

Cyclic Carbonates from CO₂ and Epoxides Catalyzed by Tetra- and Pentacoordinate Amidinate Aluminum Complexes

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S Supporting Information

ABSTRACT: A series of mono-, bi-, and trimetallic alkylaluminum complexes $((L_1)AlMe_2 (1), (L_1)Al_2Me_5 (2))$ $(L_2)AlMe_2$ (3), $(L_2)Al_2Me_5$ (4), $(L_2)_2AlMe$ (5), $(L_2)_2Al_3Me_7$ (6)) supported by amidine ligand precursors ((E)-N-(2,6diisopropylphenyl)-N'-(pyridin-2-yl)acetimidamide (L₁H) and (E)-N-(2,6-diisopropylphenyl)-N'-(pyridin-3-yl)acetimidamide (L_2H) were obtained in excellent yields and characterized by spectroscopic and X-ray diffraction methods. These complexes were studied as catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide in the presence of tetrabutylammonium iodide as cocatalyst. The reactions were carried out at 50 °C and 1 bar CO₂ pressure in the absence of solvent, and we were able to achieve an



extensive variety of terminal epoxides with moderate to excellent yields and high selectivities using aluminum complexes 2 and 6.

INTRODUCTION

Carbon dioxide (CO_2) as a sustainable C1 feedstock is a starting material for the synthesis of organic molecules and/or materials, and its chemical utilization is a challenge for the scientific community,¹⁻⁷ even though the CO₂ molecule possesses high thermodynamic stability and its use as a substrate is limited by kinetic barriers. Given that, it is necessary to develop new catalytic systems enabling transformation to overcome the associated energy barriers, $^{8-11}$ even though the catalytic transformation of \overline{CO}_2 has been widely studied to obtain a variety of different products, such as amines, amides, methanol, and formic acid.¹²⁻¹⁷ One of these processes is the reaction between epoxides and carbon dioxide to afford either cyclic^{18,19} or linear polycarbonates^{20–25} (Scheme 1), which are highly exothermic processes and have 100% atom economy. Cyclic carbonates stand out for their promising use as electrolytes in batteries²⁶⁻²⁹ and generally as aprotic solvents.³⁰⁻³² Over the last two decades, several research groups have been accessed a variety of catalytic





systems formed by the combination of Lewis acids and nucleophiles (most of them operate at 25 °C and 1 bar of CO₂ pressure) for the synthesis of cyclic carbonates from epoxides and carbon dioxide. These systems are principally based on metal complexes that include mainly aluminum,³³⁻³⁶ chromium, 37,38 and cobalt 39,40 in combination with a nucleophile as a cocatalyst, bifunctional systems, $^{41-43}$ and organocatalysts.44-46

Amidinic catalysts have recently been used for several reactions, such as olefin polymerization^{47–50} (Figure 1, I^{48}), ring-opening polymerization of cyclic esters^{51–54} (Figure 1, II⁵¹), and benzamidinate complexes have been applied in the transformation of CO₂ into cyclic carbonates⁵⁵ (Figure 1, III). One of the most interesting properties of the amidinic systems is their capacity to coordinate to different metallic centers, which has allowed incorporation of different elements from the traditional transition metals and expanded the study to elements of greater abundance such as zinc^{56–59} (Figure 1, IV^{59}), magnesium^{60–62} (Figure 1, V^{60}), and aluminum^{63–66} (Figure 1, VI^{66}).

Amidinate units have turned out to be quite versatile ancillary ligands allowing the tuning of coordinations mode by their stereoelectronic properties.⁶⁷ The exploration of various amidinate aluminum complexes for catalytic purposes has had a great effect on the development of exceptional catalytic

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R = Mes, R' = Cy, n = 1

Figure 1. Examples of complexes with amidinic ligands.

properties.^{68–71} Recently, our research group reported the use of mono- and binuclear amidinate aluminum complexes as catalysts for polymerizations and copolymerizations of lactones,⁷² and later these complexes were examined as catalysts for the preparation of cyclic carbonates from the reaction between epoxides and carbon dioxide using TBAI as a cocatalyst (Figure 1, VI⁶⁶). On the basis of these types of amidine complexes, we initiated related studies investigating a tuning of such systems for the catalytic formation of cyclic carbonates from epoxides and CO₂, changing the coordination modes of the alkyl aluminum derivatives under the influence of the size of their polynuclear structures.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of the Ligand Precursors L_1H and L_2H . The synthesis of the two related *N*-(pyridin-*x*-yl)acetimidamide (x = 2, 3) L_1H and L_2H was investigated with respect to their ability to coordinate on aluminum centers by reaction with AlMe₃, forming catalytically active organometallic compounds to generate cyclic carbonates from CO₂ and epoxides. When L_1H and L_2H link to the metal center, they show the same coordination mode (κ^2 -NN) and formation of six-membered (L_1H) or four-membered (L_2H) metallacycles.

The preparation of the L_1H and L_2H ligand precursors was carried out via a reaction between the corresponding aminopyridine and (*E*)-*N*-(2,6-diisopropylphenyl)acetimidoyl chloride⁷³ in toluene in the presence of Et₃N under reflux, affording L_1H and L_2H in 67 and 70% yields, respectively (Scheme 2).

