One-component aluminium(heteroscorpionate) catalysts for the formation of cyclic carbonates from epoxides and carbon dioxide

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**Abstract:** New neutral and zwitterionic chiral NNO-donor scorpionate ligands (**1** and **2**) have been designed to obtain new mononuclear and dinuclear NNO-heteroscorpionate aluminium complexes. Reaction of **1** with [AlR3] (R = Me, Et) in a 1:1 or 1:2 molar ratio afforded the neutral mononuclear alkyl complexes [AlR2(*κ*2-bpzappe)], R = Me (**3**), Et (**4**) and bimetallic complexes [{AlR2(*κ*2-bpzappe)}(*µ*-O){AlR3}], R = Me (**5**), Et (**6**). By reaction of complexes (**3****6**) with PhCH2Br, mononuclear and dinuclear zwitterionic aluminium complexes [AlR2(*κ*2-bbpzappe)]Br, R = Me (**7**), Et (**8**), and [{AlR2(*κ*2-bbpzappe)}(*µ*-O){AlR3}]Br, R = Me (**9**), Et (**10**), were synthesised. Both, neutral aluminium complexes in the presence of Bu4NBr and zwitterionic aluminium complexes were investigated as catalysts for cyclic carbonate formation from epoxides and carbon dioxide. Amongst them, complex **10** was found to be an efficient one-component catalysts for the synthesis of cyclic carbonates from both monosubstituted and internal epoxides and showing broad substrate scope.

Introduction

The use of carbon dioxide (CO2) as a universal renewable resource is a challenge for chemists. It requires efficient strategies for the conversion of CO2 into economically competitive products to help to stabilise and reduce atmospheric carbon dioxide levels to mitigate the greenhouse effect and develop an alternative and sustainable raw material.[1] One of the most promising reactions in this field is the synthesis of cyclic carbonates from epoxides and CO2,[2] where the driving force is provided by release of the ring strain energy in the three-membered ring of the epoxide to afford the more stable five-membered cyclic compound. This overcomes the thermodynamic inertia of a stable molecule such as CO2 (Scheme 1). Different catalytic systems for this reaction have been designed, including metal complexes,[3] bifunctional catalysts[4] and organocatalysts.[5] Bifunctional systems, or one-component catalysts, have been less developed probably owing to their more synthetically demanding preparation, although bifunctionality has proven to be highly useful in various cases to create more powerful catalysts.[4]

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**Scheme 1.** Synthesis of cyclic carbonates from epoxides and CO2.

Among these catalysts, heteroscorpionate aluminium complexes in combination with quaternary ammonium salts show relatively high catalytic activity.[6] Various metal centres can be incorporated into the heteroscorpionate ligand and the versatility of the heteroscorpionate moiety permits control of the spatial arrangement of the functional groups attached to it.[7] Therefore, the catalytic activity of heteroscorpionate complexes can be tuned further by suitable functionalisation.[8]



**Scheme 2.** Bimetallic aluminium heteroscorpionate catalysts.

In previous work, we designed and synthesised bimetallic aluminium heteroscorpionate complexes containing an oxo-bridge between the two aluminium centres and investigated their application as catalysts for the conversion of epoxides into the corresponding cyclic carbonates (Scheme 2).[6a] Notably, a combination of some of these compounds and tetrabutylammonium bromide (TBAB) forms a very efficient catalyst system for the conversion of a broad range of internal epoxides to cyclic carbonates with, unusually, higher catalytic activity for the synthesis of cyclopentene carbonate than for cyclohexene carbonate.[6a]

With the aim of developing new aluminium heteroscorpionate complexes as bifunctional catalysts for CO2 fixation, we report here the design of a new heteroscorpionate precursor that makes possible, the synthesis and characterisation of a series of neutral and zwitterionic chiral heteroscorpionate alkyl aluminium complexes. Some of these complexes behave as one-component catalysts, comprising an electrophilic metal ion and a nucleophilic quaternary ammonium salt in the same molecule for the coupling of CO2 with epoxides. These catalysts exhibit excellent activity to form the corresponding five-membered cyclic carbonates products. Intramolecular cooperative catalysis is suggested to contribute to the observed high activity and excellent stereochemical control.

Results and Discussion

**Syntheses and structural characterisation.** The synthesis of the heteroscorpionate precursor 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(dimethylamino)phenyl]-1-phenylethanol (bpzappeH) (**1**), was achieved through an efficient synthetic route previously reported for the synthesis of alcohol-containing heteroscorpionate ligands.[9] Thus, the one-pot reaction of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[10] with *n*BuLi, followed by the addition of [4-(dimethylamino)phenyl](phenyl)methanone and then saturated aqueous ammonium chloride, afforded the desired compound (bpzappeH) (**1**), which was isolated as a pale yellow solid in good yield (90%) after the appropriate work-up (Scheme 3). The salt N-benzyl-4-[2,2-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1-hydroxy-1-phenylethyl]-N,N-dimethylbenzenaminium bromide (bbpzappeH)Br (**2**) was prepared by reaction of compound **1** with an excess of (bromomethyl)benzene in acetonitrile at 60 ºC. After the appropriate workup, the ammonium bromide (**2**) was isolated as a green-yellow solid in 70% yield (Scheme 3). Compounds **1** and **2** were isolated as racemic mixtures.

 **Scheme 3.** Synthesis of bpzappeH (**1**) and (bbpzappeH)Br (**2**).

The alcohol functionalised heteroscorpionate compounds were characterised spectroscopically (see the Experimental Section). The 1H and 13C-{1H} NMR spectra of **1** and **2** contain two sets of signals for the pyrazole rings, indicating that the two pyrazole rings are not equivalent. The quarternisation of the amine moiety gave rise to two signals from the methyl groups from the amine moiety and resulted in the methylene protons from the benzyl group becoming an AB system (Figure 1). 1H NOESY-1D experiments were also performed to confirm the assignment of the signals for the Ph, ArNMe2, ArNMe2CH2Ph, Me3, Me5 and H4 groups. 1H-13C heteronuclear correlation (g-HSQC) experiments enabled the assignment of the resonances corresponding to different carbons (see the Experimental Section). It is worth noting that ligand precursor **2** was found to be metastable, slowly loosing benzyl bromide to reform compound **1** in solution. Nevertheless, compound **2** could be characterised by 1H-NMR.

The mononuclear and dinuclear alkyl-aluminium neutral complexes [AlR2(*κ*2-bpzappe)], R = Me (**3**), Et (**4**) and [{AlR2(*κ*2-bpzappe)}(*µ*-O){AlR3}], R = Me (**5**), Et (**6**) were synthesised by reaction of the neutral alcohol containing heteroscorpionate precursor **1**, with one or two equivalents of the corresponding trialkylaluminium compound (Scheme 4). The reactions were carried out in dry toluene and complexes **3****6** were isolated as racemates in excellent yields (~90%) after the appropriate workup, as light yellow solids. Reaction of neutral complexes **3****6** with PhCH2Br in dry acetonitrile afforded the mononuclear and dinuclear zwitterionic aluminium complexes [AlR2(*κ*2-bbpzappe)]Br, R = Me (**7**), Et (**8**), and [{AlR2(*κ*2-bbpzappe)}(*µ*-O){AlR3}]Br, R = Me (**9**), Et (**10**) respectively in quantitative yields (Scheme 4). These complexes were found to be stable in solution and did not decompose to a mixture of neutral complexes and benzyl bromide, in contrast to ligand precursor **2**. In the dinuclear complexes **5**, **6**, **9** and **10** the second aluminium centre is coordinated through a dative bond to the oxygen atom of the alkoxide moiety (Scheme 4).

