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Influence of the Counterion on the Synthesis of Cyclic Carbonates Catalyzed by Bifunctional Aluminum Complexes

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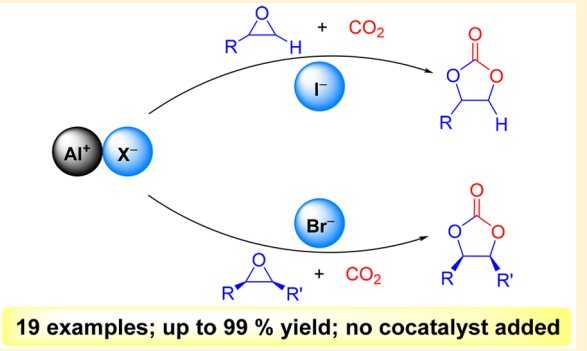
Supporting Information

ABSTRACT: New bifunctional aluminum complexes have been prepared with the aim of studying the effect of a counterion on the synthesis of cyclic carbonates from epoxides and carbon dioxide (CO_2). Neutral ligand **1** was used as a precursor to obtain four novel mesylate, chloride, bromide, and iodide zwitterionic NNO ligands (**2**−**5**). The reaction of these ligands with 1 or 2 equiv of AlR_3 (R = Me, Et) allowed the synthesis of mono- and bimetallic bifunctional aluminum complexes [$AlR_2(\kappa^2$-mbpzappe)]X [X = Cl, R = Me (**6**), Et (**7**); X = Br, R = Me (**8**), Et (**9**); X = I, R = Me (**10**), Et (**11**)] and [{$AlR_2(\kappa^2$-mbpzappe)}(μ-O){AlR_3}]X [X = $MeSO_3$, R = Me (**12**), Et (**13**); X = Cl, R = Me (**14**), Et (**15**); X = Br, R = Me (**16**), Et (**17**); X = I, R = Me (**18**), Et (**19**)] via alkane elimination. These complexes were studied as catalysts for the synthesis of cyclic carbonates from epoxides and CO_2. Iodide complex **11** showed to be the most active catalyst for terminal epoxides, whereas bromide complex **9** was found to be the optimal catalyst when internal epoxides were used, showing the importance of the nucleophile cocatalyst on the catalytic activity.

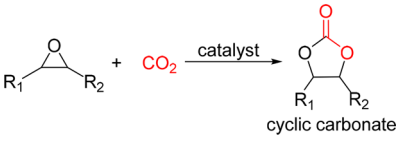


INTRODUCTION

A steady increase of carbon dioxide (CO_2) emissions from fossil fuels has been responsible for the excessive accumulation of CO_2 in the atmosphere, which is triggering severe climate problems and has become an important concern for a sustainable society.[1−4] Although large-scale processes would barely have an influence on the global concentration of CO_2 in the atmosphere, the growth of effective technologies for the chemical transformation and utilization of CO_2 into high-value-added products could be one of the most important processes to preserve fossil resources and to achieve the balance of the carbon cycle on Earth.[5−8] It is worth highlighting that CO_2 is an abundant, inexpensive, nonflammable, and safe substrate that is considered to be a renewable C1 building block for organic synthesis. However, new catalyst systems for CO_2 utilization need to be developed because of its thermodynamics.[9−11]

The reaction of CO_2 and epoxides to produce cyclic carbonates (Scheme 1) is a promising process because of its high atom economy and the considerable industrial potential of cyclic carbonates.[12−16] For example, cyclic carbonates already have interesting applications such as polar aprotic solvents in chemical processes,[17−19] electrolytes in lithium-ion batteries,[20,21] and useful intermediates in organic synthesis.[22−25]

Scheme 1. Reaction of CO_2 and Epoxides for the Synthesis of Cyclic Carbonates



Over the last 2 decades, several research groups have focused their attention on the preparation of efficient homogeneous metal-based catalytic systems supported by salen,[26−29] porphyrin,[30−33] aminophenolate,[34] and other ligands[35−38] or organocatalysts[39−43] that have shown high catalytic activity and selectivity for cyclic carbonate synthesis. Bifunctional metal systems,[44−47] which contain both the metal center and nucleophile cocatalyst within the same molecular structure,

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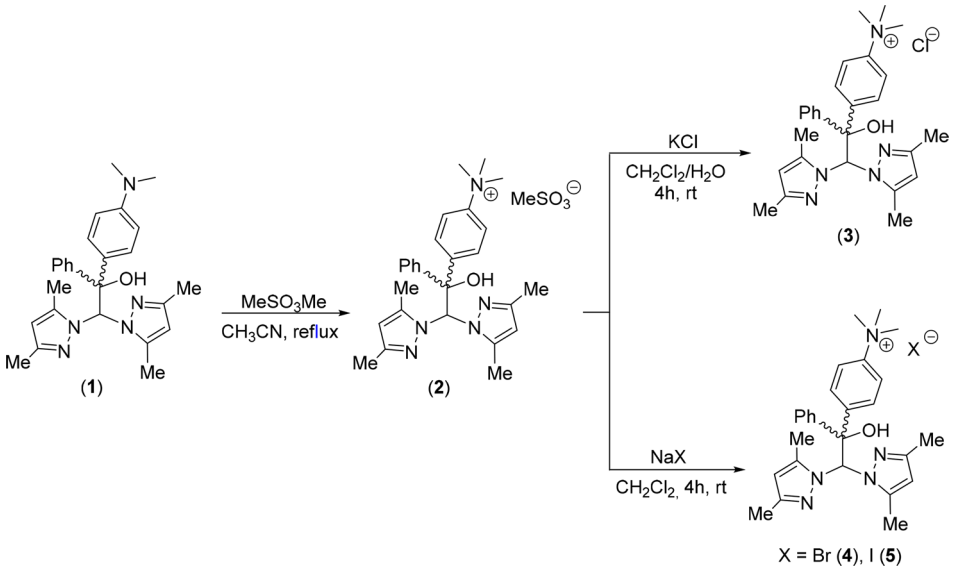
Scheme 2. Synthesis of Zwitterionic Ligands 2−5



have been far less studied for the synthesis of cyclic carbonates, although these types of catalysts could display greater catalytic activity for this transformation than the two-component catalyst systems.[44,48−50]

In recent years, our research group has developed a range of heteroscorpionate complexes that have displayed high catalytic activity in different catalytic applications such as the ring-opening polymerization (ROP) of cyclic esters,[51−53] ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides,[54,55] hydroamination of aminoalkenes,[56] and hydroalkoxylation/cyclization of alkynyl alcohols.[57] However, we have recently focused our attention on CO_2 fixation into cyclic carbonates catalyzed by organoaluminum heteroscorpionate complexes, which have displayed high catalytic activity for this transformation.[58−60] Thus, in this work we aim to study the influence of a counterion on the catalytic activity of bifunctional aluminum heteroscorpionate complexes for the synthesis of cyclic carbonates from terminal and internal epoxides.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. The syntheses of zwitterionic ligands **2**−**5** are presented in Scheme 2. The compound 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-[4-(dimethylamino)phenyl]-1-phenylethanol (**1**, bpzappeH) was synthesized as previously reported[60] and used as the starting material for synthesis of the zwitterionic ligand precursor 4-[2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-hydroxy-1-phenylethyl]-*N*,*N*,*N*-trimethylbenzenaminium methanesulfonate [**2**, (mbpzappeH)$MeSO_3$], which was synthesized by the reaction of **1** with an excess of methylmethanesulfonate in dry acetonitrile under reflux. After the appropriate workup, compound **2** was obtained as a yellow solid in 80% yield (Scheme 2).

The reaction of **2** with an excess of potassium chloride in CH_2Cl_2/H_2O (1:1) provided 4-[2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-hydroxy-1-phenylethyl]-*N*,*N*,*N*-trimethylbenzenaminium chloride [**3**, (mbpzappeH)Cl] as a yellow solid (Scheme 2). On the other hand, the treatment of **2** with an excess of sodium bromide or sodium iodide in dry CH_2Cl_2 at room temperature for 4 h afforded the desired compounds 4-[2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-hydroxy-1-phenylethyl]-*N*,*N*,*N*-trimethylbenzenaminium bromide [**4**, (mbpzappeH)Br] and 4-[2,2-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-hydroxy-1-phenylethyl]-*N*,*N*,*N*-trimethylbenzenaminium iodide [**5**, (mbpzappeH)I] as yellow solids (Scheme 2). All zwitterionic ligand precursors **2**−**5** were isolated as racemic mixtures.

The solution-state structures of compounds **2**−**5** were characterized by spectroscopic methods (see the Experimental Section). ^1H and $^{13}C\{^1H\}$NMR of these compounds showed two sets of signals for the pyrazole rings, which indicated that the pyrazole rings are not equivalent. The ^1H and $^{13}C\{^1H\}$-NMR spectra of compound **2** show the signal for the methyl group from the mesylate anion. This resonance disappears in the ^1H and $^{13}C\{^1H\}$NMR spectra of compounds **3**−**5** (Figure 1), confirming exchange of the counterions. ^1H one-dimensional nuclear Overhauser spectroscopy (1D NOESY) NMR experiments allowed assignment of the signals corresponding to the Ph, NPh, Me^3, Me^5, H^4, and $MeSO_3^-$ groups, and $^1H-^{13}C$ heteronuclear correlation (g-HSQC) NMR experiments allowed assignment of the carbon resonances.

