). Anal. Calcd. For C₂₂H₄₃N₇SiZr: C, 50.34; H, 8.26; N, 18.68. Found: C, 50.35; H, 8.41; N, 18.61. ¹H NMR (C₆D₆, 297 K), δ 5.78 (m, 1H, -CH₂-CH=CH₂), 5.46 (s, 2H, H⁴), 4.94 (m, 2H, -CH₂-CH=CH₂), 3.27 [s, 12H, Zr(NMe₂)₃], 3.12 [s, 6H, Zr(NMe₂)₃], 2.15 (m, 1H, -CH₂-CH=CH₂), 2.09 (s, 6H, Me³), 1.99 (s, 6H, Me⁵), 0.31 (s, 6H, SiMe₂). ¹³C {¹H} NMR (C₆D₆, 297 K), δ 146.3 (C³), 140.9 (C⁵), 136.1 (-CH₂-CH=CH₂), 112.6 (-CH₂-CH=CH₂), 105.7 (C⁴), 65.5 (C^a), 44.6, 43.7 [Zr(NMe₂)₃], 24.9 (-CH₂-CH=CH₂), 12.2 (Me³), 11.9 (Me⁵), -0.6 (SiMe₂).

Synthesis of [Zr(NMe₂)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 (C₆D₆, 297 K), δ 6.11 (dd, ³J_{H-H} = 10.9 Hz, ³J_{H-H} = 6.2 Hz, 1H, H^d), 5.99 (dd, ³J_{H-H} = 10.9 Hz, ³J_{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(NMe₂)₃], 2.88 (s, 1H, H^f), 2.68 (s, 1H, H^c), 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-CH₂-), 0.90 (m, 2H, H^g), 0.27, 0.26 (s, 6H, SiMe₂), 0.14 (t, ³J_{H-H} = 7.1 Hz, 2H, Si-CH₂-CH₂-). ¹³C {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-CH₂-), 13.4 (C^g), 12.2, 12.1 (Me^{3,3'}), 11.4, 11.2 (Me^{5,5'}), -2.7 (Si-CH₂-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 MoK α radiation source ($\lambda = 0.71073$ Å). Data were integrated using SAINT³⁰ and an absorption correction was performed

with the program SADABS.³¹ The structures were solved by direct methods using WINGX package,³² and refined by full-matrix least-squares methods based on F^2 .

Final R(F), wR(F2) 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.

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CONFLICT OF INTEREST

There are no conflicts to declare

Supporting Information Available: 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 ^{13}C NMR spectroscopic data and spectra of cyclic carbonates **8a–8e**, **10a–10e**, **12a–12e** and **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Unprecedented NNC-Scorpionate Zirconium-based Bicomponent System for the Very Efficient CO₂ Fixation into a Variety of Cyclic Carbonates

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The reaction of the bis(3,5-dimethylpyrazol-1-yl)methane modified by organosilyl groups with [Zr(NMe₂)₄] cleanly afforded the first zirconium complexes containing organosilyl derived bis(pyrazol-1-yl)methanides that act as robust monoanionic κ^3 -NNC scorpionates. These scorpionate zirconium amides in combination with TBAB constitute the first systems that behave as highly efficient and selective catalysts for CO₂ fixation into five-membered cyclic carbonates, through the cycloaddition reaction of CO₂ to mono-, di- and challenging biorenewable tri-substituted terpene derived epoxides, under mild and solvent-free conditions.