**Figure 1.** 1H NMR spectra of bpzappeH (**1**) and (bbpzappeH)Br (**2**).



**Ph**

**OH**

**NMe2**

**Ph**

**Me3‘**

**Me3,5,5‘**

**H4**

**H4‘**

**CH**

**NMe2**

**CH2Ph**

**Ph**

**Ph**

**CH**

**H4‘**

**H4**

**Me5‘**

**Me5**

**Me3,3‘**

The solution-state structures of complexes **3**–**10** were characterised by spectroscopic methods. The 1H and 13C{1H} NMR spectra of **3**–**10** show two sets of pyrazole resonances, indicating that the pyrazole rings are inequivalent. The 1H NMR spectra of these complexes show two singlets for each of the H4, Me3 and Me5 pyrazole protons and one singlet for the signals corresponding to the alkyl ligands. It is worth highlighting that some pyrazole proton and alkyl ligands signals appear as broad resonances (Figure 2), indicating the possible existence of fluxional behaviour due to a slow exchange process between the coordinated and the non-coordinated pyrazole ring. This behaviour has previously been observed in other heteroscorpionate aluminium complexes.[6a,11]

 **Scheme 4.** Synthesis of aluminium scorpionate complexes **3****10**.







**CH**

**Hp,p‘**

**NMe2**

**AlMe2**

**AlMe3**

**Me3‘**

**Me3**

**Me5,5‘**

**Hm**

**Hm‘**

**Ho**

**Ho‘**

**H4,4‘**

**Figure 2.** 1H NMR spectra of [{AlMe2(*κ*2-bpzappe)}(*µ*-O){AlMe3}] (**5**) and [{AlMe2(*κ*2-bbpzappe)}(*µ*-O){AlMe3}]Br (**9**).

**Ph**

**CH2Ph**

**Ph**

**NMe2**

**AlMe2**

**AlMe3**

**Me5**

**Me3,3‘,5‘**

**CH**

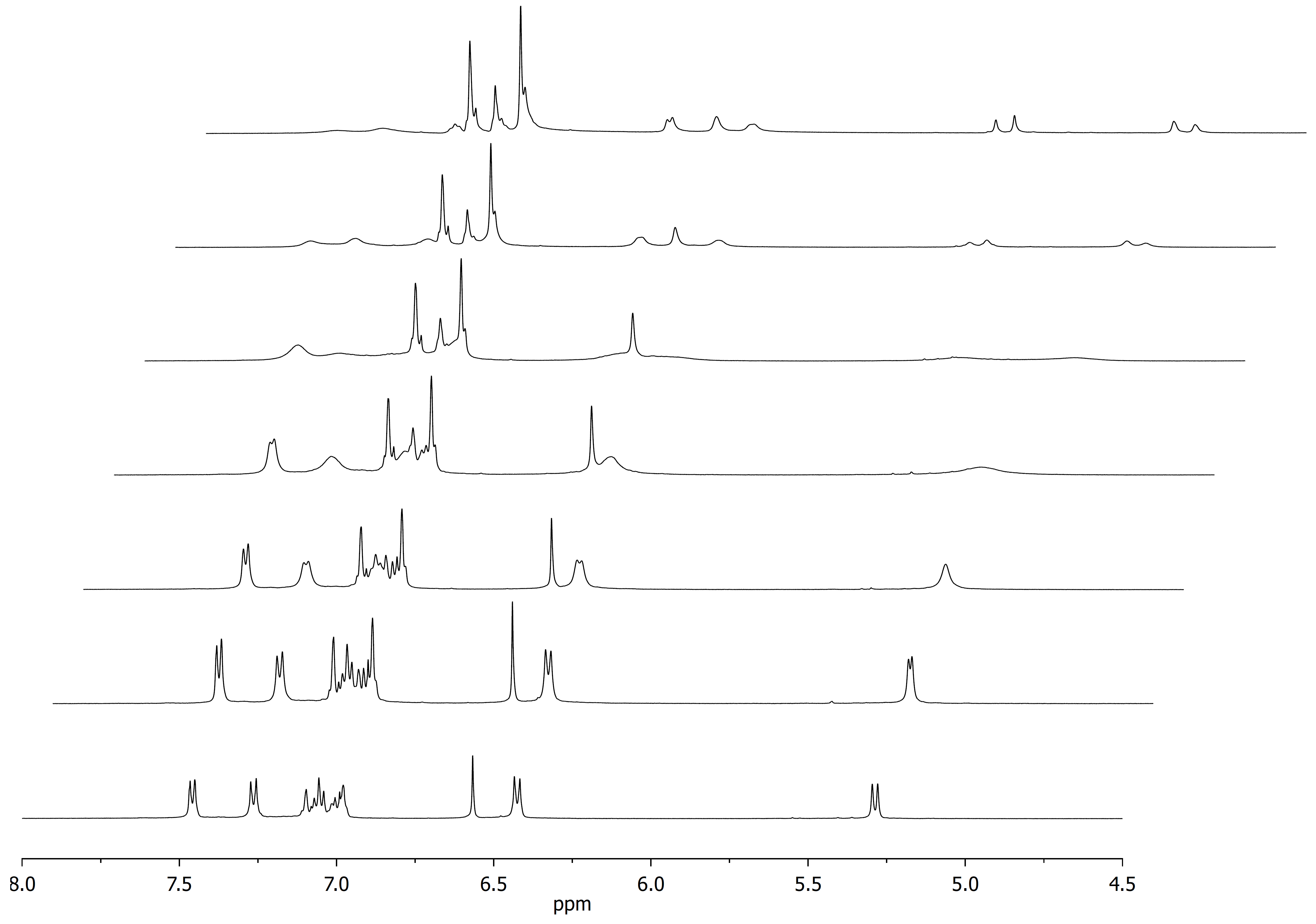
**H4**

**H4‘**

For the unequivocal assignment of most NMR resonances corresponding to the pyrazole rings and alkyl groups, NOESY-1D NMR and 1H-13C heteronuclear correlation (g-HSQC) experiments were carried out (see Experimental Section). Based on the data obtained, a tetrahedral disposition for each aluminium atom could be proposed, with the heteroscorpionate ligand coordinated in a *k*2-NO coordination mode for the monometallic complexes **3**, **4**, **7** and **8**, or a *k*2-NO-*µ*-O coordination mode, bridging the two aluminium centres for complexes **5**, **6**, **9** and **10** (Scheme 4).

To investigate the dynamic behaviour observed in complexes **3**–**10**, a VT-NMR study was carried out and the spectra obtained for compound **4** are shown in Figure 3. The VT NMR analysis showed that the resonances of the pyrazole rings broaden and become resolved indicating the presence of two diastereoisomers (Scheme 5) at –93 ºC (Figure 3). Therefore, there is an exchange process between the coordinated and the non-coordinated pyrazole rings, involving an interconversion from one diastereoisomer to the other. It is worth mentioning that the methine carbon bridging the two pyrazole rings is a stereocentre due to the coordination mode of heteroscorpionate ligand. For complexes **3**–**10**, there are four stereoisomers due to the presence of a racemic heteroscorpionate ligand (Scheme 5).