The reaction of zwitterionic heteroscorpionate ligand precursors **2**−**5** with 1 or 2 equiv of AlR_3 (R = Me, Et) in dry acetonitrile afforded the desired bifunctional mono- and dinuclear alkylaluminum complexes [$AlR_2(\kappa^2$-mbpzappe)]X [X = Cl, R = Me (**6**), Et (**7**); X = Br, R = Me (**8**), Et (**9**); X = I, R = Me (**10**), Et (**11**)] and [{$AlR_2(\kappa^2$-mbpzappe)}(μ-O)-{AlR_3}]X [X = $MeSO_3$, R = Me (**12**), Et (**13**); X = Cl, R = Me (**14**), Et (**15**); X = Br, R = Me (**16**), Et (**17**); X = I, R = Me (**18**), Et (**19**)] (Scheme 3) in yields higher than 80%. In bimetallic complexes **12**−**19**, the second aluminum center is coordinated through a dative bond to the oxygen atom of the alkoxide moiety (Scheme 3). These complexes are stable in the solid state at room temperature for weeks.

Complexes **6**−**19** were characterized spectroscopically. ^1H and $^{13}C\{^1H\}$NMR spectra of these complexes showed the resonances for the pyrazole rings, the methyl groups from the ammonium moiety, and the aromatic rings and one set of resonances for the alkyl ligands (Figure 2). It is worth highlighting that a fluxional behavior due to a quick exchange process between the two pyrazole rings is possible for these

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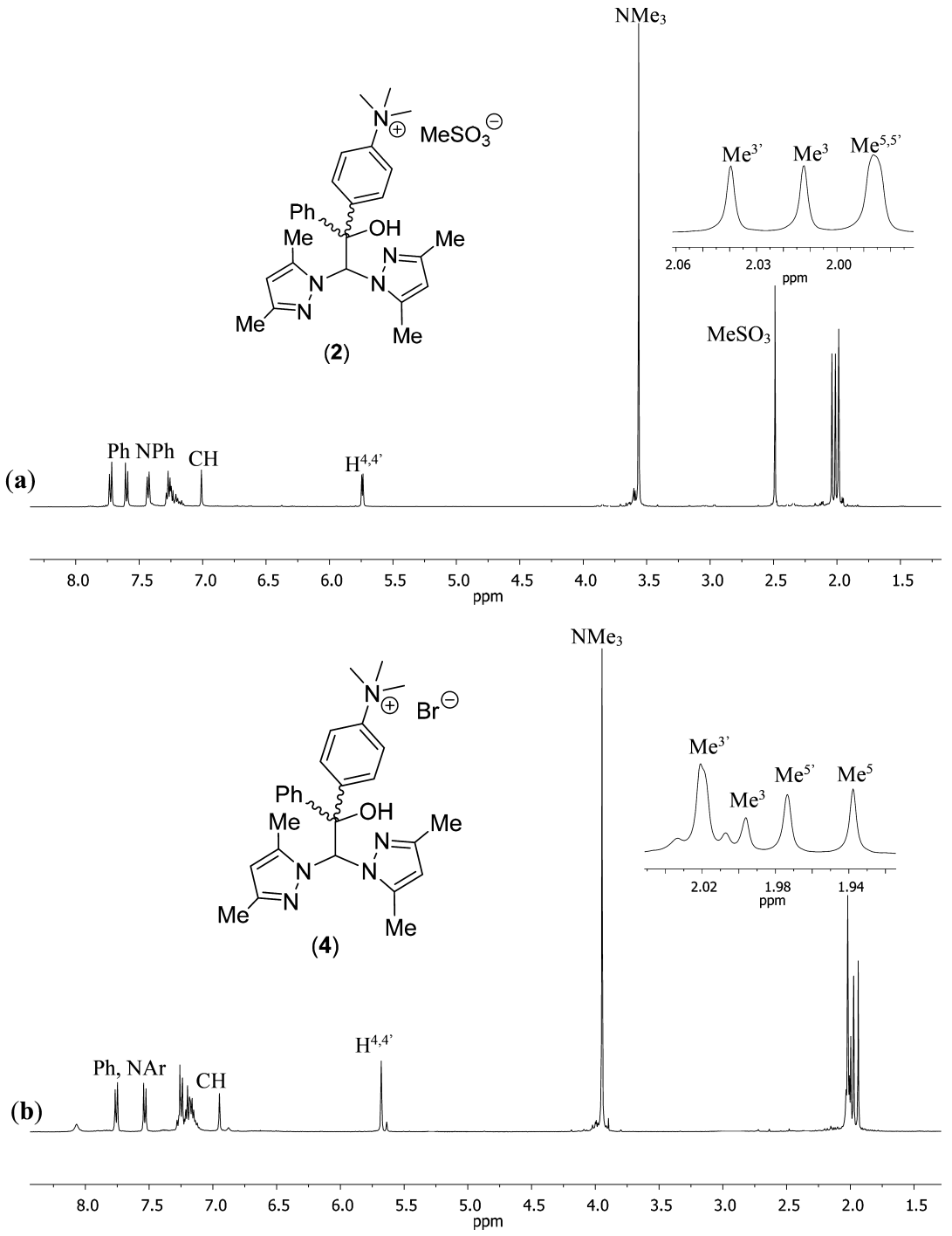

Figure 1. ^{1}H NMR spectra of (a) **2** and (b) **4** in $CDCl_3$.

complexes. This behavior has already been observed in other aluminum heteroscorpionate complexes.[58−60]

1D NOESY NMR experiments afforded unequivocal assignments for most ^{1}H NMR resonances, and the $^{13}C\{^{1}H\}$ NMR signals were assigned by $^{1}H-^{13}C$ g-HSQC NMR experiments (see the Experimental Section). The NMR results are consistent with a tetrahedral environment for each aluminum center, in which the heteroscorpionate ligand is coordinated to the aluminum center in a κ^2-NO coordination mode for monometallic compounds **6**−**11** or in a κ^2-NO-μ-O coordination mode for bimetallic complexes **12**−**19**, bridging the two aluminum atoms (Scheme 3).

To study the dynamic behavior of complexes **6**−**19**, a variable-temperature (VT) NMR study for complex **11** was carried out (Figure 3). VT NMR analysis showed that the signals of the pyrazole rings broaden and become resolved, which indicates the presence of two diastereoisomers (Scheme 4) at −95 °C (Figure 3). Therefore, a fast exchange process between the coordinated and noncoordinated pyrazole rings is observed, which involves interconversion from one diastereoisomer to the other. Notably, because of the coordination mode of the heteroscorpionate ligands, the methine carbon atom between the two pyrazole rings is a chiral center. Thus,

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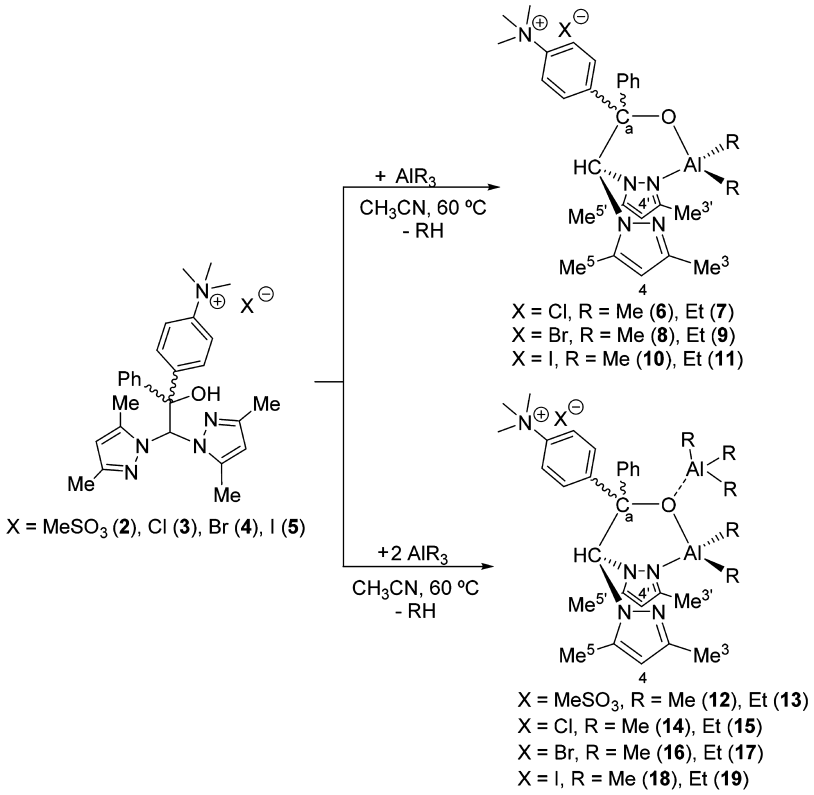
Scheme 3. Synthesis of Aluminum Complexes 6−19



