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Efficient CO$_2$ Fixation into Cyclic Carbonates Catalyzed by NNO-Scorpionate Zinc Complexes

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A series of new chiral zwitterionic NNO-scorpionate mononuclear zinc alkyls [Zn(R)(κ^3-NNO)]Br have been developed in very high yields, via suitable quaternization in the scorpionate ligand. These zwitterionic complexes performed as bifunctional catalysts and exhibited improved catalytic activity for the fixation of CO$_2$ into cyclic carbonates compared to the neutral analog mono- [Zn(R)(κ^3-NNO)] and binuclear [Zn(R)(κ^2-NNμ-O)Zn(R)$_2$] compounds. The catalyst system showed a broad substrate scope and functional group tolerance under mild and solvent-free conditions. Published article available at: https://pubs.rsc.org/en/content/articlelanding/2019/dt/c9dt01844a#!divAbstract

Introduction

During the last few years the production of high-value added organic chemicals and/or materials through the employment of carbon dioxide has received great attention[1] by many research groups, on view of the number of reviews[2a] and books[2b] that have appeared in this expanding field. Carbon dioxide is an attractive molecule that can be used as C$_1$ building block[1] considering its low cost, high abundance, low toxicity and renewability, in conjunction with the environmental concerns, as this gas represents one of the most important greenhouse gases in our atmosfere.[1] In this context, an effective conversion of CO$_2$ into fuels, chemicals and polymers, in concurrence with carbon capture and storage strategies, would benefit in the desired progression from a fossil fuel-based industry to a sustainable and circular one.[3] However, it results critical to overcome the very low thermodynamics of CO$_2$ (ΔH^o_f = −394 kJ·mol^{-1} and ΔG^o_f = −395 kJ·mol^{-1})[4] to be considered as a viable feedstock, and this is only possible through the design of effective catalysts that reduce its kinetic barrier. In addition, the employment of high-free-energy reactants thermodynamically assists the conversion of carbon dioxide into industrially demanded products.

One of the most representative processes that utilizes CO$_2$ is the production of cyclic carbonates (CCs)[5] or polycarbonates (PCs)[6] from epoxides and carbon dioxide (Scheme 1), with the formers leading important commercial applications as they can act as electrolytes in

lithium-ion batteries, sustainable polar aprotic solvents, chemical intermediates in organic synthesis, antifoam additives and plasticizers.[7] Additionally, they can also be used as starting materials for the synthesis of polyurethane and urea derivatives,[8] and when copolymerized with cyclic esters, they allow polymeric materials for biomedical applications.[9] Therefore, the yearly market demand of organic carbonates is currently increasing, with an estimated annual production higher than 10 Mt/y by 2030.[10] Nonetheless, although the production of these interesting high-tech supplies implies 100% atom-economy with highly favorable reaction enthalpy, unfortunately, the current industrial processes are net CO$_2$ emitters, -requiring high reaction temperatures and pressures.[1] To overcome all the limiting features described above, a large number of catalyst systems which combine a Lewis acid and a nucleophile as a co-catalyst, have been reported for the efficient and selective production of both CCs[5] and PCs[6] from epoxides and carbon dioxide. Furthermore, the use of biologically benign metals such as zinc[11] results also necessary to avoid potential health risks related with the toxicity concerns.[12]

In this context, highly effective organozinc initiators have been described for the ring-opening copolymerization (ROCOP) process of CO$_2$ and cyclohexene oxide (CHO) for polycarbonates production.[13] Alternatively, the employment of discrete zinc-based catalysts for CO$_2$ fixation into cyclic carbonates has been also addressed, with particular prevalence on monometallic species.[2,5,14] For instance, efficient Zn(II)-NN'O Schiff-base catalysts[15a] have been recently reported to promote the cycloaddition of CO$_2$ and aliphatic and internal epoxides, in the presence of tetrabutylammonium bromide as cocatalyst (100 bar CO$_2$ pressure, 100 °C, 2 mol % catalyst loading). Moreover, several bicomponent NNN-based organozinc complexes have been also described as efficient catalyst in this process, such as that bearing imine-benzotriazole phenoxide ligands[15b] for the coupling of propylene oxide and styrene oxide with CO$_2$ (7 bar, 50 °C, 1-5 mol %), zinc(II) acetate complexes containing NNN bis(pyrazol-1-yl)pyridine-based planar ligands[15c] (10 bar, 75 °C, 0.1 mol %) and NOO zinc(II) complexes of arylhydrazones of β-diketones (40 bar, 80 °C, 1 mol %).[15d] Interestingly, alternative air-stable NNOO-donor salen derived Zn(II) based catalysts have been also recently communicated for propylene carbonate production (50 bar, 80 °C, 0.1-0.2 mol %).[15e]

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However, very high pressure or temperature were frequently needed. Also, special interest has recently received bimetallic zinc based systems,[16] such as the bicomponent bis-(Zn–salphen)/$^nBu_4NI$, which has proved excellent turnover frequencies (up to 14 800 h^{-1}) under mild conditions (1 bar of CO_2, 45 °C).[16c] However, less attention has been focused into bifunctional zinc catalysts,[17] which comprise the co-catalyst within the same moiety, and have proved that the cooperative effect between the functional groups can improve the catalytic performance and selectivity in this reaction.

On the other hand, our reach group has extensively been exploring the synthesis of well-defined alkyl/amide complexes based on biocompatible metals such as magnesium[18] and zinc,[19] supported by NNN and NNO-scorpionate ligands of the type [M(R)(κ^3-NNX)] (M = Mg, Zn; X = N, O), which have resulted effective living initiators for the hetero- and isoselective ROP of *rac*-lactide (*rac*-LA).[18-20] Appropriately, taking advance on our previous experience in the development of organo-zinc scorpionate systems, we focus now our efforts on the design of efficient zinc-based scorpionate catalysts for the CO_2 fixation into cyclic carbonates under mild conditions. Herein we report the synthesis and structural characterization of a new family of chiral zwitterionic NNO-heteroscorpionate zinc alkyls of the type [Zn(R)(κ^3-NNO)]Br. The application of these bifunctional species, as well as the analogs neutral mono- [Zn(R)(κ^3-NNO)] and binuclear [Zn(R)(κ^2-NNμ-O)Zn(R)$_2$] complexes for the production of cyclic carbonates from epoxides and carbon dioxide has been also studied in detail.
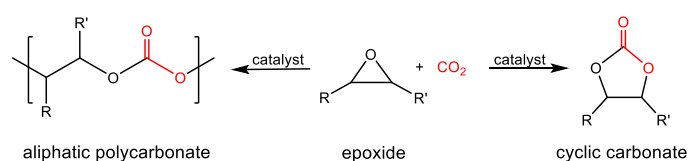

Scheme 1 Reaction of epoxides and CO_2 to produce cyclic- and polycarbonates.