 **Scheme 5.** Structures for the four stereoisomers of complex **4**.

**Figure 3.** VT-NMR study in the region from 8.0 to 4.5 ppm for compound **4** in toluene-d8.

**40 ºC**

**60 ºC**

**20 ºC**

**0 ºC**

**25 ºC**

**93 ºC**

**80 ºC**

**Ph**

**Ph**

**Ph**

**CH**

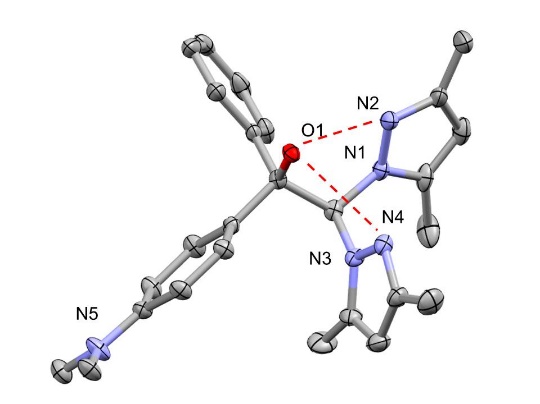
**H4,4‘**

**Ph**

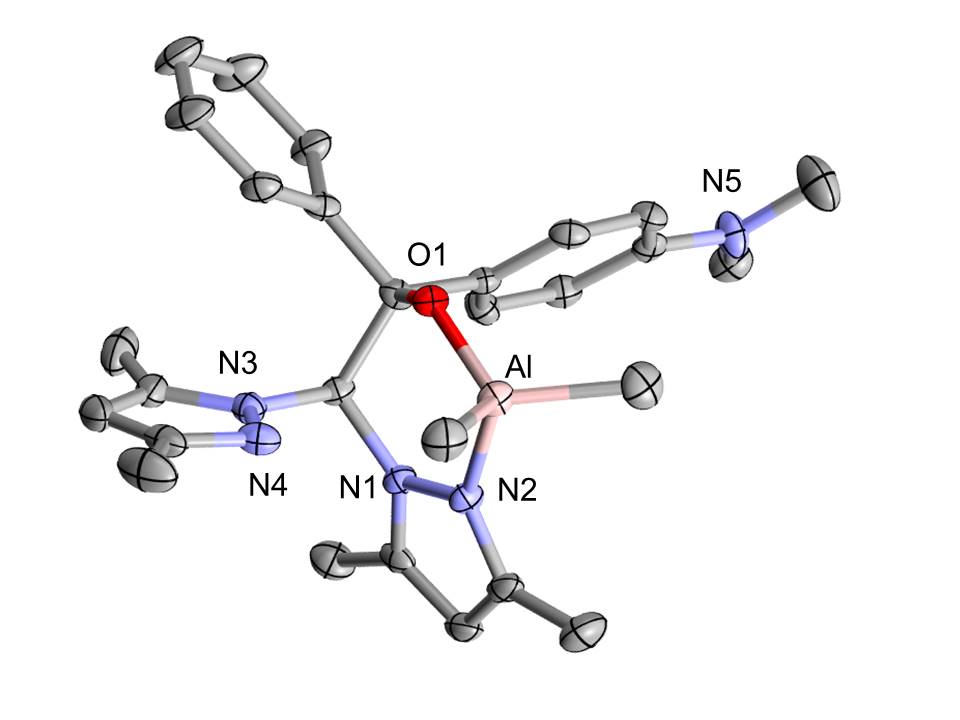
**Ph**

**CH**

**H4,4‘**

** Figure 4.** MERCURYperspectives drawing of compound **1**. Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity. Note: Mercury is Crystal Structure Visualisation Software of Cambridge Structural Database.

The solid-state structures of ligand **1** and complex **3** were determined by single crystal X–ray diffraction.[12] The corresponding MERCURY drawings of **1** and **3** are depicted in Figures 4 and 5, respectively. The crystallographic data and selected bond interatomic distances and angles are given in Tables S1–S3 of the supporting information. Compound **1** crystallises in monoclinic group *P*21/*c*. In ligand **1**, the pyrazole rings are oriented in a quasi-parallel disposition with respect to each other with a dihedral angle of 83.69º. This disposition is due to the presence of strong hydrogen bonds involving O1, N2 and N4 (red lines in figure 4) with bond lengths of 2.722 and 2.984 Å. Moreover, these molecules pack with stacking interactions between pyrazole rings with distances around 3.568 Å.

 **Figure 5.** MERCURYperspectives drawing of compound **3**. Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity. Note: Mercury is Crystal Structure Visualisation Software of Cambridge Structural Database.

In complex **3**, the heteroscorpionate ligand is *κ*2-NO coordinated to the aluminium centre through O1, and N2 atoms (Figure 5). This compound crystallises in the *P*-1 triclinic group in which, the aluminium centre is coordinated to two alkyl ligands. Therefore, this complex consists of mononuclear entities in which the aluminium atom adopts a distorted tetrahedral geometry. The dihedral angle between the N2-Al-O1 and C27-Al-C28 planes has a value of 86.28º which is consistent with a tetrahedral geometry. The Al-N and Al-O distances are 1.986(3) and 1.747(2), respectively. Furthermore, the Al-C distances, 1.952(4) Å and 1.970(4) Å are in good agreement with literature data. The crystalline structure is consistent with those proposed in Scheme 4 on the basis of solution-state NMR data.

**Synthesis of cyclic carbonates.** The synthesis of styrene carbonate **12a** from styrene oxide **11a** and carbon dioxide at 25 oC and one bar carbon dioxide pressure under solvent free conditions for 24 hours using 5 mol% of catalyst was chosen as the reaction to screen complexes **3**–**10** as catalysts (Scheme 6) and the reactions were monitored by 1H NMR spectroscopy. The results are shown in Table 1 (See Supporting Information for further details). It is worth noting that no polycarbonate formation was detected under the aforementioned reaction conditions and selectivity towards the cyclic carbonate was always >99%. This result suggests that the functional unit is not near enough to the metal center to copolymerise terminal epoxides and CO2, as reported by Lu and Darensbourg.[13]