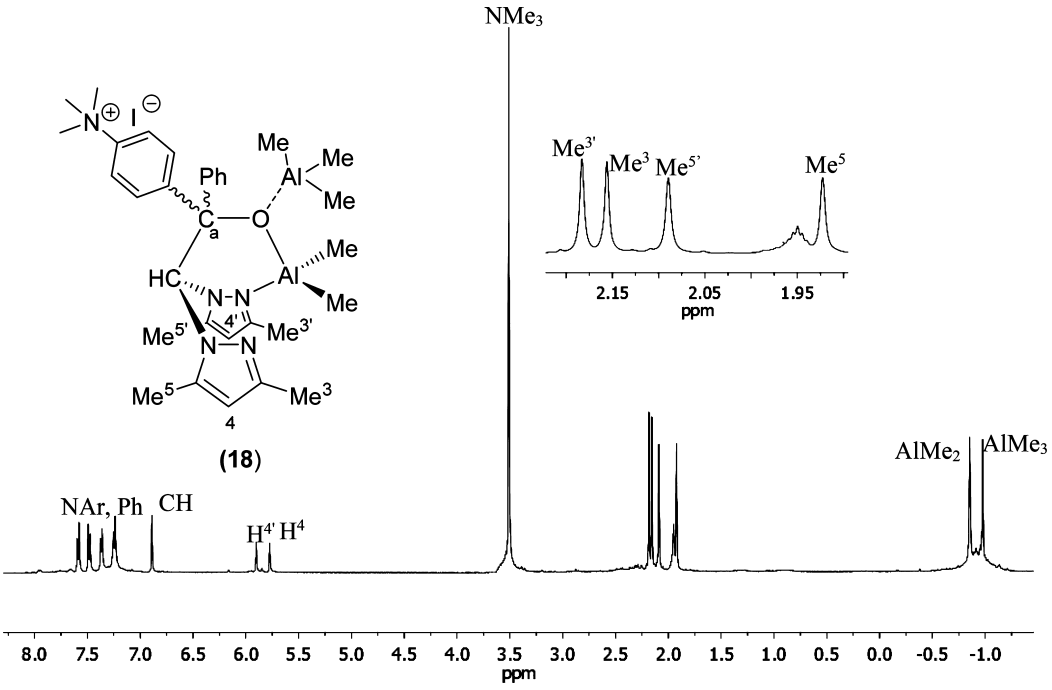


Figure 2. ^{1}H NMR spectrum of **18** in CD_3CN.

because the heteroscorpionate ligand is racemic, there are four possible stereoisomers for complexes **6−19** (Scheme 4).

The solid-state structure of complex **11** was confirmed by single-crystal X-ray diffraction analysis. The corresponding ORTEP diagram is represented in Figure 4. The crystallographic data and selected interatomic distances and angles are given in Tables S1 and S2. In complex **11**, the heteroscorpionate ligand is coordinated in a κ^2-NO coordination mode to the aluminum center through the O1 and N1 atoms (Figure 4). The dihedral angle between the N1−Al−O1 and C28−Al−C30 planes has a value of 92.4(2)°, which is consistent with a distorted tetrahedral geometry. The Al1−N1 and Al1−O1 distances are 1.978(5) and 1.751(4) Å, respectively. Moreover, the Al−C distances [1.965(6) and

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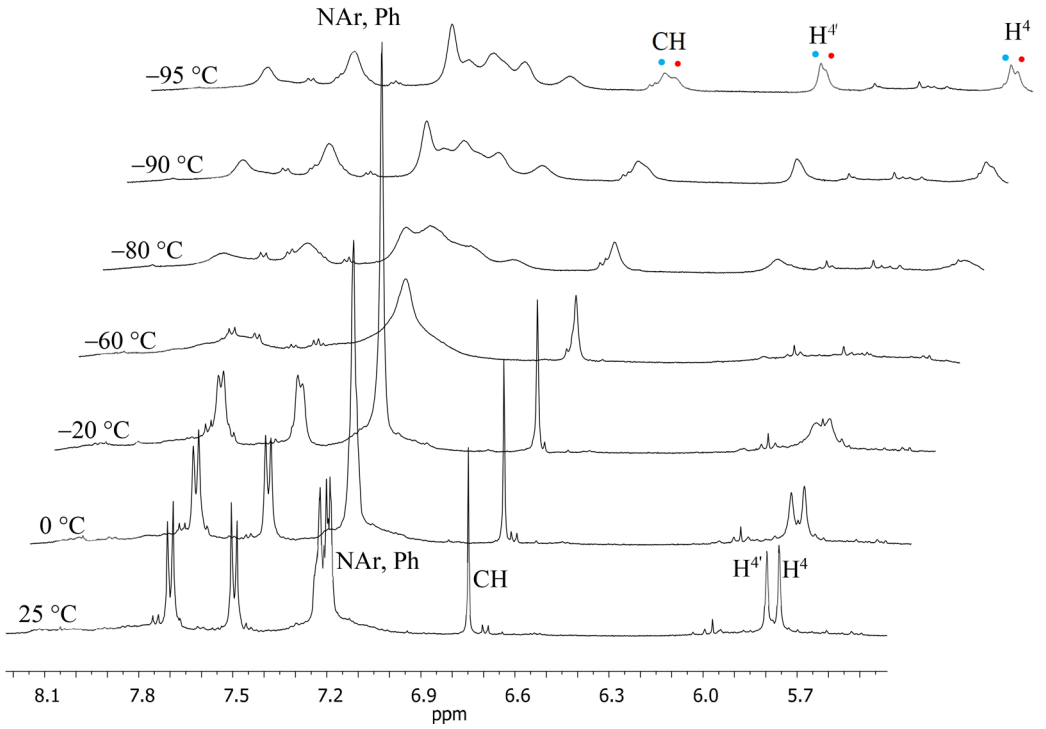
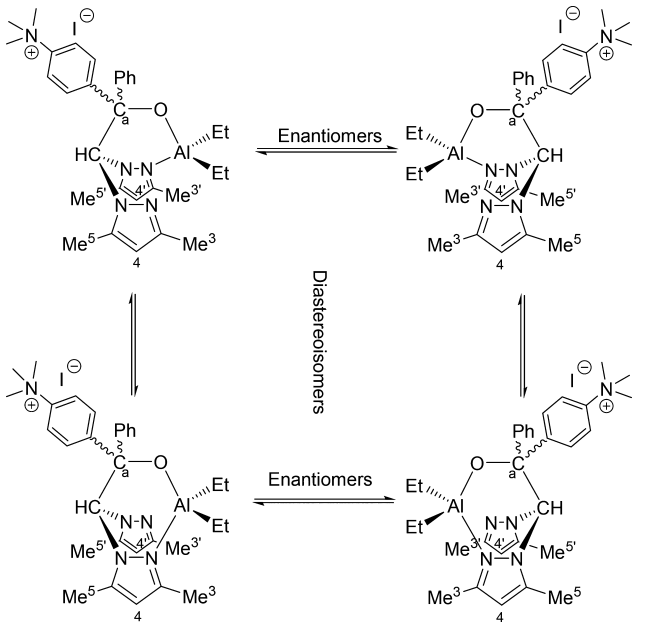


Figure 3. VT NMR study for compound **11** in CD_2Cl_2: (light-blue ●) major isomer; (red ●) minor isomer.

Scheme 4. Structure for the Four Stereoisomers of Complex 11



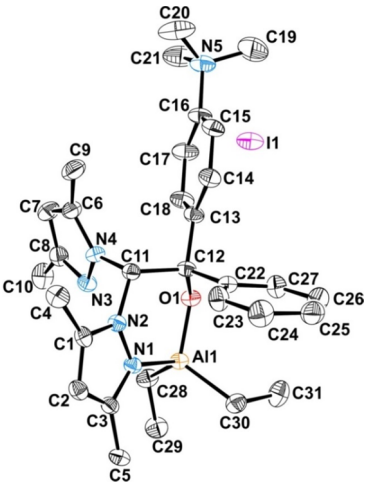
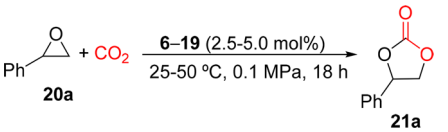


Figure 4. ORTEP diagram for compound **11**. Hydrogen atoms are omitted. Thermal ellipsoids are shown at 30%.

Scheme 5. Synthesis of 21a Catalyzed by Compounds 6–19



1.960(6) Å] are in good agreement with the previously reported aluminum scorpionate complexes.[58−60]

Synthesis of Cyclic Carbonates. With the aim of studying the influence of an anion on the synthesis of cyclic carbonates, complexes **6–19** were screened as catalysts for the synthesis of styrenecarbonate (**21a**) from styrene oxide (**20a**) and CO_2 at 25 °C and 0.1 MPa CO_2 pressure under solvent-free conditions (Scheme 5), and the reactions were monitored by ^{1}H NMR spectroscopy. In order to keep the aluminum loading constant, reactions were carried out using 5 mol % monometallic complexes **6–11** and 2.5 mol % bimetallic complexes **12–19**. The results obtained are presented in Table 1 (see the Supporting Information for further details). Polycarbonate formation was not observed under the aforementioned reaction conditions, and the selectivity toward the cyclic carbonates was always higher than 99%. This suggests that the nucleophile is not close enough to the aluminum atom to carry out the copolymerization of terminal epoxides and CO_2.[61,62]

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Table 1. Synthesis of 21a Catalyzed by 6−19[a]

entry	catalyst	cocatalyst	conversion (%) 25 °C[b]	50 °C[b]
1	**6**		10	50
2	**7**		15	60
3	**8**		35	95
4	**9**		38	98
5	**10**		42	97
6	**11**		56	99
7[c]	**12**		1	5
8[c]	**13**		2	7
9[c]	**14**		5	43
10[c]	**15**		10	55
11[c]	**16**		27	79
12[c]	**17**		30	82
13[c]	**18**		33	85
14[c]	**19**		42	90
15[c,d]	**16**	Bu_4NBr	33	89
16[c,d]	**17**	Bu_4NBr	38	84
17[c,e]	**18**	Bu_4NI	37	92
18[c,e]	**19**	Bu_4NI	48	94

[a]Reactions were carried out at 0.1 MPa CO_2 pressure for 18 h using 5 mol % complex unless specified otherwise. [b]Conversion of the crude mixture was determined by ^1H NMR spectroscopy after 18 h. [c]Complex: 2.5 mol %. [d]Bu_4NBr: 2.5 mol %. [e]Bu_4NI: 2.5 mol %.