 ${\bf L_1H}$ and ${\bf L_2H}$ were characterized spectroscopically by oneand two-dimensional NMR techniques (¹H NMR, ¹³C{¹H} NMR, ¹H NOESY-1D and ¹H-¹³C heteronuclear correlation (g-HSQC)), FT-IR, mass spectroscopy, and X-ray diffraction studies. The ¹H NMR spectra of these ligands gave rise to broad singlets at 9.54 ppm (L₁H) and 9.26 ppm (L₂H) (Experimental Section), ascribed to the N–H group of the amidine moiety, in good agreement with signals for other amidines.⁷⁴ ¹H NOESY-1D experiments were carried to

Scheme 2. Synthesis of L_1H and L_2H Amidine Ligand Precursors^{*a*}



^aReaction i: toluene, Et₃N, reflux. Reaction ii: water/CH₂Cl₂.

allocate most of the ¹H NMR resonances, and $^{1}H^{-13}C$ heteronuclear correlation (g-HSQC) experiments were used to assign the signals of the corresponding carbon atoms (see the Supporting Information).

The solid-state structures of ligand precursors L_1H and L_2H were determined by single-crystal X-ray diffraction studies. Crystal structures, crystallographic data, and selected bond angles and distances are given in Figures S3 and S6 and Tables S1 and Table S2 in the Supporting Information, respectively.

Synthesis and Structural Characterization of Complexes 1–6. The mono- and dinuclear alkyl aluminum complexes 1 and 2 were prepared via the reactions of the *N*-(pyridin-2-yl)acetimidamide ligand precursor L_1H with 1 or 2 equiv of AlMe₃ (Scheme 3). The reactions were carried out in dry CH₂Cl₂ for 2 h at room temperature. Complexes 1 and 2 were obtained in high yields (\geq 95%) as light pink solids. Alternatively, 2 could be obtained by the addition of 1 equiv of AlMe₃ to 1, under the same reaction conditions. In the dinuclear complex 2 the second aluminum center is coordinated through a dative bond to the nitrogen atom of the imino moiety.

The imino and pyridine nitrogen atoms have free electron pairs that cause two isomers, a four-membered (Figure 2a) and a six-membered (Figure 2b) metallacycle. However, the reaction between L_1H and 1 equiv of AlMe₃ afforded only one complex, which corresponded to the six-membered metallacycle type. Apparently, this arrangement is thermodynamically more stable, which can also be derived from the ¹H NMR spectrum of **1**. The formation of a six-membered

Scheme 3. Preparation of 1 and 2



Figure 2. Structural isomers of 1: (a) four-membered metallacycle; (b) six-membered metallacycle.

metallacycle became also evident for 1 and 2 from their X-ray structure determinations.

The protonolysis reaction of *N*-(pyridin-3-yl)acetimidamide with the protio ligand L_2H in the presence of 1 equiv of AlMe₃ in dry CH₂Cl₂ for 2 h at room temperature afforded the formation of complex 3 in quantitative yield. The structure of 3 consists of a four-membered metallacycle.⁷² The addition of another 1 equiv of AlMe₃ to 3, or the direct reaction of L_2H with 2 equiv of AlMe₃, resulted in the formation of complex 4 (four-membered metallacyclic AlMe₃ adduct), which was isolated as a white solid in 98% yield (Scheme 4).

Scheme 4. Aluminum Complexes 3–6 Bearing the L₂H Ligand Precursor



On the basis of the ability of aluminum centers to form pentacoordinate complexes, $^{75-78}$ we pursued the notion to access metallacyclic complexes of the type $(L_n)_2$ AlMe (n = 1, 2), which are expected to possess coordination number 5. Unfortunately, the reaction of L_1 H with 0.5 equiv of AlMe₃ in dry CH₂Cl₂ for 2 h at room temperature did not reveal the presence of new complexes but resulted in the formation of 1 and free ligand. However, the reaction of L_2 H with 0.5 equiv of AlMe₃ under the same reaction condition afforded the $(L_2)_2$ AlMe complex 5 in 90% yield as a colorless solid (Scheme 4).

The structure of **5** shows two pyridinic nitrogen atoms capable of forming an adduct with the Lewis acid $AlMe_3$, similarly to **1**. The reaction of **5** with 2 equiv of $AlMe_3$, in CH_2Cl_2 at room temperature for 2 h furnished complex **6** as a white solid in quantitative yield (Scheme 4). In comparison to **5**, **6** bears two additional $AlMe_3$ units, which are bound to the pyridine nitrogen atoms.

The solution-state structures of 1-6 were studied by spectroscopic methods. In the ¹H NMR spectra of 1-6 the signal for the H_N proton of the amidine ligand precursor was missing, thus supporting the formation of amidinate complexes (Figure 3). Moreover, these compounds exhibited signals for



Figure 3. $^1\!H$ NMR of complex 6 in C_6D_6 (a) and $^1\!H$ NMR of complex 2 in C_6D_6 (b).

the AlMe moieties (Figure 3) as part of a unique set of resonances that indicated the presence of a single isomer. The pentacoordinate species 5 and 6 showed a singlet at -0.10 ppm for 5 and at -0.19 ppm for 6 (Figure 3b), respectively, which belonged to the methyl group.

For unequivocal assignment of most of the NMR resonances ${}^{13}C{}^{1}H$ NMR spectra and two-dimensional NMR experiments were carried out for 1–6. These data supported structural arrangements with tetrahedral coordination geometries for the mononuclear complexes 1 and 3, in which the amidinate ligand was bound to the aluminum atom in κ^2 -NN coordination to the metal center. In the dinuclear aluminum complexes 2 and 4 the amidinate ligand was found attached in a κ^2 -NN- μ -N coordination mode, whereas the amidinate complexes 5 and 6 displayed pentacoordination.

