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Toward a Neutral Single-Component Amidinate Iodide Aluminum Catalyst for the CO₂ Fixation into Cyclic Carbonates

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tested and found to be active as catalysts for the cyclic carbonate formation from epoxides at 80 °C and 1 bar of CO2 pressure. A first series of experiments were carried out with 1.5 mol % of the alkyl complex 2 and 1.5 mol % of tetrabutylammonium iodide (TBAI) as a cocatalyst; subsequently, the reactions were carried out with 1.5 mol % of iodide complex 3 as a single-component catalyst. Compound 3 is one of the first examples of a



nonzwitterionic halide single-component aluminum catalyst producing cyclic carbonates. The full catalytic cycle with characterization of all minima and transition states was characterized by quantum chemistry calculations (QCCs) using density functional theory. QCCs on the reaction mechanism support a reaction pathway based on the exchange of the iodine contained in the catalyst by 1 equiv of epoxide, with subsequent attack of I^- to the epoxide moiety producing the ring opening of the epoxide. QCCs triggered new insights for the design of more active halide catalysts in future explorations of the field.

INTRODUCTION

The interest in the use and capture of CO₂ has grown enormously over the past few years¹⁻⁴ as an inexpensive, nontoxic, and abundant renewable source which can be employed as C1 chemical feedstock for the preparation of high added value products such as methanol,^{5,6} formic acid,⁷ lactams,⁸ and cyclic carbonates.⁹⁻¹¹ Among these transformations, the cyclization of epoxides and CO₂ to prepare cyclic carbonates (Scheme 1) has been extensively explored due to their role as intermediates in the production of fine chemicals, $^{12-14}$ as electrolytes in lithium-ion batteries, 15,16 and as green solvents.¹⁷

A large number of catalytic systems have been developed for the preparation of cyclic carbonates including organocatalysts $^{18-21}$ and metal complexes. $^{22-32}$ These generally act as

Scheme 1. General Synthesis of Cyclic Carbonates from Substituted Epoxide and CO₂



Lewis acids in the activation of the epoxides for their transformation to cyclic carbonates. The choice of the metal center is essential, and aluminum, an abundant element in the earth's crust, is one of the most suited metals for cyclic carbonates formation. $^{33-36}$ Moreover, regarding the use of ligands, Schiff base ligands have been widely investigated, promoting increasing reactivity of the catalysts.^{37,38} Among the catalytic systems reported in the literature, the bimetallic aluminum(salen) complex (Figure 1a) was found to be an excellent catalyst for the preparation of cyclic carbonates under mild reaction conditions.³⁹ Kleij and co-workers reported an aluminum catalyst supported by a tripodal amino phenolate ligand (Figure 1b) which displayed remarkable catalytic activity for a wide range of different epoxides toward the selective formation of cyclic carbonates.⁴⁰ We recently reported a trinuclear amidinate aluminum complex (Figure 1c) which was found also to be active for this kind of transformation.³³

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Figure 1. Double-component (a-c) or one-component (d-f) zwitterionic aluminum catalysts for the preparation of cyclic carbonates.

Scheme 2. Synthesis of the Amidinate Ligand Precursor 1



Although all of these species are active catalysts for the synthesis of cyclic carbonates, they do require a nucleophile source as a cocatalyst. In the quest for single-component catalysts, zwitterionic aluminum complexes have been proposed which already incorporate the nucleophile in their structure. Interestingly, in some cases, these catalysts can be more effective than neutral two-component systems due to cooperative effects among the functional groups which give rise to increasing selectivity and catalytic activity.^{41–48} Notably, such one-component aluminum complexes were reported by North and co-workers (Figure 1d), displaying excellent activities,^{46,47} as has been the aluminum(salen) complex e in Figure 1 bearing appended quaternary ammonium salt as substituents.³⁸ Finally, a bifunctional aluminum complex supported by a heteroscorpionate ligand was found to efficiently catalyze the generation of bioderived cyclic carbonates (Figure 1f).⁴²