As can be seen in Table 1, monometallic complexes **6**−**11** and bimetallic complexes **14**−**19** showed moderate catalytic activity at 25 °C after 18 h using a catalyst loadings of 5 and 2.5 mol %, respectively (Table 1, entries 1−6 and 9−14). However, aluminum mesylate complexes **12** and **13** displayed very low catalytic activity for the synthesis of **21a** under these reaction conditions (Table 1, entries 7 and 8) because of the low nucleophilicity of the mesylate anion. Moreover, aluminum iodide complexes **10**, **11**, **18**, and **19** displayed higher catalytic activity than their corresponding aluminum bromide complexes **8**, **9**, **16**, and **17** and aluminum chloride complexes **6**, **7**, **14**, and **15** for the synthesis of **21a** (Table 1, entries 1−6 and 9−14). These results may be due to the higher nucleophilicity and leaving group ability of the iodide anion compared to the chloride and bromide anions. The order of the catalytic activity I > Br > Cl could also be explained by the electrostatic interaction between the halide anion and ammonium cation (ion-pairing effect). A stronger interaction between the ammonium cation and halide anion will result in a less active catalyst. Therefore, the higher catalytic activity of iodide with respect to bromide and chloride may be explained by a weaker electrostatic interaction between the iodide anion and ammonium cation that makes iodide to move away from the organometallic complex, and therefore the nucleophilic attack on the epoxide is accelerated.[63−66]

In order to improve the catalytic activity of complexes **6**−**19**, the effect of increasing the reaction temperature to 50 °C was studied while keeping the CO_2 pressure constant at 0.1 MPa (Table 1). As expected, the catalytic activity of these complexes increased and almost quantitative conversion of **20a** was achieved after 18 h when monometallic aluminum bromide and iodide catalysts **8**−**11** were used (Table 1, entries 3−6). In order to keep the concentration of the counterion constant at 5 mol % in complexes **8**−**11** and **16**−**19**, 2.5 mol % tetrabutylammonium bromide (Bu_4NBr) and tetrabutylammonium iodide (Bu_4NI) was added to the reaction catalyzed by bimetallic complexes **16**−**19** (Table 1, entries 15−18). This resulted in a slight increase of the catalytic activity displayed by complexes **16**−**19**, although their performances were still lower than those displayed by monometallic complexes **8**−**11**. Among the catalysts screened for the synthesis of **21a** from **20a** and CO_2, complex **11** showed to be the most active catalyst and was chosen for further optimization. It is important to note that the influence of the counterion on the reaction of CO_2 with **20a** is clear, with the order of the catalytic activity being I > Br > Cl.

Then, the effect of the catalyst loading of complex **11** and reaction temperature was studied (Table 2). Reactions were carried at 1.0 MPa CO_2 pressure using **20a** as the substrate to avoid epoxide loss during the reaction due to its volatility, which would result in low isolated yields.[58,60] As can be seen in Table 2, low-to-moderate conversions were obtained at any catalyst loading for reactions carried out at 25 °C. However, when the reaction temperature was increased at 50 °C, almost quantitative conversions were achieved with catalyst loadings higher than 1.5 mol % (Table 2, entries 3−5). In an attempt to further reduce the catalyst loading and get quantitative conversion, reactions were performed at 85 °C, and as can be seen in Table 2, 98% conversion was achieved at 1.0 MPa CO_2 pressure after 18 h using 0.5 mol % catalyst loading.

Table 2. Optimization of Reaction Conditions for the Synthesis of 21a Catalyzed by 11[a]

entry	**11** (mol %)	conversion (%) 25 °C[b]	50 °C[b]	85 °C[b]
1	0.5	6	45	98
2	1.0	14	78	98
3	1.5	20	89	98
4	2.5	29	96	99
5	5.0	79	99	99

[a]Reactions were carried out at 1.0 MPa CO_2 pressure for 18 h. [b]Conversion of the crude mixture was determined by ^1H NMR spectroscopy after 18 h.

Once the reaction conditions for the preparation of **21a** were optimized, the transformation of a variety of terminal epoxides **20a**−**20m** into their corresponding cyclic carbonates **21a**−**21m** using 0.5−1.0 mol % complex **11** at 85 °C and 1.0 MPa CO_2 pressure for 18 h was investigated, and the results are collected in Figure 5. Generally, good-to-excellent yields were obtained for the synthesis of cyclic carbonates **21a**−**21m** from their corresponding terminal epoxides **20a**−**20m** under these reaction conditions. It is worth highlighting that catalyst **11** was tolerant to aryl and alkyl epoxides and those functionalized with halide, alcohol, ether, ester, and alkene groups, which indicates that this catalyst is highly versatile and selective because no polycarbonate was observed during the reactions.

In order to further extend the substrate scope, the synthesis of disubstituted cyclic carbonates from their corresponding internal epoxides was studied. First, we optimized the reaction conditions for the synthesis of cyclohexene carbonate (**23a**) from cyclohexene oxide (**22a**) and CO_2 (Scheme 6) using the mono- and dinuclear aluminum chloride, bromide, and iodide complexes **6**−**11** and **14**−**19**, and the results are shown in Table 3. The reactions were performed in a sealed reactor at 85 °C and 1.0 MPa CO_2 pressure for 24 h under solvent-free conditions.

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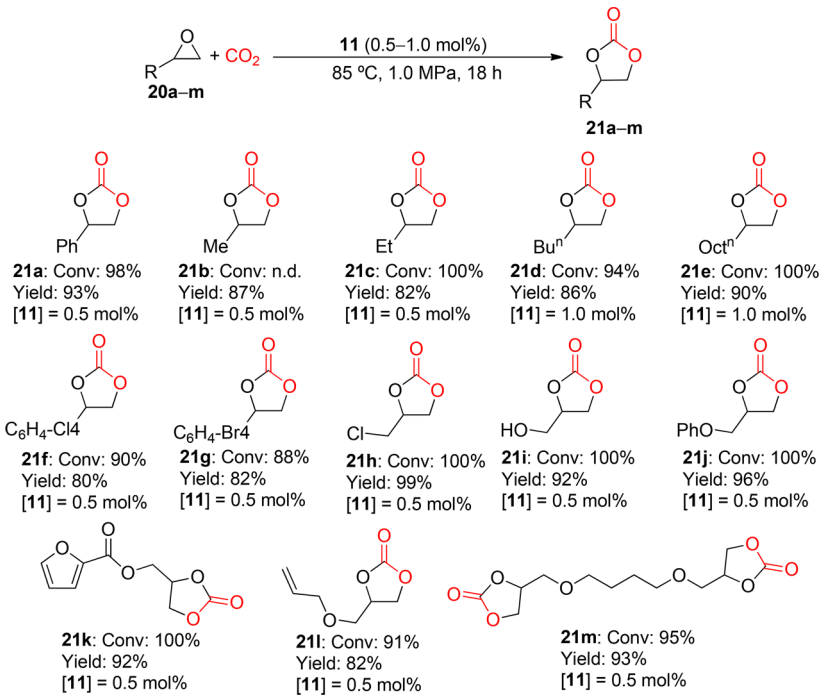

Figure 5. Synthesis of cyclic carbonates **21a–21m** from epoxides **20a–20m** and CO_2 catalyzed by complex **11**.

Scheme 6. Synthesis of 23a

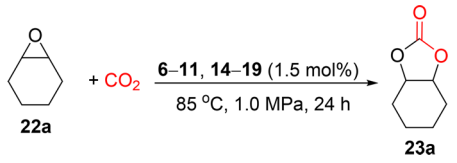

Table 3. Synthesis of 23a Catalyzed by Complexes 6–11 and 14–19[a]

entry	catalyst	cocatalyst	conversion (%)[b]
1	**6**		7
2	**7**		14
3	**8**		70
4	**9**		85
5	**10**		52
6	**11**		63
7[c]	**14**		10
8[c]	**15**		23
9[c]	**16**		60
10[c]	**17**		65
11[c]	**18**		50
12[c]	**19**		58
13[c,d]	**16**	Bu_4NBr	58
14[c,d]	**17**	Bu_4NBr	66
15[c,e]	**18**	Bu_4NI	69
16[c,e]	**19**	Bu_4NI	73

[a]Reactions were carried out at 85 °C and 1.0 MPa CO_2 pressure for 24 h using 1.5 mol % complex unless specified otherwise. [b]Conversion of the crude mixture was determined by ^1H NMR spectroscopy after 24 h. [c]Complex: 0.75 mol %. [d]Bu_4NBr: 0.75 mol %. [e]Bu_4NI: 0.75 mol %.