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | |  | |  |
| **Table 1.** Synthesis of **12a**catalysed by **2**–**10**.[a] | | | | | | | |
| Entry | Cat. | Cocat. | 25 oC (%)[b] | 25 oC (%)[b],[c] | | 25 oC (%)[b],[d] | 50 oC (%)[b] |
| 1 | **2** | - | 3 | 1 | | 1 | 12 |
| 2 | **3** | Bu4NBr | 15 | 8 | | 14 | 90 |
| 3 | **4** | Bu4NBr | 32 | 15 | | 20 | 92 |
| 4[e] | **5** | Bu4NBr | 22 | 18 | | 21 | 84 |
| 5 | **5** | Bu4NBr | 33 | 18 | | 24 | 91 |
| 6[e] | **6** | Bu4NBr | 28 | 16 | | 24 | 92 |
| 7 | **6** | Bu4NBr | 42 | 17 | | 27 | 95 |
| 8 | **7** | - | 15 | 13 | | 14 | 94 |
| 9 | **8** | - | 21 | 13 | | 12 | 95 |
| 10[e] | **9** | - | 27 | 17 | | 20 | 72 |
| 11 | **9** | - | 28 | 18 | | 23 | 97 |
| 12[e],[f] | **9** | Bu4NBr | 27 | 19 | | 25 | 99 |
| 13[e] | **10** | - | 26 | 15 | | 18 | 80 |
| 14 | **10** | - | 38 | 16 | | 20 | 98 |
| 15[e],[f] | **10** | Bu4NBr | 39 | 17 | | 22 | 100 |
| [a] Reactions carried out at 1 bar CO2 pressure for 24 hours using 5 mol% of complex and 5 mol% of Bu4NBr cocatalyst unless specified otherwise. [b] Conversion determined by 1H NMR spectroscopy or gas chromatography of the crude reaction mixture after 24h. [c] Using propylene carbonate as a solvent. [d] Using acetonitrile as a solvent. [e] 2.5 mol% of complex. [f] 2.5 mol% of complex + 2.5 mol% of Bu4NBr. | | | | | | | |

When neutral complexes **3**–**6** were used as catalyst, TBAB was added as a cocatalyst. Complexes **3**–**10** displayed from low to moderate catalytic activity for the synthesis of styrene carbonate **12a** under these conditions. As can be seen in Table 1, when 5 mol% of complexes **7**–**10** was used in the absence of TBAB, similar conversion to the combination of neutral complexes **3**–**6** and TBAB was obtained, thus showing that catalysts **7**–**10** are indeed one-component catalysts. Control experiments showed that ligand **2** was not catalytically active (Table 1, entry 1). The low catalytic activity appeared to be related to the low solubility of the catalysts in the epoxide. Therefore, the use of a solvent was investigated in order to increase the conversion to the cyclic carbonate. However, the use of a solvent was detrimental and the conversion was lower than that obtained at 25 oC under solvent free conditions (Table 1). Thus, the effect of increasing the reaction temperature to 50 oC was studied.



**Scheme 6.** Synthesis of cyclic carbonates using catalysts **2**–**10**.

As can be seen in Table 1, complexes **3****10** gave almost complete conversion of styrene oxide to styrene carbonate at 1 bar pressure of carbon dioxide and 50 oC after 24 h. Notably, reactions catalysed by complexes **3****6** and TBAB again gave similar conversions to reactions catalysed by one-component catalysts **7****10**. Since compounds **5**–**6** and **9**–**10** are bimetallic, experiments in which the concentration of aluminium was 5 mol% were carried out using an Al:TBAB ratio of 2:1 (Table 1, entries 4, 6, 10 and 13). The results showed that bimetallic complexes **9**–**10** are more active than mononuclear complexes **7**–**8** at room termperature. The same trend was observed when acetonitrile or propylene carbonate were used as a solvent. On the other hand, when the reaction was carried out at 50 oC, mononuclear complexes **7**–**8** displayed higher catalytic activity than bimetallic complexes **9**–**10** (Table 1, entries 8–10 and 13). However, complexes **7**–**8** benefit from a bromide concentration of 5 mol%. Therefore, in order to keep the bromide concentration constant at 5 mol%, 2.5 mol% of TBAB was added to reactions catalysed by complexes **9** and **10** (Table 1, entries 12 and 15) and the results showed that bimetallic complexes **9**–**10** displayed higher catalytic activity than monometallic complexes **7**–**8**. Amongst complexes **9**–**10**, complex **10** was the most active catalyst.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | | | |  | |  |
| **Table 2.** Synthesis of **12a**catalysed by **10**.[a] | | | | | | |
| Entry | **10** (mol%) | 25 oC (%)[b] | 50 oC (%)[b] | | 80 oC (%)[b] | |
| 1 | 0.5 | 6 | 48 | | 92 | |
| 2 | 1 | 10 | 65 | | 97 | |
| 3 | 1.5 | 18 | 70 | | 98 | |
| 4 | 2.5 | 26 | 80 | | 98 | |
| 5 | 5 | 38 | 98 | | 99 | |
| [a] Reactions carried out at 1 bar CO2 pressure for 24 hours. [b] Conversion determined by 1H NMR spectroscopy or gas chromatography of the crude reaction mixture after 24h. | | | | | | |

Since complex **10** was the most active one-component catalyst, it was studied for further optimisation. Firstly, the effect of the reaction temperature and the amount of catalyst **10** was investigated in reactions carried out at 1 bar pressure of carbon dioxide with styrene oxide **11a** as substrate. The results are shown in Table 2. It is apparent that reactions carried out at 25 oC and 50 oC using less than 5 mol% of catalyst **10** gave lower conversions than 98%. However, when the reaction temperature is increased to 80 oC, 92–99% conversion could be obtained using 0.5–5mol% of complex **10**.



**Figure 6.** Effect of water on the synthesis of styrene carbonate **11a** catalysed by complex **10**.

Then, the effect of adding water to the reaction mixture was investigated as we have previously shown that small amounts of water are beneficial when using alkyl aluminium complexes.[6] As shown in Figure 6, the addition of small amounts of water has a beneficial effect on the synthesis of styrene carbonate from styrene oxide and carbon dioxide catalysed by complex **10** and the addition of 0.2 mol% water increased the conversion from 21% to 35%. However, addition of more than 0.2 mol% of water was detrimental, probably due to hydrolysis of aluminium complex **10**. Therefore, it seems that complex **10** is a precatalyst and the catalytically active species contains aluminium-oxo units.

Having optimised the reaction conditions for the synthesis of styrene carbonate **12a** from styrene oxide **11a**, we investigated the conversion of a range of terminal epoxides (**11b**–**l**) into their corresponding cyclic carbonates (**12b**–**l**) using 0.5–1 mol% of catalyst **10** at 80 oC for 24 hours (Scheme 6) and the results are shown in Figure 7. In order to overcome potential issues due to the volatility of some aliphatic epoxides, reactions were carried out in a sealed reactor at 80ºC and 10 bar carbon dioxide pressure. However, a few experiments were carried out at 1 bar pressure of carbon dioxide using substrates with high boiling points to study how complex **10** performs for substrates **11a**,**h**,**i**,**l** (Figure 7). In all cases, good to excellent conversions and yields of these substrates into their corresponding cyclic carbonates **12a**,**h**,**i**,**l** were obtained under these reaction conditions.



**Figure 7.** Synthesis of cyclic carbonates **12a**–**l** from epoxides **11a**–**l** and carbon dioxide catalysed by complex **10**.

In general, good to excellent conversions and yields of terminal epoxides **11b**–**l** into the corresponding cyclic carbonates **12b**–**l** were obtained under these reaction conditions. It is worth noting that complex **10** is not only tolerant of aryl epoxides but also alkyl epoxides and those functionalised with alcohols, ethers and halides, showing that the catalyst is highly versatile under these reaction conditions. Notably, catalyst is **10** highly selective towards cyclic carbonate formation and no polycarbonate or other side-product is observed during the reaction.