Given these activities aimed at single-component catalytic systems, we focused on the development of a neutral (nonzwitterionic) and bifunctional iodide aluminum catalyst for the formation of cyclic carbonates from epoxides and CO_2 in the absence of a cocatalyst. To the best of our knowledge, there are only a few examples of neutral aluminum complexes that are able to catalyze the formation of cyclic carbonates without adding a cocatalyst,^{49,50} and in particular, only two examples of nonzwitterionic halide aluminum complexes have been reported to date that achieve good catalytic transformation and selectively by themselves in the absence of a cocatalyst.^{51,52} The concept

behind this work is toward the formation of neutral singlecomponent catalysts by employing a nucleophile already contained in the molecular structure of the catalyst. Due to the relatively long Al–I distance and the pronounced mismatch in chemical hardness, dissociation of the Al–I bond (for instance promoted by an exchange reaction) can take place more easily comparing other Al–X (X = F, Cl, Br) bonds without the need of a cocatalyst. Indeed, experimental and computational evidence presented in this work shows that the release of the iodide takes place even at room temperature.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of Ligand Precursor 1. The one-step synthesis of the new bis(amidine) ligand precursor 1 is shown in Scheme 2. The N',N''-(naphthalene-1,8-diyl)bis(N-(2,6-dimethylphenyl)acetimidamide) ligand (1) was prepared by the reaction of 1,8diaminonaphthalene with 2 equiv of (E)-N-(2,6dimethylphenyl)acetimidoyl chloride⁵³ and Et₃N in dry toluene under reflux (Scheme 2) according to a modified protocol with respect to that previously reported.⁵⁴ After the appropriate workup, compound 1 was isolated as an orange solid in 76% yield.

The molecular structure of ligand precursor 1 was characterized by mass spectrometry (MS), nuclear magnetic resonance (NMR) spectroscopy (¹H NMR, ¹³C{¹H} NMR, ¹H NOESY-1D, ¹H-¹³C g-HSQC), and X-ray diffraction. In the ¹H

NMR spectrum of this compound, two resonances at 11.14 and 8.78 ppm are assigned to the N–H groups as previously observed for other bis(amidine) ligands.^{54,55} The low field shift of one of these resonances (11.14 ppm) arises due to the formation of an intramolecular hydrogen bond (HB) between the N–H group and the nitrogen atom of the amidine moiety. The presence of the HB is confirmed in the solid-state structure of compound 1 shown in Figure 2, in which the presence of an



Figure 2. Molecular structure of ligand 1. Only one molecule (molecule "A") is shown. Thermal ellipsoids are set at 30% probability. Selected bond distances are reported in Å, and angles are reported in deg: N1–C1 1.286(3), N2–C1 1.373(3), N3–C3 1.356(3), N4–C3 1.298(3), N2–H2…N4 1.88(3), C3–N4–C39 121.7(2), C3–N3–C21 122.8(2).

intramolecular hydrogen bond N–H…N was found in both crystallographically independent molecules "A" and "B" [molecule "A": N2A–H2A…N4A 1.88(3) Å, 144(2)°; molecule "B": N2B–H2B…N4B 1.94(3) Å, 150(2)°]. These two independent molecules of **1** present similar structural data. For this reason, only one molecule ("A") is discussed (see the Supporting Information for further details).

The two NCN amidine fragments of this compound are notably different; whereas the bond length N1–C1 (1.286(3) Å) is comparable to a normal double C=N bond, the distance N2–C1 is significantly longer (1.373(3) Å) and closer to that of a single C–N bond. In the other NCN fragment, the inverse situation is observed, the bond N3–C3 (1.356(3) Å) being longer than N4–C3 (1.298(3) Å).

Synthesis and Structural Characterization of Complexes 2 and 3. The preparation of the alkyl aluminum complex 2 was carried via protonolysis of the ligand precursor 1 with 1 equiv of $AlMe_3$ in dry CH_2Cl_2 at room temperature (Scheme 3). The resulting complex 2 was isolated as a yellow



crystalline solid in quantitative yield and characterized by NMR and MS. In the ¹H NMR spectrum of this complex, the disappearance of the resonance corresponding to the N–H group of the ligand precursor 1 confirms the formation of the amidinate complex 2 (see page S5 of the Supporting Information), while both the ¹H and ¹³C{¹H} NMR resonance patterns support the existence of an approximate plane of symmetry in the molecule. Additionally, the signal at –0.52 ppm in the ¹H NMR spectrum corresponds to the methyl group coordinated to the aluminum atom. The spectroscopic evidence reveals a pentacoordinate coordination geometry for the aluminum center with the amidinate ligand adopting a κ^4 -NNNN coordination mode.