As can be seen in Table 3, chloride complexes **6**, **7**, **14**, and **15** showed very low catalytic activity for the synthesis of **23a** (Table 3, entries 1, 2, 7, and 8), whereas aluminum bromide complexes **8**, **9**, **16**, and **17** were more active than the iodide ones **10**, **11**, **18**, and **19** (Table 3, entries 3–6 and 9–12), indicating the importance of the anion for the synthesis of cyclic carbonates. As previously mentioned, aluminum iodide complexes **10**, **11**, **18**, and **19** displayed higher catalytic activity when terminal epoxides were used as substrates (Table 1). However, bromide complexes **8**, **9**, **16**, and **17** showed to be more efficient when using internal epoxides (Table 3). The effect of adding Bu_4NBr or Bu_4NI into reactions catalyzed by bimetallic complexes **16–19** to have a bromide or iodide concentration of 1.5 mol % was studied (Table 3, entries 13–16). The addition of more nucleophiles slightly improved their catalytic activity, but complex **9** showed the highest catalytic activity for the synthesis of **23a** (Table 3, entry 4). According to these results, the order of the catalytic activity for internal epoxides was Br > I > Cl, showing that not only is the balance between the nucleophilicity, leaving group ability, and electrostatic interactions between the cation and anion important but also the steric hindrance of the epoxide is crucial, and a smaller nucleophile is needed in order to obtain good yields of disubstituted cyclic carbonates.

After the reaction conditions were optimized, the formation of six disubstituted cyclic carbonates **23a–23f** from their corresponding internal epoxides **22a–22f** and CO_2 was studied (Figure 6). The reactions were performed using 1.5–2.5 mol % complex **9** at 85 °C and 1.0 MPa CO_2 pressure for 24 h. Cyclic carbonates **23a–23d** were obtained in good yields (65–86%) in the presence of 1.5 mol % catalyst **9**. However, 2.5 mol % complex **9** was required to obtain reasonable yields of cyclic carbonates **23e** and **23f** possibly because of the greater steric hindrance of their corresponding epoxides. *cis*- and *trans*-epoxides **22c** and **22d** were used for synthesis of their corresponding cyclic carbonates **23c** and **23d**. The cyclic carbonate product **23c** was isolated as a 94:6 mixture of *cis*/*trans*-cyclic carbonate (see the Supporting Information). In a similar way, the *trans*-cyclic carbonate **23d** was obtained as a 5:95 mixture of *cis*/*trans*-cyclic carbonate, which confirmed

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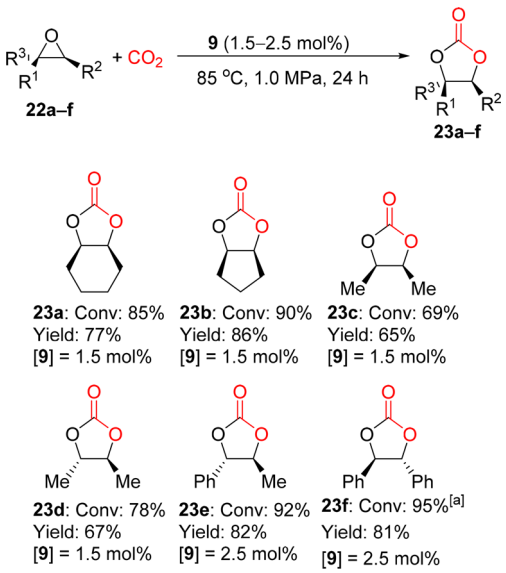


Figure 6. Synthesis of cyclic carbonates **23a**–**23f** from epoxides **22a**–**22f** and CO_2 catalyzed by complex **9**. [a]95 °C.

that the reactions occurred with retention of the epoxide stereochemistry. Therefore, two inversions of stereochemistry at the less-hindered carbon atom of the epoxide take place during the catalytic cyclic carbonate synthesis. As previously observed for monosubstituted cyclic carbonates, no polycarbonate formation was observed.

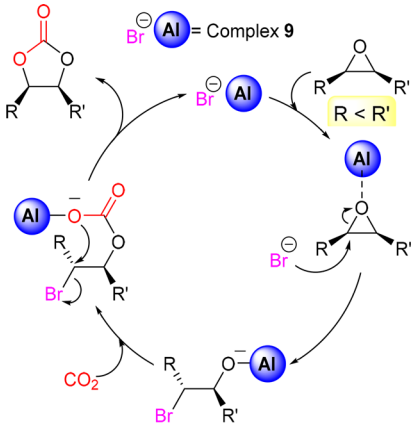
Considering that the synthesis of disubstituted cyclic carbonates takes place with retention of the epoxide stereochemistry, a plausible mechanism for the cyclic carbonate formation catalyzed by complex **9** is shown in Scheme 7, which is consistent with the catalytic cycle previously reported for cyclic carbonate formation using other aluminum complexes.[58−60]

CONCLUSIONS

New bifunctional alkylaluminum heteroscorpionate complexes supported by zwitterionic ligands containing a mesylate, chloride, bromide, or iodide anion have been developed. Single-crystal X-ray studies and NMR spectroscopy confirmed a κ^2-NO coordination mode of the heteroscorpionate ligand for the monometallic complexes and a κ^2-NO-μ-O coordination mode for the bimetallic complexes, in which the second aluminum center is coordinated through a dative bond to the oxygen atom of the alkoxide moiety.

These complexes were able to promote cyclic carbonate formation from epoxides and CO_2 without the need for the addition of an external nucleophile cocatalyst. The catalysts showed to be very selective toward cyclic carbonate synthesis, and no polycarbonate was observed during the reaction. This study has allowed us to conclude that iodide bifunctional aluminum complex **11** is the optimal catalyst for the synthesis of a wide variety of monosubstituted cyclic carbonates from terminal epoxides and CO_2 in good-to-excellent yields. On the other hand, bifunctional aluminum bromide complex **9** was the optimal catalyst for disubstituted cyclic carbonate synthesis from CO_2 and internal epoxides.

Scheme 7. Proposed Mechanism for the Synthesis of Cyclic Carbonates from Epoxides and CO_2 Catalyzed by Complex 9



EXPERIMENTAL SECTION

All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (*n*-hexane or THF) or over $CaCl_2$ (acetonitrile) and distilled under nitrogen from sodium (toluene), a sodium−potassium alloy (*n*-hexane), or $CaCl_2$ (acetonitrile). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. Microanalyses were carried out with a PerkinElmer 2400 CHN analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent. 1D NOESY NMR spectra were recorded using standard *VARIAN-FT* software with the following acquisition parameters: irradiation time = 2 s and number of scans = 256. 2D NMR spectra were acquired using standard *VARIAN-FT* software and processed using an IPC-Sun computer. Commercially available chemicals (Alfa, Aldrich, and Fluka) were used as received.

Synthesis of (mbpzappeH)MeSO$_3$ (2). In a 250 mL Schlenk tube, compound **1** (1.00 g, 2.33 mmol) was dissolved in dry acetonitrile (70 mL). Methylmethanesulfonate (0.59 mL, 6.99 mmol) was added, and the mixture was heated to acetonitrile under reflux and stirred for 16 h. Then, the solvent was removed under vacuum, and the crude residue was washed with hexane (3 × 25 mL) to remove excess methylmethanesulfonate. The resulting solid was dried, and compound **2** was isolated as a yellow solid. Yield: 77% (0.97 g, 1.80 mmol). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.73−7.20 (m, 9H, NPh, Ph), 7.01 (s, 1H, CH), 5.75 (s, 1H, H$^{4\prime}$), 5.74 (s, 1H, H^4), 3.56 (s, 9H, NMe_3), 2.49 (s, 3H, $MeSO_3$), 2.04 (s, 3H, Me$^{3\prime}$), 2.01 (s, 3H, Me$^{3\prime}$), 1.99 (s, 6H, Me$^{5,5\prime}$). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 147.4, 147.3, 146.7, 146.0, 143.6, 141.4, 141.1, 139.8 (C^{ipso,P}-NPh, C$^{3,3\prime}$, C$^{5,5\prime}$, C^{ipso}-Ph), 128.4−119.5 (NPh, Ph), 106.0 (C$^{4\prime}$), 105.6 (C^4), 81.3 (C^a), 71.7 (CH), 56.8 (NMe_3), 39.0 (CSO_3), 12.6 (Me$^{3\prime}$), 12.5 (Me^3), 10.2 (Me$^{5\prime}$), 10.0 (Me^5). Elem anal. Calcd for $C_{28}H_{37}N_5O_4S$ (539.06): C, 62.33; H, 6.86; N, 12.99. Found: C, 62.43; H, 6.97; N, 12.78.