Result and discussion

### Syntheses and catalytic activity of neutral scorpionate zinc complexes

The reaction of the previously reported alcohol heteroscorpionate precursors bpzampeH[21] (**1**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(dimethylamino)phenyl]ethanol}, bpzaepeH[21] (**2**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(diethylamino)phenyl]ethanol}, bpzimeH[21] (**3**) {2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[1-methyl-1*H*-imidazol-2-yl]ethanol}with [ZnR$_2$] in different stoichiometries (see Scheme 2) afforded the mononuclear monoalkyl zinc complexes [Zn(R)(κ^3-NNO)] (**4–12**) (κ^3-NNO = bpzampe, R = Me **4**, Et **5**, CH$_2$SiMe$_3$ **6**; bpzaepe, R = Me, **7**, Et **8**, CH$_2$SiMe$_3$ **9**; bpzime, R = Me, **10**) and the bimetallic trisalkyls [Zn(R)(κ^2-NNμ-O)Zn(R)$_2$] (**11–14**) (κ^2-NNμ-O = bpzampe, R = Me **11**, Et **12**; bpzaepe, R = Me **13**, Et **14**).[21]

Initially, mononuclear **4–10** and binuclear **11–14** alkyl zinc complexes were screened for the conversion of styrene oxide **15a** into styrene carbonate **16a** at room temperature and one bar carbon dioxide pressure, in the absence of any solvent for 3, 6 and 24 hours in a 1:1 molar ratio for complexes **4–14** and Bu$_4$NBr as co-catalyst, using 5 mol % of catalyst loading (see Scheme 3) and the results are presented in Table 1. For all complexes studied, the only species identified by ^{1}H NMR analysis were unreacted epoxide and styrene carbonate, while the formation of polycarbonate was not detected (selectivity > 99%). Conversions were determined by ^{1}H NMR analysis for each reaction without further purification.
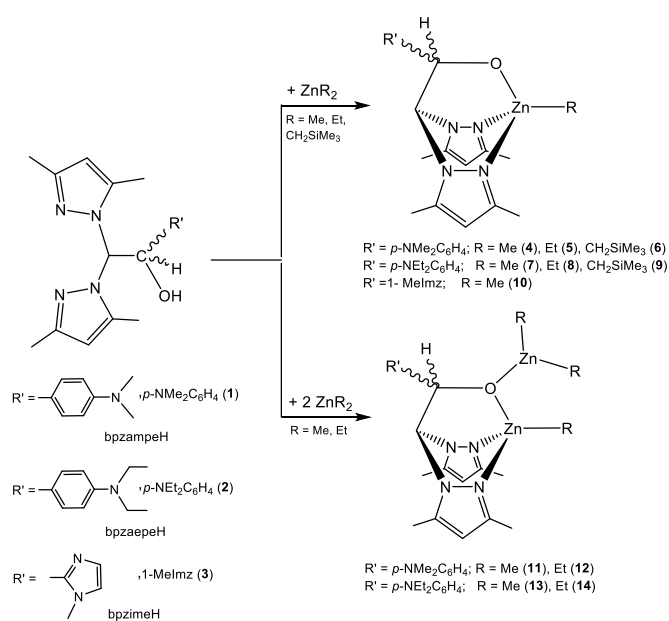
Scheme 2 Synthesis of the compounds **4-14**.[21]

The neutral binuclears **11–14** showed moderate activity values after 24 h (39-53%) (Table 1, entries 8, 12-14), considering the mild reaction conditions initially established at 25 °C and one bar CO_2 pressure. Contrarily, the neutral mononuclears **4–10** displayed lower levels of conversion (20-30%) in 24 h under otherwise identical reaction conditions (Table 1, entries 1-7). Interestingly, as the bimetallics **11–14** benefit from a zinc concentration of 10 mol % under these conditions, we decided to investigate for the most active derivative, complex **11**, whether the two zinc centers function separately or cooperatively, by changing the complex **11**/Bu$_4$NBr ratio. A control experiment for **11** maintaining the concentration of Bu$_4$NBr constant to 10 mol % (2 equivalents of Bu$_4$NBr per equivalent of catalyst **11**) revealed a slight increase in conversion (Table 1, entry 9), which is not consistent with a mechanism in which the two zinc centers act independently.[22]
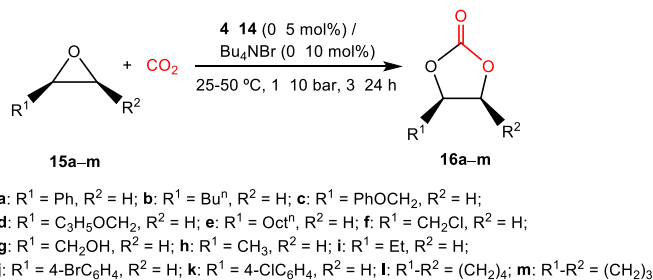
Scheme 3 Cyclic carbonate synthesis catalyzed by neutral complexes **4–14**.

In addition, we also performed a control experiment for **11** keeping the concentration of zinc constant at 5 mol % during the catalyst screening (Table 1, entry 10). This result showed that the activity of the analog monometallic **4** (Table 1, entry 1) is in fact lower than that observed for the bimetallic **11** per zinc center at 25 °C and 1 bar CO_2 pressure (32 and 39 % conv., respectively), evidencing an intramolecular cooperative effect between the two zinc centers. However, under these conditions, the monometallic complex **4** benefits now from a bromide concentration of 5 mol % versus a 2.5 mol % in the bimetallic **11**. Thus, to maintain the concentration of

bromide constant at 5 mol %, 2.5 mol % of external Bu_4NBr was added to the reaction mixture (Table 1, entry 11), given as a result an additional slight increase in the catalytic activity of **11** in comparison with **4** (32% and 42 % conv., respectively), which newly support this intramolecular cooperation between metal centers.

Table 1 Conversion of epoxide **15a** into styrene carbonate **16a** using catalysts **4–14**[a]

Entry	Catalyst	conv. 3 h[b] (%)	conv. 6 h[b] (%)	conv. 24 h[b] (%)
1	**4**	3	7	32
2	**5**	3	6	29
3	**6**	5	9	20
4	**7**	2	5	20
5	**8**	5	6	25
6	**9**	4	8	30
7	**10**	2	5	30
8	**11**	14	19	49
9[c]	**11**	12	22	53
10[d]	**11**	4	8	39
11[e]	**11**	5	9	42
12	**12**	10	15	39
13	**13**	10	14	38
14	**14**	12	19	42
15[f]	**4**	57	70	100
16[f]	**11**	73	90	100

[a] Reactions carried out at 25 °C and one bar CO_2 pressure using 5 mol % of complexes **4–14**/5 mol % of Bu_4NBr as co-catalyst unless specified otherwise. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] 5 mol % of complex + 10 mol % of Bu_4NBr. [d] 2.5 mol % of complex. [e] 2.5 mol % of complex + 5 mol % of Bu_4NBr. [f] Reactions carried out at 50 °C and 10 bar CO_2 pressure using 5 mol % of complex **4** or **14**/5 mol % of Bu_4NBr.

This effect was initially investigated by Coates *et al.* when β-diketiminato (BDI) zinc complexes[22b] were used as catalysts for the ROCOP of CHO and CO_2 for PCs production, and kinetic investigations revealed a necessary interaction between two zinc centers. This aspect has been also confirmed by North *et al.* in the case of bimetallic aluminum(salphen) complexes for the synthesis of CCs from epoxides and carbon dioxide,[22a] and very recently in our group when using bimetallic zinc scorpionate complexes **11–14** in the ring-opening polymerization of *rac*-lactide for the production of hetero-enriched poly(*rac*-lactides).[21] The effect of the alkyl group attached to the zinc center (Zn-R) could also be studied for the two neutral families assessed **4–10** and **11–14**. Thus, the presence of the methyl group had a favorable effect on the catalytic activity of derivatives **4** and **11** (Table 1, entries 1 and 8, respectively), possibly due to the presence of the less sterically hindered methyl substituent around the zinc coordination sphere, a determining aspect during the initial coordination of the epoxide to the metal center.