With the aim of obtaining a single-component catalytic system to be active without the need of a cocatalyst, we decided to replace the methyl group by an iodide ligand at the aluminum center. This was accomplished by the reaction of complex **2** with 1 equiv of I_2 in CH_2Cl_2 (Scheme 4) according to a method

Scheme 4. Synthesis of Iodide Aluminum Complex 3



recently published by Nembenna and co-workers.⁵⁶ Compound **3** was isolated in high yield (96%) and characterized spectroscopically and by X-ray diffraction. The clean conversion of complex **2** to **3** can be readily followed by ¹H NMR, monitoring the disappearance of the signal corresponding to the methyl group at the aluminum center. Furthermore, the ¹H NMR resonance pattern of **3** is consistent with an effective C_s symmetry on the NMR time scale as also found for complex **2** (The exact point group of both **2** and **3** being C_1 .).

Compounds 2 and 3 crystallize in a $P2_1/c$ space group (see Tables S4 and S5 in the Supporting Information). The crystal structures of catalysts 2 and 3 are depicted in Figures 3 and 4, respectively. For pentacoordinate structures, two high-symmetry molecular geometries are possible, the trigonal bipyramid and the square-based pyramid. The τ index^{57,58} is generally employed to characterize intermediate coordination geometries: $\tau = 0$ corresponds to perfect square-pyramidal geometry, whereas $\tau = 1$ indicates an ideal trigonal-bipyramidal structure. The observed τ values computed from the X-ray data for complexes 2 and 3, 0.05 and 0.14, respectively, are indicative of distorted square-based pyramid geometries for the pentacoordi-





Figure 3. Molecular structure of complex 2. Thermal ellipsoids are shown with 30% probability. Selected bond distances are reported in Å, and angles are reported in deg. Structural parameters from DFT calculations (M06-2X/def2-TZVP/LANL2DZ(I)) are given in squared brackets: Al1–N2 1.939(1) [1.936], Al1–N3 1.999(1) [1.966], Al1–N4 1.942(1) [1.976], Al1–N1 1.992(11) [2.029], Al1–C5 1.964(1) [1.959]; N4–Al1–C5 112.2(1) [110.5], N3–Al1–C5 113.2(1) [116.7], N1–Al1–N4 134.6(1) [140.6], N2–Al1–N3 131.9(1) [119.0].



Figure 4. Molecular structure of complex 3. Thermal ellipsoids are shown with 50% probability. Selected bond distances are reported in Å, and angles are reported in deg. Structural parameters from DFT calculations (M06-2X/def2-TZVP/LANL2DZ(I)) are given in squared brackets: Al1–N2 1.918(2) [1.920], Al1–N3 1.962(2) [1.941], Al1–N4 1.911(2) [1.939], Al1–N1 1.973(2) [1.982], Al1–I1 2.553(1) [2.542]; N2–Al1–N3 144.4(1) [121.9], N1–Al1–N4 136.1(1) [148.0], N1–Al1–I1 110.7(1) [102], N2–Al1–I1 107.9(1) [121.2].

nate aluminum centers. The axial site is occupied by the methyl (2) or iodide (3) moiety, while the tetradentate amidinate ligand appears at the base of the pyramid. Notably, the majority

of pentacoordinated amidinate aluminum complexes reported to date displays distorted trigonal bipyramidal geometries.^{33,59–62} In contrast, for complexes **2** and **3**, the distorted square pyramidal geometry appears to be favored by the orientation of the two amidinate units in the tetradentate ligand which is enforced by the rigid naphthalene backbone.

Optimized molecular geometries for catalysts 2 and 3 were computed at the M06-2X/def2-TZVP/LANL2DZ(I) level of theory, and although optimized DFT minima may differ from the crystal structures,⁶³ a good match for both bond lengths and bond angles was found (the corresponding data are provided in square brackets in Figures 3 and 4). Notably, the Al1–I1 bond length in complex 3 obtained by DFT studies 2.541 Å is close to the observed 2.553(1) Å, with similar distances having been observed in related compounds containing Al–I bonds.⁵⁶ A bond order of 0.87 was found for the Al–I bond, indicating partial covalency, whereas the relatively large Al–I bond distance is expected to render the iodide an efficient leaving "group/atom" in a single-component catalyst.

Catalytic Performance of 2 and 3 for the Synthesis of Cyclic Carbonates. Having prepared and characterized complexes 2 and 3, we explored their potential use as catalysts for the preparation of a range of cyclic carbonates (5a-h) from their corresponding epoxides (4a-h) and CO₂. The conversions and yields of the catalytic runs are shown in Table 1.