Synthesis of (mbpzappeH)Cl (3). Compound **2** (1.00 g, 1.86 mmol) was dissolved in 1:1 CH_2Cl_2/H_2O (25 mL), and then an excess of KCl (1.39 g, 16.60 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. Then, the organic layer was extracted and dried over $MgSO_4$. The mixture was filtered and the solvent removed under reduced pressure to give the product **3** as a white solid. Yield: 79% (0.70 g, 1.46 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 8.09 (s, 1H, OH), 7.74−7.15 (m, 9H, NPh, Ph), 6.98 (s, 1H, CH), 5.70 (s, 2H, H$^{4\prime,4}$), 3.96 (s, 9H, NMe_3), 2.04 (s, 6H, Me$^{3\prime,3}$), 2.00 (s, 3H, Me$^{5\prime}$), 1.95 (s, 3H, Me^5). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 297 K): δ 147.4, 147.1, 147.0, 146.0, 143.0, 140.9, 140.8 (C^{ipso,P}-NPh,C$^{3,3\prime}$, C$^{5,5\prime}$, C^{ipso}-Ph), 128.8−119.0 (NPh, Ph), 107.2 (C$^{4\prime}$), 106.3 (C^4), 81.4 (C^a), 74.1 (CH), 57.2 (NMe_3), 13.3 (Me$^{3\prime,3}$), 11.3 (Me$^{5\prime}$), 10.9 (Me^5). Elem anal. Calcd for $C_{27}H_{34}ClN_5O$ (479.45): C, 67.58; H, 7.09; N, 14.60. Found: C, 67.95; H, 7.32; N, 14.17.

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Synthesis of (mbpzappeH)Br (4). Compound **2** (1.00 g, 1.86 mmol) was dissolved in dry dichloromethane (25 mL), and then an excess of NaBr (1.90 g, 18.60 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. Then, the reaction mixture was filtered, and the solvent was removed under vacuum to give compound **4** as a white solid. Yield: 87% (0.85 g, 1.62 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 8.07 (s, 1H, OH), 7.76−7.15 (m, 9H, NPh, Ph), 6.95 (s, 1H, CH), 5.68 (s, 1H, $H^{4\prime}$), 5.28 (s, 1H, H^{4}), 3.95 (s, 9H, NMe_3), 2.02 (s, 3H, $Me^{3\prime}$), 2.00 (s, 3H, Me^{3}), 1.97 (s, 3H, $Me^{5\prime}$), 1.94 (s, 3H, Me^{5}). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 297 K): δ 147.5, 147.0, 146.9, 145.9, 143.0, 141.0, 140.9 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5\prime}$, C^{ipso}-Ph), 129.0−119.1 (NPh, Ph), 107.2 ($C^{4\prime}$), 106.3 (C^{4}), 82.4 (C^{a}), 74.0 (CH), 57.4 (NMe_3), 13.3 ($Me^{3\prime}$), 13.2 (Me^{3}), 11.4 ($Me^{5\prime}$), 10.9 (Me^{5}). Elem anal. Calcd for $C_{27}H_{34}BrN_5O$ (523.11): C, 61.93; H, 6.50; N, 13.38. Found: C, 62.43; H, 6.81; N, 13.17.

Synthesis of (mbpzappeH)I (5). The synthesis of compound **5** was carried out in a manner identical with that for **4**, using compound **2** (1.0 g, 1.86 mmol) and an excess of NaI (2.79 g, 18.60 mmol). Yield: 85% (0.90 g, 1.58 mmol). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.68−7.23 (m, 9H, NPh, Ph), 6.96 (s, 1H, CH), 5.74 (s, 1H, $H^{4\prime}$), 5.72 (s, 1H, H^{4}), 3.55 (s, 3H, NMe_3), 2.03 (s, 3H, $Me^{5\prime}$), 2.00 (s, 3H, $Me^{3\prime}$), 1.98 (s, 3H, Me^{3}), 1.96 (s, 3H, Me^{5}). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 147.4, 147.3, 146.8, 145.9, 143.6, 141.3, 140.9 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5\prime}$, C^{ipso}-Ph), 128.5−119.4 (NPh, Ph), 105.9 ($C^{4\prime}$), 105.5 (C^{4}), 81.3 (C^{a}), 71.6 (CH), 57.1 (NMe_3), 12.6 ($Me^{3\prime,3}$), 10.3 ($Me^{5\prime}$), 10.1 (Me^{5}). Elem anal. Calcd for $C_{27}H_{34}IN_5O$ (570.9): C, 56.75; H, 5.95; N, 12.26. Found: C, 56.81; H, 5.99; N, 12.09.

Synthesis of [AlMe$_2${κ^2-mbpzappe}]Cl (6). A solution of compound **3** (1.00 g, 2.08 mmol) was dissolved in dry acetonitrile (50 mL) and heated to 60 °C. Then, a solution of $AlMe_3$ (2 M in toluene, 0.88 mL, 2.08 mmol) was added, and the reaction mixture was stirred at this temperature for 2 h. Then, the solvent was evaporated under reduced pressure to give a yellow solid. The product was then washed with *n*-hexane (25 mL) and recrystallized from toluene at −26 °C to give compound **6** as a yellow solid. Yield: 91% (1.02 g). ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 7.83−7.11 (m, 9H, NPh, Ph), 6.74 (s, 1H, CH), 5.77 (s, 1H, $H^{4\prime}$), 5.71 (s, 1H, H^{4}), 3.98 (s, 9H, NMe_3), 2.18 (s, 3H, $Me^{3\prime}$), 2.17 (s, 3H, Me^{3}), 2.03 (s, 3H, $Me^{5\prime}$), 1.94 (s, 3H, Me^{5}), −0.88 [s, 6H, $Al(CH_3)_2$]. ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 149.6, 149.1, 146.0, 145.1, 141.6, 141.5, 140.9 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.7−118.0 (NPh, Ph), 107.0 ($C^{4\prime}$), 106.3 (C^{4}), 81.4 (C^{a}), 70.8 (CH), 57.2 (NMe_3), 13.2 ($Me^{3\prime}$), 13.1 (Me^{3}), 11.2 ($Me^{5\prime}$), 10.7 (Me^{5}), −7.6 [$Al(CH_3)_2$]. Elem anal. Calcd for $C_{29}H_{39}AlClN_5O$ (535.43): C, 64.99; H, 7.28; N, 13.07. Found: C, 65.23; H, 7.71; N, 12.84.

Synthesis of [AlEt$_2${κ^2-mbpzappe}]Cl (7). The synthesis of **7** was carried out in a manner identical with that for **6**, using compound **3** (1.00 g, 2.08 mmol) and a solution of $AlEt_3$ (1 M in hexane, 2.08 mL, 2.08 mmol). Compound **7** was isolated as a yellow solid. Yield: 91% (1.07 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.61−7.21 (m, 9H, NPh, Ph), 6.88 (s, 1H, CH), 5.89 (s, 1H, $H^{4\prime}$), 5.76 (s, 1H, H^{4}), 3.53 (s, 9H, NMe_3), 2.19 (s, 3H, $Me^{3\prime}$), 2.16 (s, 3H, Me^{3}), 2.09 (s, 3H, $Me^{5\prime}$), 1.93 (s, 3H, Me^{5}), 0.92−1.02 (m, 6H, $AlCH_2CH_3$), −0.14 (m, 4H, $AlCH_2CH_3$). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 150.3, 150.0, 149.6, 146.6, 146.5, 143.7, 142.4 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.7−119.6 (NPh, Ph), 107.0 ($C^{4\prime}$), 106.4 (C^{4}), 81.7 (C^{a}), 70.1 (CH), 57.4 (NMe_3), 13.0 ($Me^{3\prime}$), 12.9 (Me^{3}), 10.8 ($Me^{5\prime}$), 10.7 (Me^{5}), 9.3 ($AlCH_2CH_3$), 6.6 ($AlCH_2CH_3$). Elem anal. Calcd for $C_{31}H_{43}AlClN_5O$ (563.43): C, 66.02; H, 7.63; N, 12.43. Found: C, 66.23; H, 7.85; N, 12.24.

Synthesis of [AlMe$_2${κ^2-mbpzappe}]Br (8). The synthesis of **8** was carried out in a manner identical with that for **6**, using compound **4** (1.00 g, 1.91 mmol) and a solution of $AlMe_3$ (2 M in toluene, 0.95 mL, 1.91 mmol). Compound **8** was isolated as a yellow solid. Yield: 90% (1.00 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.62−7.20 (m, 9H, NPh, Ph), 6.90 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.77 (s, 1H, H^{4}), 3.54 (s, 9H, NMe_3), 2.18 (s, 3H, $Me^{3\prime}$), 2.15 (s, 3H, Me^{3}), 2.09 (s, 3H, $Me^{5\prime}$), 1.93 (s, 3H, Me^{5}), −0.85 (s, 6H, $[Al(CH_3)_2]$. ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 149.3, 149.2, 148.8, 145.9, 145.5, 143.1, 141.8 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.2−119.1 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^{4}), 81.2 (C^{a}), 69.8 (CH), 56.9 (NMe_3), 12.5 ($Me^{3\prime}$), 12.3 (Me^{3}), 10.3 ($Me^{5\prime}$), 10.1 (Me^{5}), −7.7 [$Al(CH_3)_2$]. Elem anal. Calcd for $C_{29}H_{39}AlBrN_5O$ (579.11): C, 60.09; H, 6.73; N, 12.09. Found: C, 60.30; H, 6.91; N, 11.94.