In addition, we decided to increase the initial temperature and pressure of the reaction for the most active complexes of each family (**4** and **11**) up to 50 °C and 10 bar CO_2 pressure, maintaining the catalyst loading at 5 mol % and the catalyst to co-catalyst ratio at 1:1 (see Table 1, entries 15-16). A similar trend was observed in this case, but surprisingly, both initiators reached good conversions in just 3 h, and the bimetallic catalyst **11** almost complete conversion in 6 h, under these still mild conditions (see Table 1, entry 16). Therefore,

we selected complex **11** as the most efficient neutral catalyst for reactions under these experimental conditions.

The effect of the halide counterion in the catalyst system was next assessed for complex **11** by employing different *tert*-butylammonium salts, at 50 °C and 10 bar CO_2 pressure after 3 hours. The results are shown on Table 2. Whereas fluoride counterion led to lower catalytic activity than the chloride and iodide ones, all of them resulted less active than the bromide anion (Table 2, entries 1-4), showing that the latest behaves as both a good nucleophile to ring-open the epoxide and a good leaving group for the cyclic carbonate formation. 1-methylimidazol (NMI) and 4-dimethylaminopyidine (DMAP) were also tested as co-catalysts, resulting poorly active systems (Table 2, entries 5 and 6, respectively). We therefore identified Bu_4NBr as the most efficient co-catalyst for complex **11** under these reaction conditions. Consistently, no conversion values were observed during the control experiments for complex **11** and Bu_4NBr, when both species were employed as catalyst in the absence of the other catalyst component, under these reaction conditions (Table 2, entries 7 and 8, respectively), which confirms that the presence of both catalyst components are necessary in the reaction mixture to produce the cycloaddition reaction.

The influence of reducing the catalyst loading was subsequently investigated for complex **11**. The results are also presented on Table 2. The catalyst/Bu_4NBr molar ratio was maintained at 1:1. A catalyst loading of 2.5 mol % afforded a very good conversion value (74 %) at 50 °C and 10 bar CO_2 pressure after 10 h (Table 2, entry 10), and therefore, it was identified as optimal loading for the bicomponent system **11**/Bu_4NBr under these experimental conditions.

Table 2 Studies on the influence of co-catalyst on the catalytic activity and optimization of the synthesis of styrene carbonate **16a**, using catalyst **11**[a]

Entry	**11** (mol %)	Bu_4NX (mol %)	conv.[b] (%)	TOF[c] (h^{-1})
1	5	F (5)	7	0.47
2	5	I (5)	53	3.53
3	5	Cl (5)	56	3.73
4	5	Br (5)	73	4.86
5	5	NMI (5)	18	1.20
6	5	DMAP (5)	6	0.40
7	5	0	0	0.00
8	0	Br (5)	4	0.27
9	1[d]	Br (1)	44	4.40
10	2.5[d]	Br (2.5)	74	2.96
11	5[d]	Br (5)	97	1.94
12	7.5[d]	Br (7.5)	95	1.27

[a] Reactions carried out at 50 °C and 10 bar CO_2 pressure for 3 h using 5 mol % of complex **11** and 5 mol % of Bu_4NX as co-catalyst unless specified otherwise. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] TOF = moles of product/(moles of catalyst·time). [d] Reaction time extended up to 10 h.

Having optimized the reaction conditions, we endeavor the preparation of thirteen cyclic carbonates **16a-16m** derived from monosubstituted epoxides **15a-15k**, which include alkyl, aryl and functionalized with alcohol, ether and halide groups, as well as internal epoxides **15l** and **15m**, using an equimolecular loading 2.5-5 mol % of the bimetallic complex **11** and Bu_4NBr at 10 bar of CO_2

pressure and 50 °C (see Figures S1-S13 in the Electronic Supporting Information, ESI†). The results are presented on Table 3. For each cyclic carbonate, the reactions were carried out for 15-24 h, then analyzed for conversion and purified for yield calculation.

To our delight, catalyst **11** proved to be an efficient and versatile catalyst for all epoxides assessed, since it gave very good to excellent conversions and yields to the corresponding cyclic carbonate under these reaction conditions. Interestingly, both the functionalized epoxides **15f** and **15g** (Table 3, entries 6 and 7) and aryl substituted epoxides **15j** and **15k** (Table 3, entries 10 and 11) yielded excellent conversions, and very good conversions were achieved for the alkyl/aryl derivatives **15a**-**15e, 15h** and **15i** (> 90 %, Table 3, entries 1-5, 8 and 9), evidencing an excellent broad substrate scope.

Table 3 Conversion of epoxides **15a-15m** into cyclic carbonates **16a-16m** using catalyst **11** and Bu₄NBr[a]

| Entry	Epoxide	conv.[b] (%)	Yield[c] (%)	TOF[d] (h^{-1})
1	**15a** (R^1 = Ph)	90	85	2.40
2	**15b** (R^1 = Bu^n)	95	87	2.53
3	**15c** (R^1 = PhOCH₂)	100	98	2.67
4	**15d** (R^1 = C₃H₅OCH₂)	100	99	2.67
5	**15e** (R^1 = Oct^n)	100	96	2.67
6	**15f** (R^1 = CH₂Cl)	100	97	2.67
7	**15g** (R^1 = CH₂OH)	100	97	2.67
8	**15h** (R^1 = CH₃)	99	98	2.64
9	**15i** (R^1 = Et)	100	98	2.67
10	**15j** (R^1 = 4-BrC₆H₄)	99	91	2.64
11	**15k** (R^1 = 4-ClC₆H₄)	100	94	2.67
12	**15l**[e] (R^1-R^2 = (CH₂)₄)	90	62	0.75
13	**15m**[e] (R^1-R^2 = (CH₂)₃)	83	57	0.70

[a] Reactions carried out at 50 °C and 10 bar CO₂ pressure for 15 h using 2.5 mol % of complex **11** and 2.5 mol % of Bu₄NBr as co-catalyst unless specified otherwise. [b] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] Yield of pure isolated cyclic carbonate. [d] TOF = moles of product/(moles of catalyst time). [e] Reaction time and catalyst loading were increased up to 24 h and 5 mol %, respectively.

Considering the high catalytic activity observed by the bicomponent system **11**/Bu₄NBr, we decided to extend this reaction to internal epoxides such as cyclohexene oxide **15l** and cyclopentene oxide **15m**. It is well-known that these substrates are more challenging reagents for cyclic carbonate synthesis, and in fact, as far as we are aware, very few examples of bimetallic zinc-based complexes have been reported for the successful production of cyclohexene and cyclopentene carbonates under the present mild conditions (20 bar of CO₂, 80 °C, 24 h).[16d] Therefore, we maintained the reaction temperature at 50 °C and 10 bar of CO₂ pressure, however, the cocatalyst loading and the reaction time were increased up to 5 mol % and 24 h, respectively. Interestingly, complex **11** showed very high conversion values for cyclohexene oxide (90%) and cyclopentane oxide (83%), (Table 3, entries 12 and 13, respectively), as a result of the added benefit for the existence of the two metal centers in this complex. By comparing the NMR spectra of cyclic carbonates **16l** and **16m** with those reported in the literature, we could confirm that the *cis*-isomer was the only isomer formed for cyclohexene[23] and cyclopentene[24] carbonates (Figures S12 and 13, respectively, in the

ESI†), indicating that the bicomponent system **11**/Bu₄NBr efficiently catalyzes the synthesis of these two cyclic carbonates with retention of the epoxide stereochemistry through a double inversion process.[23a]