The molecular geometries and atom-labeling schemes for the complexes 1 and 2 are shown in Figures 4 and 5, respectively. The molecular structures of both complexes confirmed the formation of the six-membered metallacycle, similarly to the previously reported carbaalumazenes.^{79–81} The crystallographic data and selected bond angles and distances are given in Tables S3 and S4 in the Supporting Information, respectively. In compound 1, Al1 presents a distortedtetrahedral geometry in which the amidinate bite angle N1– Al1–N3 is 92.8(1)° and the C8–Al1–C9 angle is 116.6(1)°, which are not close to the ideal tetrahedral angle of 109.5°. The bond distances Al1–N1(iminic) and Al1–N3(pyridinic) are 1.904(2) and 1.931(2) Å, respectively.

The molecular structure of 2 is shown in Figure 5. The bond distance Al2-N2 is 0.11 Å longer than the Al1-N1 distance, which confirms that the Al2 center is coordinated through a



Figure 4. Molecular structure of 1. Thermal ellipsoids are shown with 15% probability, and hydrogen atoms has been omitted for clarity. Selected bond distances (Å) and angles (deg): N1–Al1 1.904(2), N3–Al1 1.931(2), C3–N2 1.366(2), N2–C1 1.324(2), C1–C2 1.494(2); N1–Al1–N3 92.8(1), C8–Al1–C9 116.6(1), C3–N2–C1 124.7(2).



Figure 5. Molecular structure of 2. Thermal ellipsoids are shown with 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N1–Al1 1.914(1), N2–Al2 2.024(2), N3–Al1 1.930(1), C3–N2 1.393(2), N2–C1 1.349(2), C1–C2 1.494(2); N1–Al1–N3 90.5(1), C8–Al1–C9 122.5(1), C3–N2–C1 122.0(1).

dative bond to the nitrogen atom from the imino moiety, generating a greater distortion in the ideal tetrahedral geometry of Al1 in 2. The N1–Al1–N3 bite angle and C8–Al1–C9 angle are $90.5(1)^{\circ}$ and $122.5(1)^{\circ}$ respectively, which are farther from 109.5° than the equivalent angles of 1.

The molecular geometries and atom-labeling schemes for complexes 5 and 6 are shown in Figures 6 and 7, respectively. The crystallographic data and selected bond angles and distances are given in Tables S5 and S6 in the Supporting Information, respectively. Compound 5 presents a C2/c space group and roughly C_2 symmetry. The angular structure parameter (τ value)^{82,83} allows distinguishing between the geometries of a trigonal bipyramid and a square pyramid in pentacoordinated structures. A value of 1 shows a perfect trigonal-bipyramidal geometry, and a value of 0 indicates a perfect square-pyramidal structure.

The τ values for **5** and **6** (0.55 and 0.61, respectively) confirm that the geometry for the pentacoordinated aluminum center is a slightly distorted trigonal bipyramid, in which both bidentate amidinate ligands occupy an equatorial and an axial site, similar to what has already been reported for these types of complexes,⁸⁴ and the remaining equatorial site is occupied by the methyl group. In this particular case, in which the ligand L_2H is asymmetric, the nitrogens substituted by a pyridinic ring occupy the axial positions in the structure and the



Figure 6. Molecular structure of **5**. Thermal ellipsoids are shown with 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N2–Al1 2.019(1), N1–Al1 1.943(1), C8–Al1 1.968(2), C2–C1 1.498(2); N2–Al1–N2A 149.9(1), N1–Al1–N1A 126.4(1), C8–Al1–N1 116.8(1), N1–Al1–N2A 99.5(1), N2–Al1–N1A 99.5(1), N1–Al1–N2 66.4(1).



Figure 7. Molecular structure of 6. Thermals ellipsoids are shown with 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N2-Al1 2.015(1), N3-Al2 2.022(1), N6-Al3 2.018(1), N1-Al1 1.935(1), C8-Al1 1.949(1), C71-Al3 2.002(1), C2-C1 1.489(2); N2-Al1-N5 154.5(1), N1-Al1-N4 123.3(1), C8-Al1-N1 117.7(1), N1-Al1-N5 101.1(1), N2-Al1-N4 101.1(1), N1-Al1-N2 66.3(1).

associated exocyclic angle N2–Al1–N2A is equal to 149.9(1)°, which is distorted 30.1° from the ideal structure of 180°, while the exocyclic angles between the groups at the equatorial positions N1–Al1–N1A and the two N1–Al1–C8 group are about 126.4(1)° and 116.8(1)°, respectively. As expected for a trigonal-bipyramidal geometry, the two Al1–N2 bond distances of 2.019(1) Å are longer than the two other Al1–N1 distances of 1.943(1) Å, which is typical for this type of moiety.^{84–86}

The molecular structure of 6 is displayed in Figure 7. The Al2 and Al3 centers of this compound are coordinated to the ligand by the pyridine nitrogen atom, which has the effect of approximating the trigonal-bipyramidal structure of 6 to the ideal trigonal-bipyramidal structure, and the N1-Al1-C8 and

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N1–Al1–N4 angles are $117.7(1)^{\circ}$ and $123.3(1)^{\circ}$, respectively, which are closer to 120° than the equivalent angles of 5.

The Al–Me distances on the tetracoordinated aluminum centers are slightly longer (0.012 Å average) than the Al–Me distances of pentacoordinated aluminum, probably due to the stronger electron donation of two amidinates in comparison to pyridine.

Catalytic Studies for the Synthesis of Cyclic Carbonates. Aluminum complexes 1, 2, and 4–6 were initially tested for the formation of styrene carbonate 8a from styrene oxide 7a and CO₂ at 25 °C and 1 bar of CO₂ pressure for 24 h in the absence of solvent using 5 mol % of monometallic catalysts 1 and 5, 2.5 mol % of bimetallic catalysts 2 and 4, and 1.7 mol % of trimetallic catalyst 6, with the aluminum concentration kept constant at 5 mol % and 5 mol % of tetrabutylammonium iodide (TBAI) added, as can be seen in Table 1.