Synthesis of [AlEt$_2${κ^2-mbpzappe}]Br (9). The synthesis of **9** was carried out in a manner identical with that for **6**, using compound **4** (1.00 g, 1.91 mmol) and a solution of $AlEt_3$ (1 M in hexane, 1.91 mL, 1.91 mmol). Compound **9** was isolated as a yellow solid. Yield: 88% (1.03 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.66−7.21 (m, 9H, NPh, Ph), 6.90 (s, 1H, CH), 5.89 (s, 1H, $H^{4\prime}$), 5.76 (s, 1H, H^{4}), 3.58 (s, 9H, NMe_3), 2.18 (s, 3H, $Me^{3\prime}$), 2.16 (s, 3H, Me^{3}), 2.10 (s, 3H, $Me^{5\prime}$), 1.93 (s, 3H, Me^{5}), 0.94 (t, $^{3}J_{H-H}$ = 8.0 Hz, 6H, $AlCH_2CH_3$), −0.14 (m, 4H, $AlCH_2CH_3$). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 149.8, 149.4, 149.0, 148.9, 145.9, 145.6, 143.1 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.1−119.0 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^{4}), 81.1 (C^{a}), 69.6 (CH), 56.9 (NMe_3), 12.4 ($Me^{3\prime}$), 12.3 (Me^{3}), 10.3 ($Me^{5\prime}$), 10.2 (Me^{5}), 8.8 ($AlCH_2CH_3$), 6.0 ($AlCH_2CH_3$). Elem anal. Calcd for $C_{31}H_{43}AlBrN_5O$ (607.11): C, 61.27; H, 7.08; N, 11.53. Found: C, 61.52; H, 7.27; N, 11.37.

Synthesis of [AlMe$_2${κ^2-mbpzappe}]I (10). The synthesis of **10** was carried out in a manner identical with that for **6**, using compound **5** (1.00 g, 1.75 mmol) and a solution of $AlMe_3$ (2 M in toluene, 0.88 mL, 1.75 mmol). Compound **10** was isolated as a yellow solid. Yield: 91% (1.0 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.62−7.22 (m, 9H, NPh, Ph), 6.90 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.78 (s, 1H, H^{4}), 3.54 (s, 9H, NMe_3), 2.18 (s, 3H, $Me^{3\prime}$), 2.15 (s, 3H, Me^{3}), 2.09 (s, 3H, $Me^{5\prime}$), 1.93 (s, 3H, Me^{5}), −0.85 (s, 9H, $[Al(CH_3)_3]$. ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 149.3, 149.2, 148.8, 145.7, 145.5, 143.1, 141.8 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.2−119.0 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^{4}), 81.2 (C^{a}), 69.8 (CH), 57.0 (NMe_3), 12.5 ($Me^{3\prime}$), 12.3 (Me^{3}), 10.3 ($Me^{5\prime}$), 10.1 (Me^{5}), −7.7 [$Al(CH_3)_3$]. Elem anal. Calcd for $C_{29}H_{39}AlIN_5O$ (626.90): C, 55.51; H, 6.22; N, 11.17. Found: C, 55.80; H, 6.71; N, 10.84.

Synthesis of [AlEt$_2${κ^2-mbpzappe}]I (11). The synthesis of **11** was carried out in a manner identical with that for **6**, using compound **5** (1.00 g, 1.75 mmol) and a solution of $AlEt_3$ (1 M in hexane, 1.75 mL, 1.75 mmol). Compound **11** was isolated as a yellow solid. Yield: 90% (1.03 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.64−7.21 (m, 9H, NPh, Ph), 6.89 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.77 (s, 1H, H^{4}), 3.58 (s, 9H, NMe_3), 2.17 (s, 3H, $Me^{3\prime}$), 2.16 (s, 3H, Me^{3}), 2.11 (s, 3H, $Me^{5\prime}$), 1.94 (s, 3H, Me^{5}), 0.97 (t, $^{3}J_{H-H}$ = 8.4 Hz, 6H, $AlCH_2CH_3$), −0.14 (m, 4H, $AlCH_2CH_3$). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 149.8, 149.4, 149.0, 146.0, 145.8, 143.1, 141.8 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.1−119.0 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^{4}), 81.1 (C^{a}), 69.5 (CH), 57.1 (NMe_3), 12.4 ($Me^{3\prime}$), 12.3 (Me^{3}), 10.4 ($Me^{5\prime}$), 10.3 (Me^{5}), 8.8 ($AlCH_2CH_3$), 6.0 ($AlCH_2CH_3$). Elem anal. Calcd for $C_{31}H_{43}AlIN_5O$ (654.90): C, 56.80; H, 6.57; N, 10.75. Found: C, 56.93; H, 6.94; N, 10.41.

Synthesis of [{AlMe$_2$(κ^2-mbpzappe)}(μ-O){AlMe$_3$}]MeSO$_3$ (12). The synthesis of **12** was carried out in a manner identical with that for **6**, using compound **2** (1.00 g, 1.86 mmol) and a solution of $AlMe_3$ (2 M in toluene, 1.86 mL, 3.72 mmol). Compound **12** was isolated as a yellow solid. Yield: 86% (1.07 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.61−7.23 (m, 9H, NPh, Ph), 6.91 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.79 (s, 1H, H^{4}), 3.52 (s, 9H, NMe_3), 2.52 (brs, 3H, $MeSO_3$), 2.19 (s, 3H, $Me^{3\prime}$), 2.17 (s, 3H, Me^{3}), 2.09 (s, 3H, $Me^{5\prime}$), 1.94 (s, 3H, Me^{5}), −0.84 [s, 9H, $Al(CH_3)_3$], −1.07 [s, 6H, $Al(CH_3)_2$]. ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 297 K): δ 149.4, 149.2, 148.9, 145.8, 145.5, 143.0, 141.9 ($C^{ipso,p}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.2−119.2 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^{4}), 81.2 (C^{a}), 69.8 (CH), 56.9 (NMe_3), 39.0 ($MeSO_3$), 12.4 ($Me^{3\prime}$), 12.3 (Me^{3}), 10.1 ($Me^{5\prime}$), 10.0 (Me^{5}), −5.5 [$Al(CH_3)_2$], −7.8 [$Al(CH_3)_3$]. Elem anal. Calcd for $C_{33}H_{51}Al_2N_5O_4S$ (667.06): C, 59.36; H, 7.64; N, 10.49. Found: C, 59.42; H, 7.89; N, 10.12.

Synthesis of [{AlEt$_2$(κ^2-mbpzappe)}(μ-O){AlEt$_3$}]MeSO$_3$ (13). The synthesis of **13** was carried out in a manner identical with that for **6**, using compound **2** (1.00 g, 1.86 mmol) and a solution of $AlEt_3$ (1 M in hexane, 3.72 mL, 3.72 mmol). Compound **13** was isolated as a

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yellow solid. Yield: 88% (1.20 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.54−7.23 (m, 9H, NPh, Ph), 6.86 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.77 (s, 1H, H^4), 3.47 (s, 9H, NMe_3), 2.67 (brs, 3H, $MeSO_3$), 2.19 (s, 3H, $Me^{3\prime}$), 2.17 (s, 3H, Me^3), 2.09 (s, 3H, $Me^{5\prime}$), 1.94 (s, 3H, Me^5), 0.90−1.30 (m, 15H, $AlCH_2CH_3$), −0.10 to −0.40 (m, 10H, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 297 K): δ 149.9, 149.8, 149.4, 146.3, 146.1, 143.3, 142.4 ($C^{ipso,P}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.7−119.4 (NPh, Ph), 106.9 ($C^{4\prime}$), 106.5 (C^4), 81.8 (C^a), 70.3 (CH), 57.3 (NMe_3), 39.5 ($MeSO_3$), 13.1 ($Me^{3\prime}$), 12.9 (Me^3), 10.7 ($Me^{5\prime}$), 10.6 (Me^5), 12.3−10.1 ($AlCH_2CH_3$), 9.6−8.8 ($AlCH_2CH_3$). Elem anal. Calcd for $C_{38}H_{61}Al_2N_5O_4S$ (737.06): C, 61.86; H, 8.28; N, 9.50. Found: C, 62.03; H, 8.71; N, 9.21.

Synthesis of [{AlMe$_2$(κ^2-mbpzappe)}(μ-O){AlMe$_3$}]Cl (14). The synthesis of **14** was carried out in a manner identical with that for **6** using compound **3** (1.00 g, 2.08 mmol) and a solution of $AlMe_3$ (2 M in toluene, 2.08 mL, 4.16 mmol). Compound **14** was isolated as a yellow solid. Yield: 91% (1.15 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.68−7.22 (m, 9H, NPh, Ph), 6.94 (s, 1H, CH), 5.91 (s, 1H, $H^{4\prime}$), 5.79 (s, 1H, H^4), 3.58 (s, 9H, NMe_3), 2.20 (s, 3H, $Me^{3\prime}$), 2.17 (s, 3H, Me^3), 2.11 (s, 3H, $Me^{5\prime}$), 1.96 (s, 3H, Me^5), −0.83 [s, 9H, $Al(CH_3)_3$], −1.03 [s, 6H, $Al(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 297 K): δ 149.4, 149.3, 148.9, 145.8, 145.5, 143.1, 141.8, ($C^{ipso,P}$-N*Ph*, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.2−119.1 (NPh, Ph), 106.5 ($C^{4\prime}$), 106.0 (C^4), 81.1 (C^a), 69.8 (CH), 57.1 (NMe_3), 12.6 ($Me^{3\prime}$), 12.4 (Me^3), 10.3 ($Me^{5\prime}$), 10.2 (Me^5), −5.6 [$Al(CH_3)_2$], −7.8 [$Al(CH_3)_3$]. Elem anal. Calcd for $C_{32}H_{48}Al_2ClN_5O$ (608.17): C, 63.21; H, 7.96; N, 11.52. Found: C, 63.43; H, 8.05; N, 11.27.