**Scheme 7.** Synthesis of disubstituted cyclic carbonates using catalyst **10**.

To further study the substrate scope of the complex **10** as catalyst, the synthesis of disubstituted cyclic carbonates from their corresponding internal epoxides was investigated (Scheme 7) and the results are shown in Figure 8. Even though these substrates are more challenging for cyclic carbonate formation, excellent catalysts have been developed over the last few years.[2,3,4,6a]



**Figure 8.** Synthesis of cyclic carbonates **14a**–**f** from epoxides **13a**–**f** and carbon dioxide catalysed by complex **10**.

We firstly optimised the reaction conditions using cyclohexene oxide as model substrate (See Supporting Information). The synthesis of cyclohexene carbonate **14a** from cyclohexene oxide **13a** was attempted using 0.5 mol% of catalyst **10** at 80 oC and 10 bar of carbon dioxide pressure for 24 hours. However, low conversion was obtained. Therefore, the reaction pressure and the catalyst loading were increased to 20 bar and 1.5 mol% respectively. Under these conditions, cyclic carbonates **14a**-**d** were obtained in 50−82% yield (Figure 8). Cyclohexene oxide **13a** and cyclopentene oxide **13b** were found to be good substrates for cyclic carbonate formation, giving cyclic carbonates **14a,b** in 75% and 82% yield respectively (Figure 8). C*is–* and *trans*–epoxybutane **13c,d** were used as substrates for the synthesis of cyclic carbonates **14c,d**. When *cis*–epoxybutane **13c** was used, the cyclic carbonate product was obtained with a 94:6 mixture of *cis–* and *trans*–cyclic carbonates **14c,d** (See Supporting Information). Similarly, when *trans*–epoxybutane **13d** was used as substrate, the cyclic carbonate was isolated in a 96:4 mixture of *trans–* and *cis*–cyclic carbonates **14c,d**, showing that the reactions occur with retention of the epoxide stereochemistry (See Supporting Information). As shown in Figure 8, the isolated yield of **14d** is slightly lower than **14c**, probably due to the fact that the synthesis of cyclic carbonates from *cis*–epoxybutane **13c** is more challenging than from *trans*–epoxybutane **13d**.[14] However, for cyclic carbonate **14f**, the yield was rather low and the effect of increasing the catalyst loading to 2.5 mol% was investigated (See Supporting Information). Using higher catalyst loading was beneficial, giving 89% isolated yield. Similarly, for cyclic carbonate **14e**, the reaction temperature and the catalyst loading had to be increased to 90 oC and 5 mol% respectively. Under these reaction conditions, 88% yield was achieved. It is worth highlighting that no polycarbonate formation was observed under the reaction conditions showing a selectivity towards cyclic carbonate formation higher than 99%. Moreover, the synthesis of cyclic carbonates **14 a–f** catalysed by complex **10** occurs with retention of the epoxide stereochemistry, indicating that there are two inversions of the stereochemistry at the less hindered carbon atom of the epoxide during the reaction. Thus, a plausible catalytic cycle for the synthesis of cyclic carbonates using scorpionate aluminium catalyst **10** is shown in Scheme 8, which is consistent with the mechanism previously proposed for cyclic carbonate formation catalysed by scorpionate aluminium complexes.



**Scheme 8.** Plausible mechanism for the synthesis of cyclic carbonates from epoxides and carbon dioxide catalysed by complex **10**

Conclusions

We have designed a new NNO-heteroscorpionate ligand to obtain novel neutral and zwitterionic aluminium heteroscorpionate complexes. NMR spectroscopy and single-crystal X-ray studies allowed us to establish a *κ*2-NO coordination mode for the mononuclear complexes and a *κ*2-NO-*μ*-O coordination mode for the dinuclear complexes.

Complexes **7****10** in the absence of a cocatalyst act as one-component catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide. The study has led to the development of the bimetallic bifunctional aluminium complex **10**, which acts as an efficient catalyst system for the synthesis of cyclic carbonates from carbon dioxide and epoxides in good to excellent yields. The catalyst system is not only active for the synthesis of cyclic carbonates from terminal epoxides, but also from internal epoxides, thus displaying a broad substrate scope.

Although there are many aluminium-based catalyst systems that have been developed for the synthesis of cyclic carbonates from epoxides and carbon dioxide,[13,6] only a few one-component catalyst systems act as efficient catalyst for the synthesis of cyclic carbonates from internal epoxides.[15]  We have shown that complex **10** is an efficient catalyst for the synthesis of cyclic carbonates from challenging internal epoxides giving good yields under optimal reaction conditions.

Experimental Section

All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (toluene, *n*-hexane) and distilled under nitrogen from sodium (toluene) or sodium-potassium alloy (*n*-hexane). Deuterated solvents were stored over activated 4Å molecular sieves and degassed by several freeze-thaw cycles. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyser. 1H and 13C NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent. NOESY-1D spectra were recorded with the following acquisition parameters: irradiation time 2 s and number of scans 256, using standard VARIAN-FT software. Two-dimensional NMR spectra were acquired using standard VARIAN-FT software and processed using an IPC-Sun computer. Commercially available chemicals (Alfa, Aldrich, Fluka) were used as received.

**Synthesis of bpzappeH (1)**.In a 250 cm3 Schlenk tube, bdmpzm (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm3) and cooled to −70 ºC. A 1.6 M solution of *n*BuLi (3.06 cm3, 4.89 mmol) in hexane was added, and the suspension was stirred for 1 h.The reaction mixture was warmed to −10 ºC and the resulting yellow suspension was added dropwise to a cooled (−10 ºC) solution of [4-(dimethylamino)phenyl](phenyl)methanone (1.10 g, 4.89 mmol) in dry THF (20 cm3). The reaction mixture was stirred for 1 h and was allowed to warm to ambient temperature. The product was hydrolyzed with 15 mL of saturated aqueous NH4Cl (which was added dropwise). The organic layer was extracted, dried over MgSO4 overnight, filtered and the solvent was removed under vacuum to give the product as a white solid. This solid was crystallised from *n*-hexane. Yield: 90% (1.88 g, 4.40 mmol). Calcd for C26H31N5O: C, 72.70; H, 7.27; N, 16.30. Found: C, 72.94; H, 7.80; N, 16.09. 1H NMR (500 MHz, CDCl3, 297 K): δ = 7.81 (s, 1H, OH), 7.31 (m, 2H, oHPh), 7.17 (m, 2H, *m*HPh), 7.14 (m, 1H, *p*HPh), 7.10 (d, 3*J*H-H = 6.4 Hz, 2H, *m*H-NPh) 6.87 (s, 1H, CH), 6.56 (d, 3*J*H-H = 6.4 Hz, 2H, *o*H-NPh), 5.69 (s, 1H, H4’), 5.64 (s, 1H, H4), 2.88 (s, 6H, N*Me2*), 2.08 (s, 3H, Me3’), 2.02 (s, 3H, Me3), 2.01 (s, 6H, Me5’,5); 13C{1H} NMR (125 MHz, CDCl3, 297 K): δ = 149.3, 146.9, 146.7, 145.5, 140.3, 140.0, 132.8 (C*ipso,p*-N*Ph* ,C3,3’, C5,5, Cipso-*Ph*), 127.8 (*m*CPh), 127.5 (*m*CN-Ph), 126.8 (*p*CPh), 126.3 (*o*CPh), 111.8 (Co-N-*Ph*), 106.1 (C4’), 106.0 (C4), 81.6 (Ca), 74.3 (CH), 40.5 (N*Me2*), 13.5 (Me3’), 13.3 (Me3), 11.2 (Me5’,5).