Table 1. Conversions and Isolated Yields of Cyclic	
Carbonates 5a-h Employing Catalysts 2 and 3 ^a	

	R + CO ₂ 4a-h	2 (1.5 mol%)/ <u>3 (1.5</u> 80 °C, 1 b	TBAI (1.5 mol%) 5 mol%) ar, 24 h	R 5a-h
entry	epoxide	2	2 conv ^b [%] (yield, %) ^c	3 conv ^b [%] (yield, %) ^c
1	4a (R = Ph)		98 (93)	50 (45)
2	4b (R = n-Bu)		94 (89)	15 (-)
3	$4c (R = CH_2Cl)$		92 (86)	90 (82)
4	$4d (R = CH_2OPh)$		100 (92)	100 (89)
5	$4e(R = 4-ClC_6H_4)$)	72 (65)	12 (-)
6	$4f(R = 4-BrC_6H_4)$		71 (66)	0 (-)
7	$4g(R = CH_2OCH)$	$_2CF_2CHF_2)$	88 (81)	10 (-)
8	$4h (R = CH_2OCH_2(CF_2))$	₃ CHF ₂)	92 (88)	0 (-)

^{*a*}Reactions were carried out at 80 °C and 1 bar of CO₂ pressure for 24 h using 1.5 mol % of complex **2** and 1.5 mol % of TBAI or 1.5 mol % of complex **3** under solvent-free conditions. ^{*b*}Determined by ¹H NMR spectroscopy of the crude reaction mixture. ^{*c*}Yield of pure isolated cyclic carbonate.

The reactions were carried out at 80 °C and 1 bar of CO_2 pressure for 24 h employing a combination of 1.5 mol % of complex 2 and 1.5 mol % of tetrabutylammonium iodide (TBAI) as a cocatalyst, while only 1.5 mol % of the single-component catalyst 3 were used under solvent-free conditions. Interestingly, no polycarbonates were obtained under these reaction conditions as expected, since these epoxide substrates generally showed selectivity toward cyclic carbonate formation.^{18–48} In general, catalyst 2 achieved moderate to excellent yields for the preparation of cyclic carbonates **5a–h** (Table 1, entries 1–8). It is worth noting that the mixed catalytic system (2/TBAI) was reactive toward the formation of a wide variety of





Figure 5. (a) ¹H NMR spectrum of 3 + 4a at 25 °C and t = 0 in a 1:1 (3/4a) molar ratio. (b) ¹H NMR spectrum of 4a in CDCl₃. (c) ¹H NMR spectrum of 3 in CDCl₃.

Scheme 5. Proposed Reaction Mechanism for the Conversion of 4a into 5a Using Catalyst 3^a



^{*a*}Main structures and mechanistic events are depicted.

cyclic carbonates functionalized with alkyl, aryl, halide, and ether groups, which demonstrates that compound **2** has a broad scope and is selective for cyclic carbonate formation. Among these cyclic carbonates, the highly fluorinated products **5g** and **5h**, which have barely been studied, were isolated in high yields, 81% and 88%, respectively (Table 1, entries 7 and 8). These latter compounds are relevant for their potential use as electrolytes in ion-lithium batteries. $^{64-66}$

On the other hand, the neutral aluminum 3 catalyst displayed selectivity toward certain functionalized epoxides. In particular, it proved to be suitable in the catalytic conversion of the epoxides 4c and 4d with CO₂ giving excellent yields (Table 1,

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Figure 6. Gibbs free energy profile for the insertion of CO_2 into epoxide 4a using complex 3. Relevant structures and transition states are shown. Gibbs free energies are reported in kcal mol⁻¹.

entries 3 and 4) in the absence of a cocatalyst. Moderate conversion and yield were observed for the transformation of 4a (Table 1, entry 1), whereas low activity was found for the other epoxide/CO₂ reactions of Table 1 (entries 2 and 5–8) possibly suggesting that electronic properties of the evaluated epoxides play a decisive role in the initial pre-equilibrium of epoxide coordination, in the nucleophilic attack of the epoxide by iodide, and in the ring-closure step, which are apparently key steps of these catalytic processes (vide infra). Finally, it is worth highlighting that these results for 3 as a catalyst provide, to our knowledge, one of the first examples of a nonionic single-component catalytic system.