Table 1. Synthesis of Styrene Carbonate 8a using Catalysts 1, 2, and $4-6^{a}$

			conversion ^b (%)	
entry	cat.	amt of cat. (mol %)	25 °C	50 °C
1	1	5.0	20	73
2	2	2.5	40	92
3	4	2.5	15	65
4	5	5.0	18	70
5	6	1.7	33	90
6 ^{<i>c</i>}	2	2.5	0	0
7^c	6	1.7	0	0
8 ^d			1	9
9 ^e	AlMe ₃	5.0	9	20

^{*a*}Reactions were carried out at 1 bar of CO₂ pressure for 24 h using 5 mol % of Bu₄NI. ^{*b*}Conversion determined by ¹H NMR spectroscopy of the reaction mixture. ^{*c*}No Bu₄NI was added. ^{*d*}5 mol % of Bu₄NI added. ^{*e*}5 mol % of both pyridine and Bu₄NI was added.

The monometallic aluminum catalysts 1 and 5 displayed low catalytic activity for the synthesis of styrene carbonate 8a under the given reaction conditions (Table 1, entries 1 and 4). Furthermore, the catalytic activities of the bimetallic aluminum complexes 2 and 4 were low to moderate (Table 1, entries 2 and 3), although a considerable increase in the catalytic activity was observed between both complexes 2 (six-membered metallacycle) and 4 (four-membered metallacycle), showing the importance of the ligand design, whereas the trimetallic aluminum complex 6 showed a 33% conversion in styrene carbonate formation (Table 1, entry 5). According to Table 1 complexes 2 and 6 were the most active catalyst for styrene carbonate production, probably due to the fact that these complexes possess higher solubilities in the epoxide.

The influence of the temperature was then tested. As can be derived from Table 1, at 50 °C almost complete conversion of styrene oxide into styrene carbonate could be achieved on applying 2 and 6 (Table 1, entries 2 and 5). The conversion using 1, 4, and 5 increased at this temperature but their conversions were slightly lower at around 75% (Table 1, entries 1, 3, and 4). Control experiments were carried out to demonstrate that neither TBAI nor complexes 2 and 6 alone showed significant catalytic activity by themselves (Table 1, entries 6–8). Furthermore, the adduct pyridine–Al(CH₃)₃ was tested and showed a lower catalytic activity in comparison to aluminum complexes 1, 2, and 4–6 (Table 1, entry 9). On the

basis of these explorations we concluded that 2 and 6 were the most active catalysts for styrene carbonate production (8a) at both 25 and 50 °C and that the number of metallic centers in the catalysts did not have a pronounced effect on the catalytic activity.

Complexes 2 and 6 were used to investigate the effect of a cocatalyst addition in the formation of styrene carbonate (Table 2). The best results were obtained with combinations

Table 2. Influ	ence of C	ocatalyst .	Addition	on St	tyrene	
Carbonate 8a	Catalysis	Applying	Complex	es 2	and 6'	1

		$conversion^{b}$ (%)		
entry	cocat.	complex 2	complex 6	
1	Bu_4NF	0	0	
2	Bu ₄ NCl	68	65	
3	Bu_4NBr	89	83	
4	Bu_4NI	92	90	
5	PPNC1 ^c	73	70	
6	DMAP^d	0	0	

"Reactions were carried out at 50 °C and 1 bar of CO_2 pressure for 24 h using 2.5 mol % of complex **2**, 1.7 mol % of complex **6**, and 5 mol % of cocatalyst. ^bConversion determined by ¹H NMR spectroscopy of the reaction mixture. ^cBis(triphenylphosphine)iminium chloride. ^d4- (Dimethylamino)pyridine.

of 2 and 6 and TBAI (Bu_4NI) as the cocatalyst at 50 °C and 1 bar of CO₂ pressure, giving almost quantitative conversion (Table 2, entry 4). Other ammonium salts, such as TBAF and TBAC, displayed low to moderate conversions in the formation of styrene carbonate (Table 2, entries 1 and 2), while TBAB showed a higher conversion in comparison to the fluoride and chloride salts (Table 2, entry 3). PPNCl exhibited high catalytic activity under these reaction conditions (Table 2, entry 5), and DMAP failed to show any cocatalytic effect (Table 2, entry 6). Thus, TBAI turned out to be the best cocatalyst for styrene carbonate production (8a). In this way the optimum reaction conditions for the catalytic production of styrene carbonate 8a using 2 and 6 were determined.

Therefore, we subsequently explored the chemical potential for cyclic carbonate formation. The reactions of nine monosubstituted epoxides 7a-i with carbon dioxide to form the corresponding cyclic carbonates 8a-i were examined using 2.5 mol % of catalyst 2 and 1.7 mol % of catalyst 6 with 5 mol % of TBAI as cocatalyst under solvent-free conditions to study the same reaction parameters as before: for instance, whether the number of metallic centers would have any effect on the cyclic carbonate production (Figures 8 and 9).

The conversion of epoxides 7a-i into the corresponding cyclic carbonates 8a-i were pursued by ¹H NMR spectroscopy. Reactions were carried out at 50 °C and 1 bar of carbon dioxide pressure in a single glass reaction tube of a multipoint reactor (see the Supporting Information for further details). As can be seen in Figures 8 and 9, the epoxides could be converted into their corresponding cyclic carbonates from moderate to excellent yields by both complexes 2 and 6 under relatively mild reaction conditions. The formation of polycarbonates could not be observed under these conditions, and the selectivities for the cyclic carbonate formation were higher than 99%.