Syntheses and catalytic activity of bifunctional scorpionate zinc complexes

In view of the catalytic potential of complexes **4**-**14** for the successful synthesis of a range of cyclic carbonates, we endeavored to develop new zwitterionic NNO-scorpionate zinc alkyls to behave as bifunctional catalysts comprising an electrophilic metal ion and a nucleophile quaternary ammonium salt in the same molecule for coupling of CO₂ with epoxides. With this aim in mind, the salts 3-benzyl-2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-(hydroxyethyl)]-1-methyl-1*H*-imidazol-3-ium bromide [(bzbpzimeH)Br] (**17**) and the 3-butyl-2-[2,2-bis(3,5-dimethylpyrazol-1-yl)-1-(hydroxyethyl)]-1-methyl-1*H*-imidazol-3-ium bromide [(bubpzimeH)Br] (**18**) were prepared by suitable quaternization of ligand **3** with an excess amount of (bromomethyl)benzene or bromobutane respectively. Then, after the appropriate workup, ammonium bromides **17** and **18** were isolated as a white and brown solid, respectively, in very good yields (*ca*. 98%) (Scheme 4*a*). However, quaternization reactions of ligands **1** or **2** proved unsuccessful. Unfortunately, the reaction of **1**–**3** with methyl iodide in excess to obtain the analogs ammonium iodide ligands resulted also fruitless.
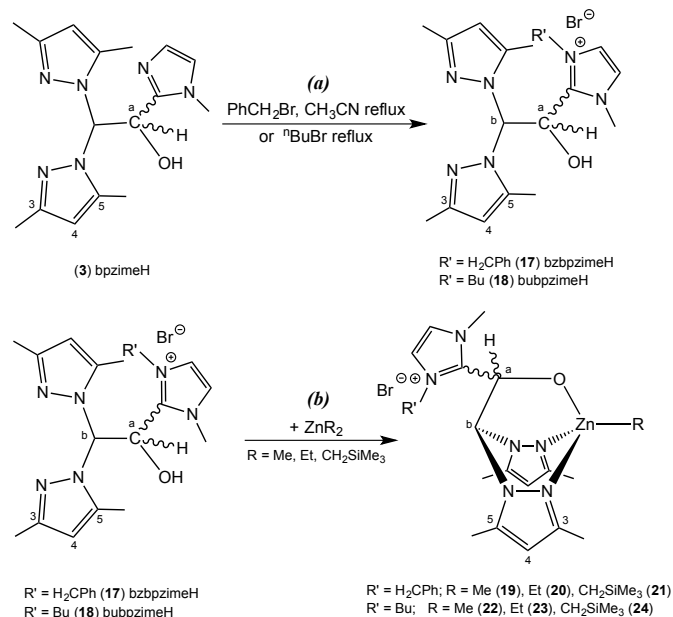

Scheme 4 Synthesis of the compounds **17** to **24**.

The alcohol-functionalized scorpionate compounds **17** and **18** were characterized spectroscopically (see Figures S14-S16 in the ESI†). The ^{1}H and ^{13}C{^{1}H} NMR spectra of both ligands exhibit two distinct sets of resonances for the two types of pyrazole rings and the ^{1}H NMR spectra show two signals from the methyl and R' groups in the imidazole moiety as a result of the quaternization. The phase-sensitive ^{1}H NOESY-1D spectra confirmed the assignments of the signals for the Me^3, Me^5 and H^4 groups of each pyrazole ring, and the ^{1}H-^{13}C heteronuclear correlation (g-HSQC) experiments enabled the assignment of the resonances corresponding to different carbon atoms (see the Experimental Section). As carbon atom (C^a) is a stereogenic center in compounds **17** and **18**, the presence in solution

of the two enantiomers was confirmed by adding a chiral shift reagent, namely (R)-(−)-(9-anthryl)-2,2,2-trifluoroethanol, giving rise to two signals for each proton in the ^{1}H NMR spectra, resulting from the two diastereoisomers of the corresponding two enantiomers.

The alcohols **17** and **18** (as racemic mixture) were subsequently reacted with [ZnR$_2$] (R = Me, Et, CH$_2$SiMe$_3$) in a 1:1 molar ratio in toluene to give, after the appropriate work-up, the mononuclear zwitterionic alkyl zinc complexes [Zn(R)(κ^3-NNO)]Br (**19–24**) (κ^3-NNO = bzbpzime, R = Me **19**, Et **20**, CH$_2$SiMe$_3$ **21**; bubpzime, R = Me, **22**, Et **23**, CH$_2$SiMe$_3$ **24**), which were isolated as white solids in good yield (*ca*. 90%) (Scheme 4b). The addition of one additional equiv. of [ZnR$_2$] to the monometallic alkyls **19–24** in order to prepare the corresponding bimetallic zwitterionic alkyl zinc complexes resulted fruitless, as untreatable mixtures were obtained.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the zwitterionic alkyls **19–24** (see Figures S17-S22 in the ESI†) contain two singlets for each of the H^4, Me^3 and Me^5 pyrazole protons, one broad singlet for each of the methine groups (CH bridge of the pyrazole rings and CH^a) and the signals corresponding to the R' moieties and the Zn-alkyl substituents. [1]H NOESY-1D experiments permitted the unequivocal assignment of all ^{1}H resonances, and the assignment of the ^{13}C{^{1}H} NMR signals was made on the basis of [1]H-^{13}C heteronuclear correlation (g-HSQC) experiments. Addition of a chiral shift reagent also confirmed the presence in solution of a racemic mixture. These results are consistent with a tetrahedral structure resulting from a κ^3-NNO coordination of the scorpionate ligand and the alkyl group to the zinc center (see Scheme 3b).[21]

Mononuclear zwitterionic complexes **19–24** were also screened for the conversion of styrene oxide **15a** into styrene carbonate **16a** at 25 °C and one bar carbon dioxide pressure, under solvent-free conditions for 3, 6 and 24 hours using 5 mol % of catalyst loading in the absence of co-catalyst (see Scheme 5). The results are presented in Table 4. As for the neutral species **4–14**, the only species identified were unreacted epoxide and styrene carbonate, with no formation of polycarbonate (selectivity > 99%), possibly due to the remote distance between the functional unit and the zinc metal center to copolymerize terminal epoxides and CO$_2$.[25] Whereas the zwitterionics **22–24** behaved as bifunctional catalysts and showed moderate activity values after 24 h under these conditions (40-50%), derivatives **19–21** did not reach any conversion values because of the lack of solubility of any complex in styrene oxide **15a** (Table 4, entries 5-7 and 2-4, respectively). Similar to what was observed for complexes **4–14**, the presence of the smaller Zn-alkyl group produced a positive result on the catalytic activity (Table 4, entry 5). Interestingly, catalysts **22–24** outperformed the catalytic activity displayed by the combination of their corresponding neutral monometallic derivatives and tetrabutylammonium bromide. Consistently, comparison of the activity data observed for the zwitterion **22** with the analog neutral **10** reveled an increase in the activity from 30 % to 47 % under otherwise identical conditions (Table 1, entry 7 and Table 4, entry 5, respectively). In the case of these bifunctional catalysts **22–24**, the pairing effect possibly generates a more Lewis acidic, and therefore a more active, zinc ion during the catalytic performance than in the case of the neutral monometallics **4–10**. As expected, a control experiment for the ligand **18** showed very low catalytic activity (Table 4, entry 1). This experiment evidenced the bifunctional nature of complex **22** as well as the cooperative effect between the functional groups in the moiety. Additionally, under the present conditions, the bifunctional catalyst **22** also demonstrated to be more efficient per Zn loading than the neutral bimetallic **11** (47 % *vs*. 42 % conv.; Table 4, entry 5 and Table 1, entry 11, respectively).
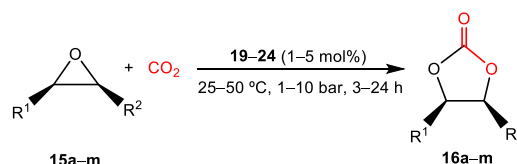
a: R^1 = Ph, R^2 = H; b: R^1 = Bu^n, R^2 = H; c: R^1 = PhOCH$_2$, R^2 = H;
d: R^1 = C$_3$H$_5$OCH$_2$, R^2 = H; e: R^1 = Oct^n, R^2 = H; f: R^1 = CH$_2$Cl, R^2 = H;
g: R^1 = CH$_2$OH, R^2 = H; h: R^1 = CH$_3$, R^2 = H; i: R^1 = Et, R^2 = H;
j: R^1 = 4-BrC$_6$H$_4$, R^2 = H; k: R^1 = 4-ClC$_6$H$_4$, R^2 = H; l: R^1-R^2 = (CH$_2$)$_4$; m: R^1-R^2 = (CH$_2$)$_3$