We then endeavored to obtain insight into the reaction mechanism by a combination of theoretical modeling and experimental studies. Initially, a series of NMR experiments were performed. The reaction between complex 3 and styrene oxide (4a) in a 1:1 molar ratio was studied spectroscopically in a Young valve NMR tube in CDCl₃ (Figure 5). First, the reaction of complex 3 (Figure 5c) with 4a (Figure 5b) was examined at room temperature and involved the immediate coordination of the epoxide upon dissociation of I⁻ with subsequent ringopening upon the nucleophilic attack of the iodide, giving rise to a ring-opened intermediate III (Figure 5a). From the NMR results in Figure 5a, no free styrene oxide was observed, but the immediate formation of an equilibrium mixture of the intermediate species II and III takes place, favoring the ring opened species III. The appearance of two new signals in the ¹H NMR at 5.18 and 4.57 ppm, respectively (Figure 5a and page S23 in the Supporting Information), belonging to the CH and CH₂ protons of the opened epoxide, confirmed the presence of intermediate alkoxide species III (Figure 5a). Formation of III was additionally supported by a DEPT-135 NMR experiment, in which a negative resonance at 70.0 ppm and a positive signal at

38.6 ppm were observed, corresponding to the CH₂ and CH groups of the opened epoxide, respectively. This also provided evidence that the iodide anion attack is directed to the carbon atom (C_{α}) with the strongest carbocation character (see page S24 in the Supporting Information), as reported in previous mechanistic studies.^{20,67} Our results therefore support the notion that styrene carbonate (**5a**) is formed starting by an S_N2 reaction of the iodine (exchanged by the epoxide) at the α -carbon of epoxide.

Based on these results, we suggest a catalytic cycle for the formation of styrene carbonate **5a** from the styrene oxide **4a** and CO_2 in the presence of catalyst **3**, a reaction mechanism which is particularly interesting since no cocatalyst (e.g., TBAI) is needed. For catalyst **3**, the nucleophile (iodide) is already contained in the structure, in contrast to many reported systems requiring a cocatalyst.^{33,39,40} Iodide was selected since it has the larger Al–I bond distance and the lowest dissociation energy compared to the chloride and bromide analogues (see the **Supporting Information**). The proposed catalytic cycle for the formation of cyclic carbonates catalyzed by **3** is shown in Scheme **5**, and the corresponding computed free energy profile is depicted in Figure 6. The reaction mechanism in Scheme **5** can be generalized for other epoxides.

In a first stage, complex 3 forms a reactive complex (I) with 1 equiv of epoxide 4a, with a free energy of -12.6 kcal mol⁻¹. Adduct I then dissociates an iodine anion (via TS1 with a ΔG_1^{\ddagger} = 19.7 kcal mol⁻¹) giving rise to the ion pair II. The cationic complex in II is stabilized by favorable π -stacking interactions between the phenyl moiety (in 4a) and the naphthalene-type moiety of the ligand. Although dispersion and the favorable Al–O interaction help stabilizing II, strong CH…CH repulsive interactions within the epoxide moiety and the ligand prevent this system from being more stable than I. The second step is the

nucleophilic attack of the dissociated iodide to the C_{α} carbon atom in the epoxide to give the ring-opened alkoxide structure III via an activation barrier of 6.1 kcal mol^{-1} . It is worth mentioning that in this step, the iodide atom can attack either C_{α} (substituted) or C_{β} . Butera et al. reported activation energies of 44.6 and 59.7 kcal mol⁻¹ for the C_{α} and C_{β} attack (for styreneepoxide and CO_2 reaction), respectively, with the attack at C_{α} thus being kinetically favored.⁶⁸ In situ NMR studies (see page S25 in the Supporting Information) corroborate the nucleophilic attack at the C_{α} atom with the appearance of a signal at 4.57 ppm in the ¹H NMR and at 38.6 ppm in the ${}^{13}C{}^{1}H$ NMR spectrum. The ring-opened structure III is highly exergonic, most likely due to the loss of the strained three-membered epoxide ring. On the basis of the energetic span model,^{69,70} species III corresponds to the TOF-determining intermediate (TDI), being the lowest (free) energy intermediate along the reaction pathway in the forward direction. In the absence of temperature, the reaction stops with the formation of III as shown by NMR experiments (Figure 5). However, in the present reaction conditions, intermediate III then inserts CO₂ forming into the Al-O bond giving the alkylcarbonate species

IV. This transformation takes place via a four-membered cyclic transition state, **TS3**, with an $\Delta G_3^{\ddagger} = 12.5$ kcal mol⁻¹ (see Figure 6). After the near-isothermic formation of **IV**, the ring-closure takes place with formation of the cyclic carbonate moiety still coordinated to the aluminum center releasing the iodide. The free activation energy of this process is $\Delta G_4^{\ddagger} = 27.0$ kcal mol⁻¹, with **TS4** being the TOF-determining transition state (TD-TS). Therefore, species **III** and **TS4** are thought to determine the turnover frequency for the catalytic fixation of CO₂ to give cyclic carbonates with a span energy (δE) of 33.2 kcal mol⁻¹.