It is worth mentioning that the epoxides 7a-e were transformed into their corresponding cyclic carbonates 8a-e in excellent yields by the catalytic systems 2/TBAI and 6/

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Figure 8. Cyclic carbonates 8a-i from epoxides 7a-i catalyzed by 2 and TBAI. Legend: (a) conversion determined by ¹H NMR of the reaction mixture; (b) yield determined on purified product.



Figure 9. Cyclic carbonates 8a-i from epoxides 7a-i catalyzed by 6 and TBAI. Legend: (a) conversion determined by ¹H NMR of the reaction mixture; (b) yield determined on purified product.

TBAI, whereas glycerol carbonate **8f** and aryl carbonates **8g**–i were obtained with lower conversions and yields. These results demonstrated that catalysts **2** and **6** are highly tolerant to alkyl epoxides, although these catalysts were not as effective with those epoxides functionalized with aryl, halide, alcohol, and ether groups, probably due to the lower solubility of these epoxides in the catalytic solutions (Figures 8 and 9). The bimetallic catalyst **2** is slightly more active than the trimetallic system **6**, allowing us to conclude that the complexes with the greatest numbers of metallic centers are not necessarily the most active catalysts.

According to the literature, most catalytic systems reported to date require a CO_2 pressure higher than 1 bar to carry out the synthesis of cyclic carbonates from epoxides and carbon dioxide, although there are a few examples of catalysts that display an excellent catalytic activity at this CO_2 pressure. For that reason, we would like to compare the activity of complexes 2 and 6 with those most active catalysts reported in the bibliography. Two of them, an Al(salen) complex⁸⁷ (Al(salen), Table 3) and a Cr(salophen) complex³⁸ (Cr, Table 3), were reported by North and co-workers and another excellent example, a bifunctional heteroscorpionate aluminum complex⁴¹ (Al, Table 3), was prepared by Otero and co-workers (the structures of these complexes are shown in the Supporting Information).

Complexes 2 and 6 showed low TOF values of 0.67 and 0.79 h^{-1} , respectively (Table 3, entries 1 and 2), which are slightly higher in comparison to that presented by the bifunctional

Table 3. Comparation of Catalytic Activities of Different Complexes a^a

entry	cat. (amt (mol %))	cocat. (amt (mol %))	conversion (%)	TON ^b	$\operatorname{TOF}^{c}(h^{-1})$
1	2 (2.5)	TBAI (5.0)	40	16	0.67
2	6 (1.7)	TBAI (5.0)	33	19	0.79
3 ^d	Al(salen) (2.5)	TBAB (2.5)	62	25	8.33
4	Cr (2.5)	TBAB (2.5)	92	37	1.54
5	Al (5.0)	TBAI (5.0)	55	11	0.45
6 ^e	2 (2.5)	TBAI (5.0)	76	30	1.25
7 ^e	6 (1.7)	TBAI (5.0)	51	30	1.25
8 ^f	2 (2.5)	TBAI (5.0)	55	22	0.92
9 ^f	6 (1.7)	TBAI (5.0)	39	23	0.96
10 ^e	Cr (2.5)	TBAB (2.5)	91	36	1.5
$11^{\rm f}$	Cr (2.5)	TBAB (2.5)	89	36	1.5

^{*a*}Reactions were carried out by using styrene oxide as the epoxide at 25 °C and 1 bar of CO₂ pressure for 24 h unless stated otherwise. ^{*b*}TON = (mol of product)/(mol of catalyst). ^{*c*}TOF = (mol of product)/((mol of catalyst) × time). ^{*d*}t = 3 h. ^{*e*}2-(4-Chlorophenyl)-oxirane (7h) as epoxide and T = 50 °C. ^{*f*}2-(4-Bromophenyl)oxirane (7i) as epoxide and T = 50 °C.

aluminum catalyst (Table 3, entry 5), whereas the Al(salen) catalyst displayed the highest TOF value (8.33 h⁻¹) (Table 3, entry 3) of all the catalysts studied for the preparation of styrene carbonate 8a at room temperature and 1 bar pressure of CO₂. On the other hand, the Cr(salophen) complex (Cr, Table 3) exhibits slightly superior values of TOF in comparison to complexes 2 and 6 for the synthesis of 4-chlorostyrene carbonate (8h) and 4-bromostyrene carbonate (8i) (Table 3, entries 6–11). In conclusion, complexes 2 and 6 displayed an intermediate catalytic activity for the synthesis of cyclic carbonates at 1 bar of CO₂ pressure.

A mechanism for the production of cyclic carbonates catalyzed by 6 is proposed in Scheme 5. It follows a scheme

Scheme 5. Catalysis of Monosubstituted Cyclic Carbonates from Terminal Epoxides and CO₂ Catalyzed by 6 under Cocatalysis of Iodide



of Lewis acid catalysis (Lewis acid Al in Scheme 5). The cycle is consistent with a catalytic scheme previously proposed by our research group for cyclic carbonates using amidinate aluminum complexes.⁶⁶

CONCLUSIONS

New amidine ligand precursors (L_1H and L_2H) were prepared, which could be reacted further to give mono-, bi-, and trimetallic amidinate aluminum complexes. NMR spectroscopy and X-ray diffraction studies have allowed us to determine the different coordination modes of these complexes. Complex 1 presents a κ^2 -NN coordination mode, while the other mononuclear complex 5 has a pentacoordinated aluminum center. For the bimetallic aluminum complexes 2 and 4, the amidinate ligands are attached to the aluminum centers in a κ^2 -NN- μ -N coordination mode, while the trimetallic aluminum complex 6 exhibits one pentacoordinated aluminum center and the other two aluminum centers present a tetrahedral structure.