Scheme 5 Cyclic carbonate synthesis catalyzed by bifunctional complexes **19–24**.

Similar to the neutral complexes, increasing the initial temperature and pressure of the reaction up to 50 °C and 10 bar CO$_2$ pressure for the most active zwitterion **22** (5 mol % loading), produced almost complete conversion in 6 h (Table 4, entry 8), under these still mild conditions. In addition, 2.5 mol % was also identified as optimal loading for the bifunctional **22** (Table S1 in the ESI†). Under these optimized reaction conditions, the bifunctional catalyst **22** converted a broad range of alkyl, aryl, functionalized and internal epoxides **15a-15m** into their corresponding cyclic carbonates **16a-16m** in good to excellent yields, similarly to the neutral bimetallic complex **11**, at 10 bar of CO$_2$ pressure and 50 °C after 15-24 hours of cycloaddition reaction, using 2.5-5 mol % of catalyst loading. The results are presented in Figure 1. Notably, catalyst **22** displayed outstanding catalytic activity with functionalized epoxides **15c-15d** and **15f-15g**, which reacted very rapidly to afford the corresponding cyclic carbonates in yields higher than 95%. In contrast, aliphatic and aromatic epoxides exhibited inferior reactivity – especially **15h** – possibly due to the lower solubility of the catalyst in the epoxide. Given the potential of complex **22** as catalyst, it was also investigated the catalytic activity towards the production of cyclic carbonates **16l-16m** from internal epoxides **15l-15m**. We were delighted to find that the bifunctional catalyst **22** resulted efficient for the synthesis of disubstituted cyclic carbonates **16l** and **16m** in good yields, with complete stereochemical preference for the *cis*-isomer, at 50 °C and 10 bar CO$_2$ pressure in 24 hours, using 5 mol % of loading (see Figures S23-S24 in the ESI†), considering that the very few examples of bifunctional zinc-based catalysts described until now for the successful production of cyclic carbonates from internal epoxides required much more energic conditions.[17]

Table 4 Conversion of epoxide **15a** into styrene carbonate **16a** using catalysts **19–24**^{a}

Entry	Catalyst	conv. 3 h^b (%)	conv. 6 h^b (%)	conv. 24 h^b (%)
1	**18**	0	2	5
2	**19**	-	-	-
3	**20**	-	-	-
4	**21**	-	-	-
5	**22**	10	23	47
6	**23**	8	20	38
7	**24**	7	17	39
8	**22**^{c}	63	87	100

^{a} Reactions carried out at 25 °C and one bar CO$_2$ pressure using 5 mol % of complexes **19–24** unless specified otherwise. ^{b} Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. ^{c} Reactions carried out at 50 °C and 10 bar CO$_2$ pressure under identical conditions.
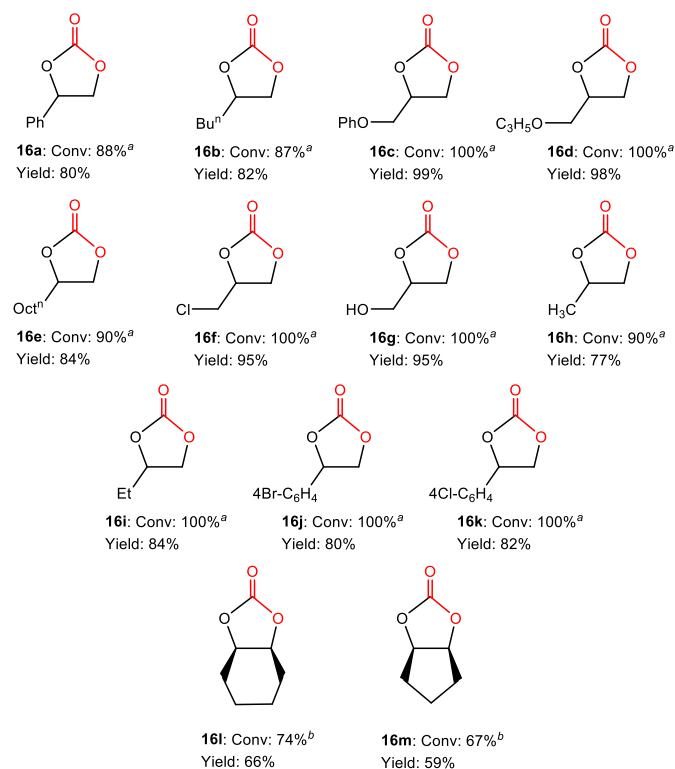
Figure 1 [a] Synthesis of cyclic carbonates **16a–16m** from epoxides **15a–15m** and carbon dioxide using a 2.5 mol % of complex **22** at 50 °C and 10 bar CO_2 pressure for 15 hours. [b] Reaction time and catalyst loading were increased up to 24 h and 5 mol %, respectively.

16a: Conv: 88%[a] Yield: 80%
16b: Conv: 87%[a] Yield: 82%
16c: Conv: 100%[a] Yield: 99%
16d: Conv: 100%[a] Yield: 98%
16e: Conv: 90%[a] Yield: 84%
16f: Conv: 100%[a] Yield: 95%
16g: Conv: 100%[a] Yield: 95%
16h: Conv: 90%[a] Yield: 77%
16i: Conv: 100%[a] Yield: 84%
16j: Conv: 100%[a] Yield: 80%
16k: Conv: 100%[a] Yield: 82%
16l: Conv: 74%[b] Yield: 66%
16m: Conv: 67%[b] Yield: 59%

Considering that complex **22** resulted very active in the synthesis of cyclic carbonates **16a−16m** with retention of the epoxide stereochemistry, a plausible mechanism for cyclic carbonate production catalyzed by this bifunctional zinc complex is presented in Scheme 6. The mechanism agrees with those previously proposed for one-component scorpionate aluminum complexes,[26] used for coupling CO_2 and epoxides into cyclic carbonates, which present the combination of a Lewis acid and a nucleophile in the same molecule. The proposal is consistent with the initial coordination of the epoxide, subsequent nucleophilic attack of the bromide to the less sterically hindered carbon atom of the epoxide, CO_2 insertion, and final ring-closing of the cyclic carbonate.