For the formation of cyclic carbonate **5a**, we explored the bifurcation of the reaction path from species **V**. In particular, the reaction product **5a** could be released from **V** via **TS5** and displacement by the iodide at the Al center with an activation Gibbs free energy of just 0.6 kcal mol⁻¹. However, since the solvent in the reaction corresponds to the epoxide itself (**4a** for the present case), the coordination of a second equiv of **4a** at the Al center in **V** was studied. This was found to give a very stable intermediate ($\Delta G^{\circ} = -26.5$ kcal mol⁻¹), and the concerted exchange between the cyclic carbonate **5a** and epoxide **4a** therefore provides a shortcut in the catalytic cycle (Scheme 5) yielding species II through **TS5'** with a relatively low activation barrier (5.6 kcal mol⁻¹).

We expect that at high concentration of epoxide the mechanism through **TS5**' should dominate, while toward the end of the reaction, when the concentration of cyclic carbonate predominates, the pathway through **TS5** may be favored.

In summary, we have demonstrated that a single-component catalyst for the fixation of CO_2 into cyclic carbonates could be obtained in the form of the amidinate aluminum complex **3** which provides one of the first examples of a nonzwitterionic single-component catalyst producing cyclic carbonates.^{51,52} Although the reaction yields are not still superior to the ones in which TBAI is employed, efforts are being made in our group to increase the reactivity of these neutral-component catalysts. These include, inter alia, the modification of the ancillary bis(amidinate) ligand.

Overall, the selectivity toward certain functionalized epoxides opens the route to a rational design of new catalysts. From the computational studies, we have characterized species III and **TS4** as the TOF-determining states. Therefore, in order to decrease the respective span energy, it is necessary to diminish the oxophilic nature on Al, thus decreasing the stability of key intermediate III. On the other hand, inclusion of suitable (strong) electron withdrawing functional groups in the epoxide helps to decrease the activation barrier for the ring closure step (**TS4**), which involves the nucleophilic attack of oxygen to an electron deficient C_{α} atom.

CONCLUSIONS

Methyl (2) and iodide (3) aluminum complexes supported by a tetradentate amidinate ligand have been synthesized. X-ray diffraction, NMR, and MS studies, supported by theoretical modeling, have established a pentacoordinate structure for the aluminum atom with a distorted square planar geometry in which the amidinate ligand is binding in a κ^4 -NNNN coordination mode to the aluminum center (complexes 2 and 3).

Complex 2 was found to be active for the preparation of eight cyclic carbonates (5a-h) from their corresponding epoxides (4a-h) and CO₂ employing tetrabutylammonium iodide (TBAI) as a cocatalyst at 80 °C and 1 bar of CO_2 pressure. This catalyst system (2/TBAI) was found to be highly reactive for the cyclic carbonate formation during this catalytic process. On the other hand, iodide complex 3 displayed elevated catalytic activity toward some cyclic carbonates without addition of any cocatalyst, thus representing one of the first examples of a nonzwitterionic aluminum complex reported to date which is active toward this transformation under the presented working conditions. Based on quantum chemical modeling, the reaction mechanism for the insertion of CO₂ into cyclic carbonates using 3 was rationalized. In particular, it was found that the TOFdetermining species are the ring-opened alkoxide structure III and the transition state TS4 of the ring closure step to yield the cyclic carbonate attached to the catalyst (V). Furthermore, we conclude that choice between two alternatives reaction pathways for the release of the cyclic carbonate depends on a dynamic equilibrium between the concentration of the epoxide and the formed cyclic carbonates along the reaction. At higher concentrations of epoxide, a shortcut in the formation of the epoxide adduct II is favored. On the other hand, near the end of the conversion (when the concentration of cyclic carbonate starts to increase), the equilibrium is shifted toward the restoration of catalyst 3 concomitant to the release of the reaction product. Computations of the reaction mechanism triggered new insights for the design of more active halide catalysts in future explorations of the field. Improvements of catalyst 3 toward a wider range of epoxides are currently under active investigations in our laboratory.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. Reagent-grade solvents were obtained from E. Merck. Toluene was distilled from benzophenone ketyl, and dichloromethane and hexane were dried using an Innovative Technology Pure Solv Model PS-MD-5. The compounds 1,8-diaminonaphthalene, AlMe₃ (TMA), I₂, epoxides, and Bu₄NI were purchased from Aldrich and used as received. The imidoyl chloride (*E*)-*N*-(2,6-dimethylphenyl)acetimidoyl chloride was prepared according to published procedures.⁵³ The following instruments were used for the physical characterization of the compounds. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts and the coupling constants are reported in parts per million (SiMe₄ as standard) and Hertz, respectively. Most of the NMR assignments were supported by additional 2D experiments,

and the numbers of scans used for ${}^{13}C{}^{1}H$ NMR ranged from 0.5 to 2 K depending on the sample concentration. Mass spectra were acquired using a Micro Tof (Bruker) or a Clarus SQ 8T GC/MS (PerkinElmer).