Aluminum complexes 1, 2, and 4–6 have carried out the synthesis of cyclic carbonates from terminal epoxides and CO_2 using tetrabutylammonium iodide as a cocatalyst. Among them, the bimetallic complex 2 and trimetallic complex 6 with TBAI showed the highest catalytic activity for the cyclic carbonate formation at 50 °C and 1 bar of CO_2 pressure in the absence of solvent. Complex 2 is slightly more active than complex 6; thus, it is possible to conclude that the number of metallic centers present in a compound do not necessarily have a direct effect on its catalytic activity. However, six-membered metallacycle (complex 2) generates a considerable increase in activity in comparison with the four-membered metallacycle analogue (complex 4).

It is worth noting that these complexes are some of the first amidinate aluminum complexes which have been used in the the formation of cyclic carbonates from epoxides and CO_2 . These amidinate ligands are easy to use and can be prepared on a huge scale, which allows us to conclude that these types of catalysts present a great potential for the synthesis of cyclic carbonates.

EXPERIMENTAL SECTION

Synthesis of (E)-N-(2,6-Diisopropylphenyl)-N'-(pyridin-2-yl)acetimidamide (L₁H). (E)-N-(2,6-Diisopropylhenyl)acetimidoyl chloride⁷¹ (0.62 g, 2.61 mmol) was added to a solution of 2aminopyridine (0.24 g, 2.61 mmol) and triethylamine (0.4 mL, 2.87 mmol) in 30 mL of toluene. The reaction mixture was stirred for 8 h under reflux. All volatiles were removed under vacuum. The solid residue was taken up in 30 mL of CH₂Cl₂ and washed twice with 15 mL of water. After drying and removal of solvent, the crude product was purified by column chromatography using silica gel (ethyl acetate) and further recrystallized with ethanol to give light yellow crystals (0.52 g, 67%). ¹H NMR (400 MHz, DMSO-d₆, 298 K): δ/ ppm 9.54 (br s, 1H, NH), 8.47 (br s, 1H, H₂), 8.26 (d, J = 4.0 Hz, 1H, H_5), 7.68 (t, J = 7.3 Hz, 1H, H_3), 7.06 (d, J = 7.5 Hz, 2H, H_{10}), 6.99– 6.90 (m, 2H, $H_{4,11}$), 2.86 (hept, J = 6.8 Hz, 2H, H_{12}), 1.78 (s, 3H, H_7), 1.12 (d, J = 6.9 Hz, 6H, H_{14}), 1.05 (d, J = 6.8 Hz, 6H, H_{13}). ¹³C{¹H} NMR (100 MHz, DMSO- d_6 , 298 K): δ /ppm 153.77 (C₁), 152.70 (C₆), 147.48 (C₅), 145.25 (C₈), 137.68 (C₃), 137.32 (C₉), 122.62 (C_{10}), 122.36 (C_{11}), 117.34 (C_4), 112.70 (C_2), 27.59 (C_{12}), 23.41 (C13), 22.57 (C14), 18.16 (C7). IR (KBr): v/cm⁻¹ 3241, 3183, 3107, 3056, 2960, 2925, 2866, 1676, 1660, 1579, 1540, 1462, 1436, 1372, 1310, 1254, 1233, 1197, 1151, 1101, 1054, 1013, 994, 955, 935, 883, 854, 807, 781, 759, 739, 703, 623, 558, 516, 500. HRMS (ESI) for $C_{19}H_{26}N_3 [M + H]^+$: m/z calcd 296.212, found 296.212.

Synthesis of (*E*)-*N*-(2,6-Diisopropylphenyl)-*N*'-(pyridin-3-yl)acetimidamide (L_2H). *N*-(2,6-Diisopropylhenyl)acetimidoyl chloride (0.62 g, 2.61 mmol) was added to a solution of 3-aminopyridine (0.24 g, 2.61 mmol) and triethylamine (0.4 mL, 2.87 mmol) in 30 mL of toluene. The reaction mixture was stirred for 8 h under reflux. All volatiles were removed under vacuum. The solid residue was taken up in 30 mL of CH₂Cl₂ and washed twice with 15 mL of water. After drying and removal of solvent, the crude product was purified by column chromatography using silica gel (ethyl acetate) to give colorless crystals (0.54 g, 70%). ¹H NMR (400 MHz, DMSO- d_6 , 298 K): δ /ppm 9.26 (br s, 1H, NH), 8.96 (d, J = 2.0 Hz, 1H, H₅), 8.35 (d, J = 8.2 Hz, 1H, H₂), 8.14 (d, J = 3.7 Hz, 1H, H₄), 7.28 (m, 1H, H₃), 7.06 (d, J = 7.6 Hz, 2H, H₁₀), 6.94 (t, J = 7.6 Hz, 1H, H₁₁), 2.87 (hept, J = 6.8 Hz, 2H, H₁₂), 1.76 (s, 3H, H₇), 1.13 (d, J = 6.9 Hz, 6H, H₁₄), 1.05 (d, J = 6.8 Hz, 6H, H₁₃). ¹³C{¹H} NMR (100 MHz, DMSO- d_6 , 298 K): δ /ppm 152.80 (C₆), 145.08 (C₈), 142.02 (C₄), 140.35 (C₅), 138.11 (C₁), 137.54 (C₉), 124.93 (C₂), 123.28 (C₃), 122.59 (C₁₀), 122.34 (C₁₁), 27.57 (C₁₂), 23.39 (C₁₃), 22.61 (C₁₄), 18.00 (C₇). IR (KBr): ν /cm⁻¹ 3282, 3236, 3175, 3117, 3056, 2959, 2926, 2867, 1664, 1607, 1583, 1547, 1484, 1459, 1436, 1421, 1374, 1311, 1260, 1235, 1200, 1186, 1159, 1101, 1047, 1023, 955, 800, 784, 758, 706. HRMS (ESI) for C₁₉H₂₆N₃ [M + H]⁺: m/z calcd 296.212, found 296.212.