Conclusions

We report here the design of new chiral zwitterionic NNO-scorpionate mononuclear zinc alkyls [Zn(R)(κ^3-NNO)]Br by suitable quaternization in the scorpionate ligand, which can act as effective catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide. The study has led to the development of the zinc alkyl derivative **22**, which acts as an efficient bifunctional catalyst under mild and solvent-free conditions for the synthesis of cyclic carbonates not only from terminal epoxides, but also from internal epoxides and carbon dioxide, thus exhibiting a broad substrate scope and functional group tolerance. The investigation also includes catalytic assessment of the analog neutral mononuclears [Zn(R)(κ^3-NNO)] and binuclears [Zn(R)(κ^2-NNμ-O)Zn(R)$_2$] in the present of Bu$_4$NBr as optimized cocatalyst, with excellent conversions reached for the same cyclic carbonates in the case of the bimetallic **11**, as a result of the beneficial intramolecular
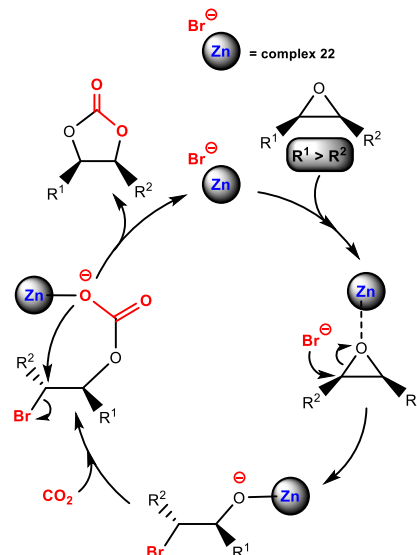
Scheme 6 Plausible mechanism for the conversion of epoxides and CO_2 into cyclic carbonates catalyzed by complex **22**.

effect between the two zinc centers. Nonetheless, the bicomponent system **11**/Bu$_4$NBr displayed lower activity than catalyst **22** considering the zinc mol % loadings, evidencing that when using these NNO-scorpionate zinc alkyls for cyclic carbonate production, a one-component complex is more efficient than a bicomponent bimetallic system.

Even though several zinc-based catalyst systems have been reported for CO_2 fixation into cyclic carbonates in the last few years,[14-17] there are still significant efforts in developing more efficient catalysts based on non-toxic and biocompatible metals such as zinc, which could catalyze this reaction under mild conditions. In this context, bifunctional catalytic systems are centering great attention in recent years, and in comparison with one-component catalysts previously reported,[17] the bifunctional derivative **22** catalyzes the cycloaddition reaction of a wider range of epoxides[17c] and CO_2 into their corresponding cyclic carbonates, in shorter reaction times and at lower temperature and carbon dioxide pressure for the most challenging epoxides (130 °C, 10 bar of CO_2, 5 h;[17a] 120 °C, 17 bar, 32-72 h;[17b] 100 °C, 30 bar, 16 h;[17c]) still using low catalyst loadings.

Experimental Section

General Procedures

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Solvents were predried over sodium wire and distilled under nitrogen from sodium (n-hexane), sodium-benzophenone (THF and diethyl ether) or diphosphorus pentaoxide (acetonitrile). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. Compounds **1**-**14** were prepared as reported previously.[21] The reagents Bu^{n}Li, 1-methyl-2-imidazolecarboxaldehyde, (bromometyl)benzene, 1-bromobutane, Li(CH$_2$SiMe$_3$), [ZnCl$_2$] and [ZnR$_2$] (R = Me, Et) were used as purchased (Aldrich).

Instruments and Measurements

NMR spectra were recorded on a Bruker Advance Neo 500 spectrometer (^{1}H NMR: 500 MHz; ^{13}C NMR: 125 MHz) and were

referenced to the residual deuterated solvent signal. ^{1}H NMR homodecoupled and NOESY-1D spectra were recorded on the same instrument with the following acquisition parameters: irradiation time 2 s and 256 scans, 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 17–24

Synthesis of (bzbpzimeH) (17). To a 250 cm^3 Schlenk tube charged with bpzimeH (**3**)[21] (1.00 g, 3.18 mmol) was added 60 mL of acetonitrile followed by the addition of 0.38 cm^3 (3.18 mmol) of benzyl bromide via syringe. The mixture was refluxed overnight. Solvent was removed under vacuum and the residue was washed with *n*-hexane (50 mL) to give **17** as a white solid. Yield 98% (1.51 g, 3.11 mmol). Anal. Calcd for $C_{23}H_{29}BrN_6O$: C, 56.91; H, 6.02; N, 17.31; Found: C, 56.41; H, 5.71; N, 17.79; ^{1}H NMR (CD$_3$CN, 297 K): δ 7.44-7.35 (m, 6H, Ph) 7.39 (s, 1 H, C=C$_{im}$), 7.18 (s, 1 H, C=C$_{im}$), 6.45 (bd, 1 H, CH^a), 6.36 (d, 1 H, CH^b), 5.89 (s, 1 H, H$^{4'}$), 5.80 (s, 1 H, H^4), 5.69 (d, 1 H, BrC$\underline{H}_2$-Ph), 5.62 (d, 1 H, BrC$\underline{H}_2$-Ph), 4.12 (s, 3 H, NMe$_{im}$), 2.28 (s, 3 H, Me$^{3'}$), 2.15 (s, 3 H, Me^3), 2.13 (s, 3 H, Me$^{5'}$), 2.11 (s, 3 H, Me^5). ^{13}C-{^{1}H} NMR (CD$_3$CN, 297 K): δ 142.0-134.1, (C$^{3\ or\ 5}$) 129.8, 129.7, 127.2 (BrCH$_2$-$\underline{Ph}$), 124.8, 122.6 (C=C$_{im}$), 106.8, 106.2 (C$^{4-4'}$), 69.8 (CH^a), 65.1 (CH^b), 51.7 (BrC$\underline{H}$-Ph), 31.3 (NMe$_{im}$), 12.6, 12.3 (Me$^{3-3'}$), 10.0, 9.9 (Me$^{5-5'}$).

Synthesis of (bubpzimeH) (18). The synthesis of **18** was carried out in an identical manner to **17**, using bpzimeH (**3**)[21] (1.00 g, 3.18 mmol) and 1-bromobutane (0.34 cm^3, 3.18 mmol). Yield 99% (1.42 g, 3.15 mmol). Anal. Calcd for $C_{20}H_{31}BrN_6O$: C, 53.22; H, 6.92; N, 18.62; Found: C, 53.01; H, 7.06; N, 18.89; ^{1}H NMR (CDCl$_3$, 297 K): δ 7.18 (s, 1 H, C=C$_{im}$), 6.89 (bs, 1 H, C=C$_{im}$), 6.63 (d, 1 H, CH^a), 6.40 (d, 1 H, CH^b), 5.82 (s, 1 H, H$^{4'}$), 5.79 (s, 1 H, H^4), 4.18 (m, 2 H, BrC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$), 4.08 (s, 3 H, NMe$_{im}$), 2.29 (s, 3 H, Me$^{3'}$), 2.20 (s, 6 H, Me$^{5-5'}$), 2.07 (s, 3 H, Me^3), 1.83 (m, 2 H, BrCH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 1.42 (m, 2 H, BrCH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$), 0.96 (t, 3 H, BrCH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$). ^{13}C-{^{1}H} NMR (CDCl$_3$, 297 K): δ 149.3, 148.7, 144.0, 141.0 (C$^{3\ or\ 5}$), 123.9, 121.2 (C=C$_{im}$), 108.1, 107.6 (C$^{4-4'}$), 70.9 (CH^a), 64.4 (CH^b), 49.1 (BrC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$), 37.9 (NMe$_{im}$), 32.0 (BrCH$_2$-$\underline{C}H_2$-CH$_2$-CH$_3$), 20.0 (BrCH$_2$-CH$_2$-$\underline{C}H_2$-CH$_3$), 13.9 (BrCH$_2$-CH$_2$-CH$_2$-$\underline{C}H_3$), 13.9, 13.8 (Me$^{3-3'}$), 9.9, 9.8 (Me$^{5-5'}$).