**Synthesis of (bbpzappeH)Br (2)**.In a 250 cm3 Schlenk tube, compound **1** (1.00 g, 2.33 mmol) was dissolved in dry acetonitrile (70 cm3). The benzyl bromide (0.83 cm3, 6.99 mmol) was added and the reaction mixture was heated to 60 ºC and stirred during 16 h. The solvent was remove under vacuum and the reaction crude was washed with hexane (3x25 cm3) to remove the excess of benzyl bromide. After drying the resulting solid, compound **2** was isolated as a green-yellow solid. Yield: 70% (0.97 g, 1.63 mmol). Calcd for C33H38BrN5O: C, 65.99; H, 6.38; N, 11.66. Found: C, 66.43; H, 6.81; N, 11.17. 1H NMR (500 MHz, CDCl3, 297 K): δ = 7.60-6.97 (m, 14H, Ph), 6.87 (s, 1H, CH), 5.75 (s, 1H, H4’), 5.67 (s, 1H, H4), 5.60 (m, 2H, *CH2*Ph), 3.94 (s, 3H, N*Me2*), 3.89 (s, 3H, N*Me2*), 2.10 (s, 3H, Me5’), 2.04 (s, 6H, Me3’,3), 1.96 (s, 3H, Me5); 13C{1H} NMR (125 MHz, CDCl3, 297 K): δ = 147.6, 147.5, 147.2, 143.0, 142.7, 141.0, 140.8, 132.6 (C*ipso,p*-N*Ph* ,C3,3’, C5,5, Cipso-Ph*,* C*ipso*-CH2Ph), 130.4-121.0(o,mC-Ph) 130.4-121.0 (o,m,pC-N*Ph*), 106.9 (C4’), 106.4 (C4), 81.4 (Ca), 73.7 (CH), 72.7 (*CH2*Ph), 53.5, 52.9 (N*Me2*), 13.5 (Me3’), 13.3 (Me3), 11.3 (Me5’), 11.0 (Me5).

**Synthesis of [AlMe2{*κ*2-bpzappe}] (3)**.In 250 cm3 Schlenk tube, bpzappeH **(1)**.(1.0 g, 2.33 mmol) was dissolved in dry toluene (70 cm3) and heated to 60 ºC. A solution of AlMe3 (2 M in toluene, 1.2 cm3 , 2.33 mmol) was added and the reaction mixture was stirred at this temperature for 2 h. The solvent was removed under reduced pressure to give complex **3** as a light yellow solid. The product was washed with n-hexane (25 mL) and recrystallised from toluene at **–**26ºC to give compound **3** as yellow crystals. Yield: 94 % (1.07 g). Calcd for C28H36AlN5O: C, 69.25; H, 7.47; N, 14.42. Found: C, 69.53; H, 7.89; N, 14.03. 1H NMR (500 MHz, C6D6, 297 K): δ = 7.58 (m, 2H, *o*HPh), 7.39 (3*J*H-H = 9.2 Hz, 2H, *m*H-NPh), 7.10 (m , 2H, *m*HPh), 7.03 (m, 1H, *p*HPh), 6.65 (s, 1H, CH), 6.50 (d, 3*J*H-H = 9.2 Hz, 2H, *o*H-NPh), 5.31 (s, 1H, H4’), 5.30 (s, 1H, H4), 2.46 (s, 6H, N*Me2*), 2.12 (s, 3H, Me3’), 2.10 (s, 3H, Me3), 1.60 (s, 3H, Me5’), 1.45 (s, 3H, Me5), -0.07 (s, 6H, [Al(CH3)2]; 13C{1H} NMR (125 MHz, C6D6, 297 K): δ = 149.4, 148.6, 148.4, 147.8, 140.8, 140.0, 134.8, (C*ipso,p*-NPh ,C3,3’, C5,5, Cipso-Ph,), 128.9 (*m*CPh), 128.3 *(mC*-NPh ), 126.7 (*p*CPh), 125.2 (*o*CPh), 111.5 (*o*C-N*Ph*), 105.9 (C4’), 105.5 (C4), 81.4 (Ca), 71.0 (CH), 39.7 (N*Me2*), 13.0 (Me3’), 12.8 (Me3), 10.2 (Me5’), 9.9 (Me5), -6.6 [Al(CH3)2].

**Synthesis of [AlEt2{*κ*2-bpzappe}] (4)**.The synthesis of **4** was carried out in an identical manner to **3**, using bpzappeH  **(1)** (1.0 g, 2.39 mmol) and AlEt3 (1 M in hexane, 2.39 cm3, 2.39 mmol). Compound **4** was isolated as a yellow solid. Yield: 84 % (1.02 g). Calcd for C30H40AlN5O: C, 70.15; H, 7.85; N, 13.63. Found: C, 70.50; H, 8.15; N, 13.13,1H NMR (500 MHz, C6D6, 297 K): δ = 7.54 (m, 2H, *o*HPh), 7.37 (d, 3*J*H-H = 9.0 Hz, 2H, *m*H-NPh), 7.13 (m, 2H, *m*HPh), 7.10 (m, 1H, *p*HPh), 6.60 (s, 1H, CH), 6.51 (d, 3*J*H-H = 9.0 Hz, 2H, *m*H-NPh), 5.30 (s, 2H, H4’,4), 2.46 (s, 6H, N*Me2*), 2.14 (s, 3H, Me3’), 2.13 (s, 3H, Me3), 1.61 (m, 6H, AlCH2*CH3*), 1.56 (s, 3H, Me5’), 1.42 (s, 3H, Me5), 0.56 (m, 4H, Al*CH2*CH3) 13C{1H} NMR (125 MHz, C6D6, 297 K): δ = 149.4, 148.7, 148.6, 148.2,140.8, 139.9, 137.5, 135.3 (*ipso,p*C-NPh ,C3,3’, C5,5, *ipso*CPh), 128.9 (*m*CPh), 127.7 (*m*C-NPh ), 126.7 (*p*CPh), 125.2 (*o*CPh), 111.5 (*o*C-NPh), 105.8 (C4’), 105.5 (C4), 81.2 (Ca), 70.7 (CH), 39.7 (N*Me2*), 13.0 (Me3’), 12.8 (Me3), 10.2 (Me5’), 9.9 (AlCH2*CH3*), 9.9 (Me5), 2.2 (Al*CH2*CH3).