Synthesis of [(L₁)AlMe₂] (1). A solution of trimethylaluminum (AlMe₃) (24.51 mg, 0.34 mmol) in dichloromethane was quickly added to a solution of L_1H (100 mg, 0.34 mmol) in dichloromethane. The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the solid was washed with hexane. Compound 1 was obtained as a pale pink solid (115 mg, 96%). Single colorless crystals for X-ray crystallography were grown from cold hexane at -30 °C. ¹H NMR (400 MHz, C₆D₆, 298 K): $\delta/$ ppm 7.53 (d, J = 5.8 Hz, 1H, H₅), 7.22 (d, J = 5.1 Hz, 1H, H₂), 7.20-7.13 (m, 3H, $H_{11,10}$), 6.93 (t, J = 7.8 Hz, 1H, H_3), 6.17 (t, J = 6.4, 1H, H₄), 3.42-3.29 (m, 2H, H₁₂), 2.11 (s, 3H, H₇), 1.30 (d, J = 6.8 Hz, 6H, H₁₄), 1.13 (d, J = 6.8 Hz, 6H, H₁₃), 0.33 (s, 6H, H₁₅). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ/ppm 170.01 (C₆), 159.36 (C₁), 144.83 (C₉), 140.90 (C₅), 140.28 (C₈), 140.18 (C₃), 127.34 (C₁₁), 124.78 (C₂), 124.63 (C₁₀), 116.20 (C₄) 28.28 (C₁₂), 25.53 (C₇), 24.89 (C₁₄), 24.64 (C₁₃), -9.16 (C₁₅).

Synthesis of $[(L_1)Al_2Me_5]$ (2). A solution of L_1H (200 mg, 0.68 mmol) in dichloromethane was added to a solution of 2 equiv of AlMe₃ (98.04 mg, 1.36 mmol) in dichloromethane. The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the solid was washed with hexane. Compound 2 was obtained as a pink solid (285 mg, 99%). Single colorless crystals for X-ray crystallography were grown from cold dichloromethane/hexane. ¹H NMR (400 MHz, C_6D_6 , 298 K): δ /ppm 7.56 (d, J = 7.7 Hz, 1H, H₅), 7.28 (d, J = 5.1 Hz, 1H, H₂), 7.08–7.02 (m, 1H, H_{11}), 6.97 (d, J = 7.6 Hz, 2H, H_{10}), 6.86 (t, J = 7.9, 1H, H_4), 6.15 (t, J = 6.5 Hz, 1H, H₃), 2.82 (br s, 2H, H₁₂), 2.18 (s, 3H, H₇), 1.05 (d, J = 6.5 Hz, 6H, H_{13}), 0.97 (d, J = 6.7 Hz, 6H, H_{14}), -0.20 (s, 9H, H₁₆), -0.48 (s, 6H, H₁₅). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ/ppm 175.97 (C₆), 157.68 (C₁), 143.08 (C₉), 140.69 (C₄), 140.34 (C_2) , 138.35 (C_8) , 128.35 (C_{11}) , 124.75 (C_{10}) , 124.04 (C_5) , 119.39 (C₃), 28.49 (C₁₂), 24.55 (C_{7,13}), 23.83 (C₁₄), -5.31 (C₁₆), -11.53 (C₁₅).

Synthesis of [(L₂)AlMe₂] (3). To a stirred solution of L₂H in C_6D_6 (12.41 mg, 0.042 mmol) was added a solution of AlMe₃ in C_6D_6 (3 mg, 0.042 mmol). After 30 min the solution was subjected to NMR spectroscopy, showing a virtually quantitative spectroscopic yield of 3 on the basis of of the ¹H NMR spectrum. ¹H NMR (400 MHz, C_6D_6 , 298 K): δ /ppm 8.59 (br s, 1H, H₃), 8.10 (d, *J* = 5.0 Hz, 1H, H₄), 7.29 (br s, 1H, H₂), 7.17–7.10 (m, 3H, H_{10,11}), 6.67 (dd, *J* = 7.8, 5.4 Hz, 1H, H₃), 3.61–3.50 (m, 2H, H₁₂), 1.60 (s, 3H, H₇), 1.41 (d, *J* = 6.7 Hz, 6H, H₁₄), 1.31 (d, *J* = 6.8 Hz, 6H, H₁₃), 0.06 (s, 6H, H₁₅).