Synthesis of [Zn(Me)(bzbpzime)] (19). In a 250 cm^3 Schlenk tube, bzbpzimeH (1.0 g, 2.06 mmol) was dissolved in dry THF (60 mL) and the solution was cooled to -70 ^{o}C. A solution of [ZnMe$_2$] (2.0 M in toluene) (1.03 mL, 2.06 mmol) was added and the mixture was allowed to warm up to room temperature and stirred during 1 h. The solvent was evaporated to dryness under reduced pressure to yield a white product. The product was washed with *n*-hexane to give compound **19**. Yield: 90% (1.05 g, 1.85 mmol). Anal. Calcd. for $C_{24}H_{31}BrN_6OZn$: C, 51.03; H, 5.53; N, 14.88; Found: C, 51.32; H, 5.68; N, 14.74; ^{1}H NMR (CD$_3$CN, 297 K): δ 7.40-7.30 (m, 6H, Ph), 7.29 (s, 1 H, C=C$_{im}$), 7.24 (s, 1 H, C=C$_{im}$), 6.25 (s, 1 H, CH^a), 6.17 (s, 1 H, CH^b), 6.06 (s, 2 H, H$^{4-4'}$), 5.55 (d, 1 H, BrC$\underline{H}_2$-Ph), 5.00 (d, 1 H, BrC$\underline{H}_2$-Ph), 3.64 (s, 3 H, NMe$_{im}$), 2.28 (s, 3 H, Me$^{3'}$), 2.23 (s, 3 H, Me^3), 2.19 (s, 3 H, Me$^{5'}$), 2.01 (s, 3 H, Me^5), -0.67 (s, 3 H, Zn-CH$_3$). ^{13}C-{^{1}H} NMR (CD$_3$CN, 297 K): δ 142.0-134.1 (C$^{3\ or\ 5}$), 129.1, 128.7, 118.1 (BrCH$_2$-$\underline{Ph}$), 124.2, 122.2 (C=C$_{im}$), 106.9, 106.2 (C$^{4-4'}$), 75.2 (CH^a), 67.3 (CH^b), 50.8 (BrC$\underline{H}_2$-Ph), 35.4 (NMe$_{im}$), 12.1, 12.0 (Me$^{3-3'}$), 10.2, 10.1 (Me$^{5-5'}$), 0.19 (Zn-Me).

Synthesis of [Zn(Et)(bzbpzime)] (20). The synthesis of **20** was carried out in an identical manner to **19**, using [ZnEt$_2$] (1.0 M in hexane) (2.06 mL, 2.06 mmol). Yield: 91% (1.08 g, 1.87 mmol). Anal. Calcd. for

$C_{25}H_{33}BrN_6OZn$: C, 51.87; H, 5.75; N, 14.52; Found: C, 52.19; H, 5.84; N, 14.61; ^{1}H NMR (CD$_3$CN, 297 K), δ 7.40-7.20 (m, 6H, Ph), 7.39 (s, 1 H, C=C$_{im}$), 7.32 (s, 1 H, C=C$_{im}$), 6.25 (s, 1 H, CH^a), 6,17 (s, 1 H, CH^b), 6.07 (s, 2 H, H$^{4-4'}$), 5.55 (d, 1 H, BrC$\underline{H}_2$-Ph), 4.96 (d, 1 H, BrC$\underline{H}_2$-Ph), 3.65 (s, 3 H, NMe$_{im}$), 2.30 (s, 3 H, Me$^{3'}$), 2.24 (s, 3 H, Me^3), 2.20 (s, 3 H, Me$^{5'}$), 1.99 (s, 3 H, Me^5), 1.27 (t, 3 H, Zn-CH$_2$C$\underline{H}_3$), 0.29 (q, 2 H, Zn-C$\underline{H}_2$CH$_3$). ^{13}C-{^{1}H} NMR (CD$_3$CN, 297 K): δ 142.0-135.0 (C$^{3\ or\ 5}$), 129.2, 128.8, 118.2 (BrCH$_2$-$\underline{Ph}$), 124.3, 122.5 (C=C$_{im}$), 106.6, 106.5 (C$^{4-4'}$), 76.2 (CH^a), 68.1 (CH^b), 50.6 (BrC$\underline{H}_2$-Ph), 35.5 (NMe$_{im}$), 13.8 (Zn-CH$_2$C$\underline{H}_3$), 12.1–9.9 (Me$^{3,3',5',5}$), −1.0 (Zn-$\underline{C}H_2$CH$_3$).

Synthesis of [Zn(CH$_2$SiMe$_3$)(bzbpzime)] (21). A solution of [(trimethylsilyl)methyllithium, Li(CH$_2$SiMe$_3$)] 0.7 M in hexane (5.88 mL, 4.12 mmol) was added to a cooled (–40 ^{o}C), stirred suspension of [ZnCl$_2$] (0.28 g, 2.06 mmol) in diethyl ether (50 mL) in a 250 cm^3 Schlenk tube. The mixture was allowed to warm up to room temperature and stirred for 2 h. An increase in turbidity was observed and this finally led to the formation of a white suspension. The suspension was filtered and the filtrate, corresponding to Zn(CH$_2$SiMe$_3$)$_2$, was added to a 250 cm^3 Schlenk tube containing a precooled (–20 °C) solution of bzbpzimeH (1.0 g, 2.06 mmol) in diethyl ether (50 mL). The mixture was allowed to warm up to room temperature and stirred during 30 minutes. The ether was evaporated to dryness under reduced pressure to yield a white product. The product was washed with cold hexane (30 mL) to give a white solid identified as **21**. Yield: 90% (1.18 g, 1.85 mmol). Anal. Calcd. For $C_{27}H_{39}BrN_6OSiZn$: C, 59.91; H, 6.17; N, 13.19; Found: C, 59.45; H, 6.37; N, 13.21; ^{1}H NMR (CD$_3$CN, 297 K), δ 7.40-7.29 (m, 6H, Ph), 7.37 (s, 1 H, C=C$_{im}$), 7.15 (s, 1 H, C=C$_{im}$), 6.30 (s, 1 H, CH^a), 6,15 (s, 1 H, CH^b), 6.06 (s, 2 H, H$^{4-4'}$), 5.90 (d, 1 H, BrC$\underline{H}_2$-Ph), 5.64 (d, 1 H, BrC$\underline{H}_2$-Ph), 3.70 (s, 3 H, NMe$_{im}$), 2.30 (s, 3 H, Me$^{3'}$), 2.23 (s, 3 H, Me^3), 2.19 (s, 3 H, Me$^{5'}$), 1.98 (s, 3 H, Me^5), -0.06 (s, 9 H, Zn-CH$_2$Si$\underline{Me}_3$), -0.79 (d, 1 H, Zn-C$\underline{H}_2$SiMe$_3$) -0.82 (d, 1 H, Zn-C$\underline{H}_2$SiMe$_3$). ^{13}C-{^{1}H} NMR (CD$_3$CN, 297 K): δ 142.0-134.0 (C$^{3\ or\ 5}$), 129.2, 128.6, 118.2 (BrCH$_2$-$\underline{Ph}$) 124.1, 122.0 (C=C$_{im}$), 106.3, 106.0 (C$^{4-4'}$), 67.9 (CH^a), 65.1 (CH^b), 52.2 (BrC$\underline{H}_2$-Ph), 36.2 (NMe$_{im}$), 12.4-9.9 (Me$^{3-3',5-5'}$), 3.6 (Zn-CH$_2$Si$\underline{Me}_3$), − 6.0 (Zn-$\underline{C}H_2$SiMe$_3$).