Synthesis of N', N''-(Naphthalen-1,8-diyl)bis(N-(2,6dimethylphenyl)acetimidamide) (naphbamH) (1). (E)-N-(2,6-Dimethylphenyl)acetimidoylchloride⁵³ (1.0 g, 5.51 mmol) was added to a solution of 1,8-diaminonaphthalene (0.4 g, 2.76 mmol) and triethylamine (0.8 mL, 5.80 mmol) in 30 mL of toluene. The reaction mixture was stirred for 12 h under reflux. All volatiles were removed under vacuum. The solid residue was taken up in 30 mL of Et₂O and washed with 15 mL of a saturated solution of Na₂CO₃. Then the organic layer was washed with 20 mL of water and dried over MgSO4. After that, solvent was removed, and the crude product was recrystallized with CH_2Cl_2 /hexane (1:2) to give orange crystals (0.94 g, 76%). ¹H NMR $(400 \text{ MHz}, [D_6]\text{DMSO}) \delta/\text{ppm} = 11.13 (s, 1H, NH_b), 8.96 (d, J = 8.0$ Hz, 1H, H₉), 8.77 (s, 1H, NH_a), 7.44-6.74 (m, 11H, H_{1-3,7,8,15-17,25-27}), 2.29 (s, 6H, H_{19,29}), 2.13 (s, 3H, H₂₂), 1.90 (s, 6H, H_{20,30}), 0.83 (s, 3H, H₁₂). ¹³C{¹H} NMR (100 MHz, [D₆]DMSO) $\delta/\text{ppm} = 157.01 \ (C_{21}), \ 152.33 \ (C_{11}), \ 149.05 - 135.08$ $(C_{4-6,10,13,14,18,23,24,28})$, 128.31–113.55 $(C_{1-3,7-9,15-17,25-27})$, 19.23 $(C_{19,29})$, 18.51 $(C_{20,30})$, 18.30 (C_{22}) , 18.08 (C_{12}) . MS (ESI) $C_{30}H_{32}N_4$ [M]: m/z calcd: 448.260; found: 448.262

Synthesis of Complex {AlMe(κ^4 -naphbam)} 2. A solution of trimethylaluminum (TMA) (24.5 mg, 0.34 mmol) in CH₂Cl₂ was quickly added to a solution of 1 (152.5 mg, 0.34 mmol) in CH₂Cl₂. The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under vacuum, and the solid was washed with hexane. Compound 2 was obtained as a light-yellow solid (164.2 mg, 99%). Single colorless crystals for X-ray crystallography were grown from cold hexane at $-30 \,^{\circ}\text{C}$. ¹H NMR (400 MHz, CDCl₃) δ /ppm = 7.44 (d, J = 8.0 Hz, 2H, H₃), 7.34 (t, J = 8.0 Hz, 2H, H₂), 7.10 (d, J = 8.0 Hz, 2H, H₁), 7.01 (t, J = 4.5 Hz, 2H, H₁₂), 6.94 (d, J = 4.5 Hz, 4H, H_{11,13}), 2.21 (s, 6H, H₁₅), 2.07 (s, 6H, H₈), 1.87 (s, 6H, H₁₆), -0.52 (s, 3H, H₁₇). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ /ppm = 172.61 (C₈), 142.08– 134.10 (C_{4-69,10,14}), 128.18 (C₁₂), 127.79 (C₁₃), 125.70 (C₂), 124.63 (C₁₁), 122.45 (C₃), 116.26 (C₁), 19.15 (C₁₅), 18.84 (C₁₆), 15.44 (C₈), $-5.80 (C_{17})$. **MS (ESI)** $C_{31}H_{33}AlN_4 [M]$: m/z calcd: 488.250; found: 488 251