Synthesis of [(L₂)Al₂Me₅] (4). A solution of L₂H (200 mg, 0.68 mmol) in dichloromethane was added to a solution of 2 equiv of AlMe₃ (98.04 mg, 1.36 mmol) in dichloromethane. The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the solid was washed with hexane. Compound 4 was obtained as a white solid (282 mg, 98%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ /ppm 8.39 (d, *J* = 2.5 Hz, 1H, H₅), 7.93 (dd, *J* = 5.2, 0.8 Hz, 1H, H₄), 7.12 (dd, *J* = 8.4, 7.0 Hz, 1H, H₁₁), 7.04 (d, *J* = 7.4 Hz, 2H, H₁₀), 6.74–6.70 (m, 1H, H₂), 6.42 (dd, *J* = 8.3, 5.3 Hz, 1H, H₃), 3.01 (hept, *J* = 6.9 Hz, 2H, H₁₂), 1.35 (s, 3H, H₇), 1.11 (d, *J* = 6.8 Hz, 6H, H₁₄), 1.05 (d, *J* = 6.9 Hz, 6H, H₁₃), -0.18 (s, 9H, H₁₆), -0.26 (s, 6H, H₁₅). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ /ppm 174.26 (C₆), 144.08 (C₉), 141.84 (C₁), 140.96 (C₄), 140.81

Organometallics

 (C_5) , 136.52 (C_8) , 132.39 (C_2) , 127.37 (C_{11}) , 125.76 (C_3) , 124.24 (C_{10}) , 28.50 (C_{12}) , 24.75 (C_{14}) , 23.77 (C_{13}) , 14.85 (C_7) , -7.64 (C_{16}) , -9.97 (C_{15}) .

Synthesis of [(L₂)AIMe] (5). A solution of trimethylaluminum (AlMe₃) (24.51 mg, 0.34 mmol) in dichloromethane was quickly added to a solution of 2 equiv of L2H (200 mg, 0.68 mmol) in dichloromethane. The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the solid was washed with hexane. Compound 5 was obtained as a white solid (193 mg, 90%). Single colorless crystals for X-ray crystallography were grown from cold dichloromethane/hexane. ¹H NMR (400 MHz, C_6D_6 , 298 K): δ /ppm 8.19 (br. s, 4H, H_{5,4}), 7.21–7.16 (m, 2H, H₁₁), 7.14–7.08 (m, 4H, $H_{10,12}$), 6.61–6.56 (m, 2H, H_3), 6.48 (d, J = 8.0Hz, 2H, H₂), 3.45–3.33 (m, 4H, H_{17,14}), 1.48 (s, 6H, H₇), 1.19 (d, J = 6.6 Hz, 18H, $H_{15,18,19}$), 1.10 (d, J = 6.8 Hz, 6H, H_{16}), -0.10 (s, 3H, H_{20}). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ /ppm 173.89 (C₆), 145.42 (C₅), 145.22 (C₁₃), 144.55 (C₉), 144.19 ($\overline{C_4}$), 140.78 (C₁), 138.29 (C_8) , 129.83 (C_2) , 126.92 (C_{11}) , 124.33 (C_{10}) , 123.85 (C_{12}) , 123.23 (C₃), 28.57 (C₁₇), 28.46 (C₁₄), 24.78 (C₁₈), 24.56 (C₁₉), 24.41 (C₁₅), 24.20 (C₁₆), 14.03 (C₇), -10.63 (C₂₀).

Synthesis of [(L₂)Al₃Me₇] (6). A solution of 2 equiv of AlMe₃ (23.07 mg, 0.32 mmol) in dichloromethane was added to a solution of complex 5 (100 mg, 0.16 mmol) in dichloromethane. The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the solid was washed with hexane. Compound 6 was obtained as a white solid (122.8 mg, 99%). Single colorless crystals for X-ray crystallography were grown from cold dichloromethane/hexane. ¹H NMR (400 MHz, C_6D_6 , 298 K): δ /ppm 8.16 (s, 2H, H₅), 7.82 (d, J = 5.1 Hz, 2H, H₄), 7.11-7.05 (m, 2H, H_{11}), 7.00 (d, J = 7.5 Hz, 2H, H_{10}), 6.95 (d, $J = 7.6, 2H, H_{12}$), 6.49 (d, J = 8.1 Hz, 2H, H₂), 6.32-6.26 (m, 2H, H₃), 3.19-3.04 (m, 4H, $H_{17,14}$), 1.38 (s, 6H, H_7), 1.10 (d, J = 6.6 Hz, 6H, H_{15}), 1.08–1.02 (m, 18H, $H_{18,19,16}$), -0.19 (s, 3H, H_{20}), -0.24 (s, 18H, H_{21}). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ/ppm 174.86 (C₆), 144.30 (C₁₃), 144.03 (C₉), 142.58 (C₁), 140.86 (C₅), 140.79 (C₄), 136.91 (C₈), 133.81 (C₂), 127.56 (C₁₁), 125.21 (C₃), 124.41 (C₁₀), 124.10 (C₁₂), 28.72 (C₁₇), 28.45 (C₁₄), 24.74 (C₁₅), 24.71 (C₁₆), 24.08 (C₁₈), 24.01 (C_{19}) , 14.34 (C_7) , -7.65 (C_{21}) , -10.67 (C_{20}) .

General Procedure for Catalyst Screening at 1 bar Pressure. Styrene oxide 8a (1.7 mmol), amidinate aluminum catalysts 1, 2, and 4–6 (27.7–83.0 μ mol), and TBAI (83.0 μ mol) were placed in an individual glass reaction tubes with a magnetic stirrer bar in a Carousel 12 Place Reaction Station multipoint reactor. The reaction mixture was stirred at 25–50 °C for 24 h, and then the conversion of styrene oxide 7a into styrene carbonate 8a was determined by analysis of a sample by ¹H NMR spectroscopy.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00795.

Experimental section including general descriptions, synthesis of cyclic carbonates, and X-ray structure analysis, figures referenced in the text, structural characterization data (¹H and ¹³C NMR spectra) for all compounds including cyclic carbonates **8a**–i, and X-ray crystallographic data for L₁H, L₂H, **1**, **2**, **5**, and **6** (PDF)

Accession Codes

CCDC 1862888–1862893 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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