Synthesis of [Zn(Me)(bubpzime)] (22). The synthesis of **22** was carried out in an identical manner to **19**, using bubpzimeH (1.0 g, 2.22 mmol), [ZnMe$_2$] (2.0 M in toluene) (1.1 mL, 2.22 mmol). Yield: 89% (1.05 g, 1.97 mmol). Anal. Calcd. For $C_{21}H_{33}BrN_6OZn$: C, 47.52; H, 6.27; N, 15.83; Found: C, 47.69; H, 6.30; N, 15.48; ^{1}H NMR (CD$_3$CN, 297 K), δ 7.32 (s, 1 H, C=C$_{im}$), 7.31 (s, 1 H, C=C$_{im}$), 6.92 (d, 1 H, CH^a), 6.22 (s, 1 H, H$^{4'}$), 6.12 (s, 1 H, CH^b), 6.09 (s, 1 H, H^4), 4.0 (m, 2 H, BrC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$), 3.66 (s, 3 H, NMe$_{im}$), 2.40 (s, 3 H, Me$^{3'}$), 2.31 (s, 3 H, Me$^{5'}$), 2.25 (s, 3 H, Me^5), 2.19 (s, 3 H, Me^3), 1.85-1.60 (m, 2 H, BrCH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 1.30 (m, 2 H, BrCH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$), 0.92 (t, 3 H, BrCH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$), -0.62 (s, 3 H, Zn-CH$_3$). ^{13}C-{^{1}H} NMR (CD$_3$CN, 297 K): δ 151.0 − 141.0 (C$^{3\ or\ 5}$), 128.3, 123.7 (C=C$_{im}$), 106.7, 106.1 (C$^{4-4'}$), 75.1 (CH^a), 67.3 (CH^b), 47.7 (BrC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$), 31.3 (NMe$_{im}$), 19.1 (BrCH$_2$-$\underline{C}H_2$-CH$_2$-CH$_3$), 15.5 (BrCH$_2$-CH$_2$-$\underline{C}H_2$-CH$_3$), 12.8 (BrCH$_2$-CH$_2$-CH$_2$-$\underline{C}H_3$), 13.4, 13.2 (Me$^{3-3'}$), 10.3, 10.1 (Me$^{5-5'}$), 0.1 (Zn-Me).

Synthesis of [Zn(Et)(bubpzime)] (23). The synthesis of **23** was carried out in an identical manner to **20**, using bubpzimeH (1.0 g, 2.22 mmol), [ZnEt$_2$] (1.0 M in hexane) (2.22 mL, 2.22 mmol). Yield: 87% (1.05 g, 1.93 mmol). Anal. Calcd. For $C_{22}H_{35}BrN_6OZn$: C, 48.50; H, 6.48; N, 15.42; Found: C, 48.81; H, 6.40; N, 15.73; ^{1}H NMR (CD$_3$CN, 297 K): δ 7.36 (s, 2 H, C=C^{im}), 6.27 (s, 1 H, CH^a), 6.18 (s, 1 H, CH^b), 6.07 (s, 1 H, H^4), 6.06 (s, 1 H, H$^{4'}$), 4.00 (bs, 2 H, BrC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$), 3.71 (s, 3 H, NMe$_{im}$), 2.33 (s, 3 H, Me$^{3'}$), 2.28 (s, 6 H, Me$^{5-5'}$), 2.26 (s, 3 H, Me^3), 1.85 (m, 2 H, BrCH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 1.60 (m, 2 H, BrCH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$),

1.29 (t, 3 H, BrCH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$), 0.91 (t, 3 H, Zn-CH$_2$C$\underline{H}_3$), 0.28 (q, 2 H, Zn-C$\underline{H}_2$CH$_3$). ^{13}C-{^{1}H} NMR (CD$_3$CN, 297 K): δ 150.0 – 142.0 (C$^{3 \text{ or } 5}$), 123.8, 121.6 (C=C$_{im}$), 106.8, 106.3 (C$^{4\text{-}4'}$), 75.1 (CH^a), 62.3 (CH^b), 47.8 (BrCH$_2$-CH$_2$-CH$_2$-CH$_3$), 35.6 (BrCH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 31.9 (NMe$_{im}$), 19.3 (BrCH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$), 12.7 (BrCH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$), 12.4 (Zn-CH$_2$C$\underline{H}_3$), 12.2, 12.1 (Me$^{3\text{-}3'}$), 10.5, 9.9 (Me$^{5\text{-}5'}$), -4.0 (Zn-C$\underline{H}_2$CH$_3$).

Synthesis of [Zn(CH$_2$SiMe$_3$)(bubpzime)] (24). The synthesis of **24** was carried out in an identical manner to **21**, using bubpzimeH (1.0 g, 2.22 mmol), Li(CH$_2$SiMe$_3$) 0.7 M in hexane (6.34 mL, 4.44 mmol) and [ZnCl$_2$] (0.30 g, 2.22 mmol). Yield: 87% (1.16 g, 1.92 mmol). Anal. Calcd. For C$_{24}$H$_{41}$BrN$_6$OSiZn: C, 47.80; H, 6.85; N, 13.94; Found: C, 47.63; H, 7.04; N, 13.61; ^{1}H NMR (CD$_3$CN, 297 K): δ 7.30 (s, 1 H, C=C^{im}), 7.26 (s, 1 H, C=C^{im}), 6.23 (s, 1 H, CH^a), 6.19 (s, 1 H, CH^b), 6.06 (s, 2 H, H$^{4\text{-}4'}$), 3.70 (bs, 2 H, BrC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$) 3.61 (s, 3 H, NMe$_{im}$), 2.30 (s, 6 H, Me$^{3\text{-}3'}$), 2.27 (s, 6 H, Me$^{5\text{-}5'}$), 1.80 (m, 2 H, BrCH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 1.30 (m, 2 H, BrCH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$), 0.91 (t, 3 H, BrCH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$), 0.01 (s, 9H, Zn-CH$_2$SiMe$_3$), −0.76 (s, 2H, Zn-C$\underline{H}_2$SiMe$_3$). ^{13}C-{^{1}H} NMR (CD$_3$CN, 297 K): δ 150.0 – 142.0 (C$^{3 \text{ or } 5}$), 123.9, 121.8 (C=C$_{im}$), 106.8, 106.1 (C$^{4\text{-}4'}$), 67.5 (CH^a), 63.8 (CH^b), 48.3 (BrC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$). 31.7 (NMe$_{im}$), 19.6 (BrCH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 15.2 (BrCH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$), 12.4 (BrCH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$), 12.1, 12.0 (Me$^{3\text{-}3'}$) 10.2, 10.0 (Me$^{5\text{-}5'}$), 2.9 (Zn-CH$_2$SiMe$_3$), −2.1 (Zn-C$\underline{H}_2$SiMe$_3$).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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