Synthesis of Complex {All(\kappa^4-naphbam)} 3. A solution of complex 2 (50.0 mg, 0.10 mmol) in CH₂Cl₂ was quickly added to a solution of I₂ (26.0 mg, 0.10 mmol) in CH₂Cl₂. The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under vacuum, and the solid was washed with hexane. Compound **3** was obtained as a light brown solid (60.0 mg, 96%). Single colorless crystals for X-ray crystallography were grown from cold hexane at $-30 \,^{\circ}C$. ¹H **NMR** (400 MHz, CDCl₃) δ /ppm = 7.52 (d, *J* = 8.24 Hz, 2H, H₃), 7.38 (t, *J* = 7.7 Hz, 2H, H₂), 7.20 (d, *J* = 7.6 Hz, 2H, H₁), 7.06 (d, *J* = 7.6 Hz, 2H, H₁₁), 6.99 (t, *J* = 7.3 Hz, 2H, H₁₂), 6.94 (d, *J* = 7.6 Hz, 2H, H₁₃), 2.41 (s, 6H, H₁₅), 2.15 (s, 6H, H₈), 1.84 (s, 6H, H₁₆). ¹³C{¹H} **NMR** (100 MHz, CDCl₃) δ /ppm = 175.09 (C₇), 140.20–134.22 (C_{4-69,10,14}), 128.69 (C₁₁), 127.84 (C₁₃), 125.80 (C₂), 125.58 (C₁₂), 123.61 (C₃), 116.91 (C₁), 20.68 (C₁₅), 18.78 (C₁₆), 15.79 (C₈). **MS** (**ESI**) C₃₀H₃₀AlIN₄ [M]: *m*/z calcd: 600.130; found: 600.132

General Procedure for the Synthesis of Cyclic Carbonates at **1 bar Pressure.** An epoxide 4a-h (1.7 mmol), catalyst **2** (25.5 μ mol), and TBAI (25.5 µmol) or catalyst 3 (25.5 µmol) were placed in individual glass reaction tubes with a magnetic stirrer bar in a multipoint reactor. The reaction mixture was stirred at 80 °C at 1 bar of CO₂ pressure 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 (6:1), then hexane:EtOAc (3:1), and then EtOAc to give the pure cyclic carbonate. Cyclic carbonates 5a-h are all known compounds, and the spectroscopic data for samples prepared using catalysts 2 or 3 were consistent with those reported in the literature 33,36,71-74reported in the literature.³

Computational Details. Optimization and frequency computations of fundamental structures along the potential energy surface were carried out at the density functional theory (DFT) level of theory. For geometry optimizations, the B3LYP/6-31G**-LANL2DZ(I) level of theory was used, which has been successfully applied in related systems.^{68,75,76} Although the B3LYP and M06-2X functionals perform similarly, comparison of DFT structures with X-ray data, structures **2** and **3** were optimized at the M06-2X/def2-TZVP. All computations were performed in *Gaussian16*.⁷⁷ For the computation of Gibbs free energy, all low-frequency vibrations were treated using the quasi rigidrotor harmonic oscillator (quasi-RRHO) approximation using 100 cm⁻¹ as cutoff.⁷⁸ Gibbs free energy differences (ΔG) were reported as

$$\Delta G = \Delta E + \Delta G_{\text{RRHC}}^{\text{T}}$$

where ΔE is the difference in electronic energies, and $\Delta G_{\rm RRHO}^{\rm T}$ collects the zero-point vibrational energy (ZPVE) and RRHO Gibbs free energy corrections. Gibbs free energy and ZPVE corrections were computed using a Python script developed by one of the authors.⁷⁹ Unfortunately, it was not possible to include solvent effects in the calculations due to the lack of an exact dielectric constant for this nonconventional solvent (4a).

X-ray Crystal Structure Analyses. Data sets for compounds 1 and 2 were collected with a Bruker D8 Venture CMOS diffractometer. For compound 3, data sets were collected with a Bruker APEX II CCD diffractometer. The following programs were used: data collection, APEX3 V2016.10; cell refinement, SAINT V8.37A; data reduction, SAINT V8.37A; absorption correction, SADABS V2014/7;⁸⁰ structure solution, SHELXT-2015;⁸¹ structure refinement, SHELXL-2015;⁸² and graphics, XP.⁸³ R-values are given for observed reflections, and wR2 values are given for all reflections.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03290.

NMR spectra, noncovalent intermolecular and intramolecular interactions, bond lengths, crystallographic data, NMR data for cyclic carbonates **5a-h**, and XYZ coordinates (PDF)

Accession Codes

CCDC 1923607–1923609 contain 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 Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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