Synthesis of [{AlEt$_2$(κ^2-mbpzappe)}(μ-O){AlEt$_3$}]Cl (15). The synthesis of **15** was carried out in a manner identical with that for **6**, using compound **3** (1.00 g, 2.08 mmol) and a solution of $AlEt_3$ (1 M in hexane, 4.16 mL, 4.16 mmol). Compound **15** was isolated as a yellow solid. Yield: 87% (1.23 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.60−7.20 (m, 9H, NPh, Ph), 6.88 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.76 (s, 1H, H^4), 3.52 (s, 9H, NMe_3), 2.19 (s, 3H, $Me^{3\prime}$), 2.17 (s, 3H, Me^3), 2.10 (s, 3H, $Me^{5\prime}$), 1.93 (s, 3H, Me^5), 0.90−1.40 (m, 15H, $AlCH_2CH_3$), −0.07 to −0.43 (m, 10H, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 297 K): δ 149.5, 149.0, 148.6, 146.0, 145.7, 143.1, 141.8 ($C^{ipso,P}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.1−118.8 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.8 (C^4), 81.1 (C^a), 69.5 (CH), 56.8 (NMe_3), 12.4 ($Me^{3\prime}$), 12.3 (Me^3), 10.2 ($Me^{5\prime}$), 10.1 (Me^5), 8.6, 6.0 ($AlCH_2CH_3$), 1.5 ($AlCH_2CH_3$). Elem anal. Calcd for $C_{37}H_{58}Al_2ClN_5O$ (678.31): C, 65.54; H, 8.62; N, 10.32. Found: C, 65.82; H, 8.74; N, 10.09.

Synthesis of [{AlMe$_2$(κ^2-mbpzappe)}(μ-O){AlMe$_3$}]Br (16). The synthesis of **16** was carried out in a manner identical with that for **6**, using compound **4** (1.00 g, 1.91 mmol) and a solution of $AlMe_3$ (2 M in toluene, 1.91 mL, 3.82 mmol). Compound **16** was isolated as a yellow solid. Yield: 82% (1.02 g). ^{1}H NMR (500 MHz, C_6D_6, 297 K): δ 7.55−7.20 (m, 9H, NPh, Ph), 6.88 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.77 (s, 1H, H^4), 3.48 (s, 9H, NMe_3), 2.18 (s, 3H, $Me^{3\prime}$), 2.16 (s, 3H, Me^3), 2.08 (s, 3H, $Me^{5\prime}$), 1.91 (s, 3H, Me^5), −0.85 [s, 9H, $Al(CH_3)_3$], −0.96 [s, 6H, $Al(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 297 K): δ 149.7, 149.3, 148.9, 145.6, 145.5, 143.1, 141.7 ($C^{ipso,P}$-N*Ph*, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.2−118.9 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^4), 81.2 (C^a), 69.8 (CH), 57.0 (NMe_3), 12.5 ($Me^{3\prime}$), 12.3 (Me^3), 10.2 ($Me^{5\prime}$), 10.1 (Me^5), −7.69 ($AlCH_3$). Elem anal. Calcd for $C_{32}H_{48}Al_2BrN_5O$ (652.62): C, 58.90; H, 7.41; N, 10.73. Found: C, 59.14; H, 7.54; N, 10.52.

Synthesis of [{AlEt$_2$(κ^2-mbpzappe)}(μ-O){AlEt$_3$}]Br (17). The synthesis of **17** was carried out in a manner identical with that for **6**, using compound **4** (1.00 g, 1.91 mmol) and a solution of $AlEt_3$ (1 M in hexane, 3.82 mL, 3.82 mmol). Compound **17** was isolated as a yellow solid. Yield: 87% (1.20 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.55−7.20 (m, 9H, NPh, Ph), 6.86 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.76 (s, 1H, H^4), 3.51 (s, 9H, NMe_3), 2.19 (s, 3H, $Me^{3\prime}$), 2.17 (s, 3H, Me^3), 2.09 (s, 3H, $Me^{5\prime}$), 1.92 (s, 3H, Me^5), 0.84−1.29 (m, 15H, $AlCH_2CH_3$), −0.08 to −0.33 (m, 10H, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 297 K): δ 149.9, 149.5, 149.1, 148.9, 146.0, 145.6, 143.2 ($C^{ipso,P}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.2−118.8 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^4), 81.1 (C^a), 69.5 (CH), 57.0 (NMe_3), 12.4 ($Me^{3\prime}$), 12.3 (Me^3), 10.3 ($Me^{5\prime}$), 10.1 (Me^5), 9.6 ($AlCH_2CH_3$), 8.8, 8.0 ($AlCH_2CH_3$). Elem anal. Calcd for $C_{37}H_{58}Al_2BrN_5O$ (722.76): C, 61.49; H, 8.09; N, 9.70. Found: C, 61.83; H, 8.24; N, 9.52.

Synthesis of [{AlMe$_2$(κ^2-mbpzappe)}(μ-O){AlMe$_3$}]I (18). The synthesis of **18** was carried out in a manner identical with that for **6**, using compound **5** (1.00 g, 1.75 mmol) and a solution of $AlMe_3$ (2 M in toluene, 1.75 mL, 3.50 mmol). Compound **18** was isolated as a yellow solid. Yield: 92% (1.13 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.64−7.21 (m, 9H, NPh, Ph), 6.90 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.78 (s, 1H, H^4), 3.55 (s, 9H, NMe_3), 2.18 (s, 3H, $Me^{3\prime}$), 2.15 (s, 3H, Me^3), 2.10 (s, 3H, $Me^{5\prime}$), 1.94 (s, 3H, Me^5), −0.85 [s, 9H, $Al(CH_3)_3$], −0.97 [s, 6H, $Al(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 297 K): δ 149.3, 149.2, 148.8, 145.8, 145.5, 143.1, 141.8 ($C^{ipso,P}$-N*Ph*, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.2−119.1 (NPh, Ph), 106.4 ($C^{4\prime}$), 105.9 (C^4), 81.3 (C^a), 69.8 (CH), 57.1 (NMe_3), 12.5 ($Me^{3\prime}$), 12.3 (Me^3), 10.3 ($Me^{5\prime}$), 10.2 (Me^5), −7.71 ($AlCH_3$). Elem anal. Calcd for $C_{32}H_{48}Al_2IN_5O$ (699.62): C, 54.94; H, 6.92; N, 10.01. Found: C, 55.12; H, 7.23; N, 9.74.

Synthesis of [{AlEt$_2$(κ^2-mbpzappe)}(μ-O){AlEt$_3$}]I (19). The synthesis of **19** was carried out in a manner identical with that for **6**, using compound **5** (1.00 g, 1.75 mmol) and a solution of $AlEt_3$ (1 M in hexane, 3.50 mL, 3.50 mmol). Compound **19** was isolated as a yellow solid. Yield: 89% (1.20 g). ^{1}H NMR (500 MHz, CD_3CN, 297 K): δ 7.61−7.22 (m, 9H, NPh, Ph), 6.88 (s, 1H, CH), 5.90 (s, 1H, $H^{4\prime}$), 5.77 (s, 1H, H^4), 3.53 (s, 9H, NMe_3), 2.19 (s, 3H, $Me^{3\prime}$), 2.16 (s, 3H, Me^3), 2.10 (s, 3H, $Me^{5\prime}$), 1.93 (s, 3H, Me^5), 0.90−1.32 (m, 15H, $AlCH_2CH_3$), −0.07 to −0.33 (m, 10H, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 297 K): δ 150.1, 149.7, 149.3, 146.3, 146.1, 143.4, 142.1 ($C^{ipso,P}$-NPh, $C^{3,3\prime}$, $C^{5,5}$, C^{ipso}-Ph), 129.4 (^{m}CPh), 128.0−119.2 (NPh, Ph), 106.7 ($C^{4\prime}$), 106.2 (C^4), 81.3 (C^a), 69.8 (CH), 57.2 (NMe_3), 12.7 ($Me^{3\prime}$), 12.6 (Me^3), 10.6 ($Me^{5\prime}$), 10.4 (Me^5), 9.0 ($AlCH_2CH_3$), 5.6 ($AlCH_2CH_3$). Elem anal. Calcd for $C_{37}H_{58}Al_2IN_5O$ (769.76): C, 57.73; H, 7.59; N, 9.10. Found: C, 57.88; H, 7.81; N, 8.93.

X-ray Crystallographic Structure Determination. Colorless crystals for **11** were obtained by the diffusion of acetonitrile/hexane. X-ray data for **11** were collected on a Bruker X8 APEX II CCD area detector diffractometer at T = 290 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å, sealed X-ray tube). Data were integrated using *SAINT*,[67] and an absorption correction was performed with the program *SADABS*.[68] The structures were solved by direct methods using the *WINGX* package[69] and refined by full-matrix least-squares methods based on F^2. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and thereafter treated as riding atoms. Compound **11** crystallizes with two acetonitrile molecules disordered over four positions. These positions have been refined with occupancies of 0.25 for each one, and *RIGU* instruction has been necessary. Salient crystallographic data are summarized in Table S1, and further details can be found in the Supporting Information. Selected bond lengths and angles are given in Table S2. CCDC 1881272 is for the structure of **11**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b03475.

Experimental data, workup for catalytic reactions, X-ray crystallographic data for compound **11**, and ^{1}H and ^{13}C NMR spectra for cyclic carbonates (PDF)

Accession Codes

CCDC 1881272 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cam-

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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