**Synthesis of [{AlMe2(*κ*2-bpzappe)}(*µ*-O){AlMe3}] (5)**. The synthesis of **5** was carried out in an identical manner to **3**, using bpzappeH  **(1)** (1.0 g, 2.39 mmol) and AlMe3 (2 M in toluene, 2.39 cm3, 4.78 mmol). Compound **5** was isolated as light yellow solid. Yield: 79 % (1.06 g). Calcd for C31H45Al2N5O: C, 66.76; H, 8.13; N, 12.56. Found: C, 67.24; H, 8.45; N, 12.16,1H NMR (500 MHz, C6D6, 297 K): δ = 7.64 (m, 2H, *o*HPh), 7.37 (3*J*H-H = 9.2 Hz, 2H, oH-NPh), 7.13 (m, 2H, *m*HPh), 7.02 (m, 1H, *p*HPh), 6.62 (s, 1H, CH), 6.51 (d, 3*J*H-H = 9.2 Hz, 2H, *m*H-NPh), 5.39 (s, 1H, H4’), 5.24 (s, 1H, H4), 2.33 (s, 6H, N*Me2*), 2.13 (s, 3H, Me3’), 2.05 (s, 3H, Me3), 1.53 (s, 3H, Me5’), 1.49 (s, 3H, Me5), -0.11 (s, 6H, [Al(CH3)2], -0.52 (s, 9H, [Al(CH3)3]; 13C{1H} NMR (125 MHz, C6D6, 297 K): δ = 149.4, 148.6, 148.4, 147.8, 140.8, 140.1, 134.8, (C*ipso,p*-N*Ph* ,C3,3’, C5,5, Cipso-Ar), 128.9 (*m*CPh), 128.2 (*m*C-NPh), 126.7 (*p*CPh), 125.3 (*o*CPh), 111.5 (Co-N*Ph*), 105.9 (C4’), 105.5 (C4), 81.4 (Ca), 71.0 (CH), 39.7 (N*Me2*), 13.0 (Me3’), 12.8 (Me3), 10.2 (Me5’), 9.9 (Me5), -3.7, -4.2 [Al(CH3)2],-6.6 [Al(CH3)3].

**Synthesis of [{AlEt2(*κ*2-bpzappe)}(*µ*-O){AlEt3}] (6)**.The synthesis of **6** was carried out in an identical manner to **3**, using bpzappeH  **(1)** (1.0 g, 2.39 mmol) and AlEt3 (1 M in toluene, 4.78 cm3, 4.78 mmol). Compound **6** was isolated as a yellow solid.Yield: 88 % (1.23 g). Calcd for C36H55Al2N5O: C, 68.87; H, 8.83; N, 11.16. Found: C, 69.59; H, 9.12; N, 10.54,1H NMR (500 MHz, C6D6, 297 K): δ = 7.51 (m, 2H, *o*HPh), 7.32 (3*J*H-H = 8.4 Hz, 2H, *m*H-NPh), 7.12 (m , 2H, *m*HPh), 7.02 (m, 1H, *p*HPh), 6.67 (m, 2H, *m*H-NPh), 6.55 (s, 1H, CH), 5.40 (s, 1H, H4’), 5.25 (s, 1H, H4), 2.24 (s, 6H, N*Me2*), 2.15 (s, 3H, Me3’), 2.08 (s, 3H, Me3), 1.61-1.40 (m, 15H, AlCH2*CH3*), 1.52 (s, 3H, Me5’), 1.36 (s, 3H, Me5), 0.52-0.04 (m, 10H, Al*CH2*CH3) 13C{1H} NMR (125 MHz, C6D6, 297 K): δ = 149.4, 149.1, 148.6, 148.2, 140.8, 140.1, 135.2 (*ipso,p*C-N*Ph* ,C3,3’, C5,5, *ipso*C-Ar), 128.9 (*m*C-NPh), 128.1 (*o*CPh ), 126.7 (*m*CPh), 126.4 (*p*CPh), 111.5 (*o*C-N*Ph*), 105.9 (C4’), 105.6 (C4), 81.2 (Ca), 70.7 (CH), 39.7 (N*Me2*), 13.0 (Me3’), 12.8 (Me3), 10.3 (Me5’), 10.2, 9.8 (AlCH2*CH3*), 10.1 (Me5), 2.1, -0.2 (Al*CH2*CH3).

**Synthesis of [AlMe2{*κ*2-bbpzappe}]Br (7)**.In 250 cm3 Schlenk tube, complex **3** (1.0 g, 2.06 mmol) was dissolved in dry acetonitrile (50 cm3). The benzyl bromide (0.72 cm3, 6.19 mmol) was added and the reaction mixture was stirred at 60°C for 16 h. The solvent was remove under vacuum and the reaction crude was washed with hexane (3x25 cm3) to remove the excess of benzyl bromide and compound **7** was obtained as a yellow solid. Yield: 83 % (1.12 g). Calcd for C35H43AlBrN5O: C, 64.02; H, 6.60; N, 10.67. Found: C, 64.50; H, 7.03; N, 10.32,1H NMR (500 MHz, CDCl3, 297 K): δ = 7.69 (m, 2H, *o*HPh), 7.53-7.05 (m, 12H, CH2*Ph*, HNPh, HPh), 6.77 (s, 1H, CH), 5.83 (s, 1H, H4’), 5.68 (s, 1H, H4), 5.62 (m, 2H, *CH2*Ph), 3.90, 3.88 (s, 6H, N*Me2*) 2.22 (s, 3H, Me3’), 2.19 (s, 3H, Me3), 2.15 (s, 3H, Me5’), 1.80 (s, 3H, Me5), -0.84 (s, 6H, [Al(CH3)2]; 13C{1H} NMR (125 MHz, CDCl3, 297 K): δ = 149.6, 149.3, 149.0, 145.4, 143.1, 141.8, 140.8, 137.9 (*ipso,p*C-NPh ,C3,3’, C5,5, *ipso*CPh, *ipso*C-CH2Ph), 132.7, 129.0, 128.6, 128.2, 127.8, 127.0, 125.3 (*m*C-N*Ph*, *o,m,p*CPh, *o,m.p*C-CH2Ph) 120.7 (*o*C-N*Ph*), 107.2 (C4’), 106.0 (C4), 81.4 (Ca), 72.6 (*CH2*Ph), 70.6 (CH), 53.4 (N*Me2*), 13.3 (Me3’), 13.1 (Me3), 11.5 (Me5’), 10.6 (Me5), -7.4 [Al(CH3)2].

**Synthesis of [AlEt2{*κ*2-bbpzappe}]Br (8)**.The synthesis of **8** was carried out in an identical manner to **7**, using complex **4** (1.0 g, 1.79 mmol) and benzyl bromide (0.63 cm3, 5.37 mmol). Compound **8** was isolated as a yellow solid. Yield: 84 % (1.09 g). Calcd for C37H47AlBrN5O: C, 64.90; H, 6.92; N, 10.23. Found: C, 65.09; H, 7.10; N, 10.02. 1H NMR (500 MHz, CDCl3, 297 K): δ = 7.70 (m, 2H, *o*HPh), 7.54-7.05 (m, 12H, CH2*Ph*, NPh, Ph), 6.73 (s, 1H, CH), 5.82 (s, 1H, H4’), 5.67 (s, 1H, H4), 5.65 (m, 2H, *CH2*Ph), 3.90 (s, 6H, N*Me2*), 2.22 (s, 3H, Me3’), 2.18 (s, 3H, Me3), 2.12 (s, 3H, Me5’), 1.82 (s, 3H, Me5), 0.95 (m, 6H, AlCH2*CH3*), -0.18 (m, 4H, Al*CH2*CH3); 13C{1H} NMR (125 MHz, CDCl3, 297 K): δ = 150.2, 149.5, 149.2, 145.8, 143.1, 141.5, 140.7, 135.0 (*ipso,p*C-N*Ph* ,C3,3’, C5,5, *ipso*CPh, *ipso*C-CH2*Ph*), 132.7, 129.2, 128.8, 128.6, 127.8, 127.6, 126.9 (*m*C-NPh, *o,m,p*C-Ph, *o,m,p*C-CH2*Ph*) 120.5 (*o*C-NPh), 107.0 (C4’), 106.0 (C4), 81.2 (Ca), 72.5 (*CH2*Ph), 70.0 (CH), 53.5, 53.4 (N*Me2*), 13.2 (Me3’), 13.1 (Me3), 11.4 (Me5’), 10.7 (Me5), 9.3(AlCH2*CH3*), 1.6 (Al*CH2*CH3).

**Synthesis of [{AlMe2(*κ*2-bbpzappe)}(*µ*-O){AlMe3}]Br (9)**.The synthesis of **9** was carried out in an identical manner to **7**, using complex **5** (1.0 g, 1.94 mmol) and benzyl bromide (0.68 cm3, 5.82 mmol). Compound **9** was isolated as a yellow solid. Yield: 88 % (1.16 g). Calcd for C38H53Al2BrN5O: C, 62.54; H, 7.32; N, 9.60. Found: C, 62.75; H, 7.43; N, 9.51. 1H NMR (500 MHz, CDCl3, 297 K): ).δ = 7.67-7.15 (m, 14H, CH2*Ph*, NPh, Ph), 6.88 (s, 1H, CH), 5.97 (s, 1H, H4’), 5.77 (s, 1H, H4), 5.49 (m, 2H, *CH2*Ph), 3.93, 3.89 (s, 6H, N*Me2*) 2.35 (s, 3H, Me3), 2.30 (s, 3H, Me3’), 2.28 (s, 3H, Me5’), 1.91 (s, 3H, Me5), -0.65 (s, 6H, [Al(CH3)2], -0.72 (s, 9H, [Al(CH3)3]; 13C{1H} NMR (125 MHz, CDCl3, 297 K): δ = 149.9, 149.3, 149.0, 145.3, 142.8, 141.9, 140.8, 137.8 (*ipso,p*C-NPh ,C3,3’, C5,5, *ipso,p*C-Ph, *ipso*C-CH2*Ph*), 132.6, 130.7, 129.5, 128.7, 127.8, 127.6, 127.0 (*m*C-N*Ph*, *o,m,p*C-Ph, *o,m,p*C-CH2*Ph*) 120.5 (*o*C-NPh), 107.2 (C4’), 106.0 (C4), 81.4 (Ca), 73.1 (*CH2*Ph), 71.0 (CH), 53.5, 53.4 (N*Me2*), 13.3 (Me3’), 13.1 (Me3), 11.5 (Me5’), 10.6 (Me5), -4.5 [Al(CH3)2], -7.3 [Al(CH3)3].

**Synthesis of [{AlEt2(*κ*2-bbpzappe)}(*µ*-O){AlEt3}]Br (10)**.The synthesis of **10** was carried out in an identical manner to **7**, using complex **6** (1.0 g, 1.59 mmol) and benzyl bromide (0.56 cm3, 4.77 mmol). Compound **10** was isolated as a yellow solid. Yield: 82 % (1.04 g). Calcd for C43H62Al2BrN5O: C, 64.65; H, 7.82; N, 8.77. Found: C, 65.13; H, 8.29; N, 8.32; 1H NMR (500 MHz, CDCl3, 297 K): δ = 7.85-7.25 (m, 14H, CH2*Ph*, NPh, Ph), 6.89 (s, 1H, CH), 5.98 (s, 1H, H4’), 5.83 (s, 1H, H4), 5.81 (m, 2H, *CH2*Ph), 4.05 (s, 6H, N*Me2*), 2.38 (s, 3H, Me3’), 2.35 (s, 3H, Me3), 2.30 (s, 3H, Me5’), 1.98 (s, 3H, Me5), 1.42-1.01 (m, 15H, AlCH2*CH3*), -0.01 (m, 10H, Al*CH2*CH3); 13C{1H} NMR (125 MHz, CDCl3, 297 K): δ = 150.1, 149.5, 149.2, 145.8, 143.1, 141.6, 140.8, 132.6 (*ipso,p*C-NPh, C3,3’, C5,5, *ipso*C-Ph, *ipso*C-CH2*Ph*), 130.4, 129.2, 129.0, 128.6, 127.8, 127.5, 126.9 (*m*C-N*Ph*, *o,m,p*C-Ph, *o,m,p*C-CH2*Ph*), 120.7 (*o*C-N*Ph*), 107.0 (C4’), 106.0 (C4), 81.2 (Ca), 72.5 (*CH2*Ph), 70.0 (CH), 53.6, 53.3 (N*Me2*), 13.2 (Me3’), 13.1 (Me3), 11.4 (Me5’), 10.7 (Me5), 9.4, 9.3, 9.1 (AlCH2*CH3*), 1.6 (Al*CH2*CH3).

**General procedure for catalyst screening at 1 bar pressure**

Styrene oxide **11a** (1.7 mmol), a combination of catalysts **3–6** (83.0 **mol) and Bu4NBr (26.7 mg, 83.0 **mol) or one-component catalysts **7–10** (83.0 **mol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred at 25 ºC or 50 ºC for 24 h, then the conversion of styrene oxide **11a** to styrene carbonate **12a** was determined by analysis of a sample by 1H NMR spectroscopy.

**General procedure for synthesis of cyclic carbonates at 10 bar pressure**

An epoxide **11a–l** or **13a–f** (1.7 mmol) and catalyst **10** (83.0 **mol) were placed in a multipoint reactor with a magnetic stirrer bar. The reaction mixture was stirred at 50–90 ºC for 24 h. The conversion of epoxide to cyclic carbonate was then determined by analysis of a sample by 1H NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH2Cl2 to remove the catalyst. The eluent was evaporated in *vacuo* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane:EtOAc (9:1), then hexane:EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **12a–l** and **14a–f** are all known compounds and the spectroscopic data for samples prepared using catalyst **10** were consistent with those reported in the literature.[3,6]

**X-ray crystallographic structure determination**

Colourless and yellow crystals (for **1** and **3**, respectively) were obtained by diffusion of toluene and were mounted on a glass fibre and used for data collection on a Bruker D8 Venture with Photon detector equipped with graphite monochromated Mo Kα radiation (*λ* = 0.71073 Å). Lorentz-polarisation and empirical absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares calculations on *F2* using the program SHELXS97.[16] Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent.[17] Several crystals of **3** were measured and the structure was solved from the best data we were able to collect. Attempts to solve disorder problems with one toluene solvent molecule failed in compound **3**. Instead, a new set of *F*2 (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON-94. 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. Selected bond lengths and angles are given in Tables S2 and S3 (see the Supporting Information). CCDC reference numbers for the structures of **1** and **3** are 1505774 and 1505775, respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336-033; e-mail, deposit@ ccdc.cam.ac.uk).

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