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Mono- and Dinuclear Asymmetric Aluminum Guanidinates for the Catalytic CO_2 Fixation into Cyclic Carbonates

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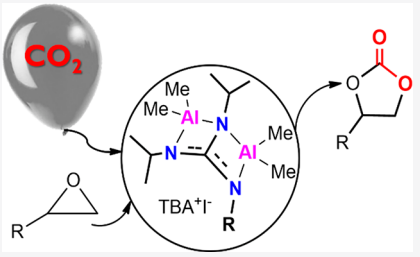
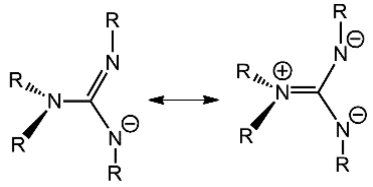
ABSTRACT: A set of trisubstituted guanidine ligands $\mathbf{L_1H_2}$−$\mathbf{L_4H_2}$ with general formula (^{i}PrHN)$_2$CNR (R = Ph (L_1H_2), R = 2,4,6-$Me_3C_6H_2$(L_2H_2), R = *p*-BrC_6H_4(L_3H_2), R = (C_5H_4)Fe(C_5H_5), Fc (L_4H_2)) was employed to synthesize a family of mono- and dinuclear asymmetric methyl aluminum guanidinato compounds ((L_2H)$AlMe_2$ (**1**), (L_4H)$AlMe_2$ (**2**), (L_1)Al_2Me_4 (**3**), (L_2)Al_2Me_4 (**4**), (L_3)Al_2Me_4 (**5**), (L_4)Al_2Me_4 (**6**), (L_1H)$_2$AlMe (**7**), (L_2H)$_2$AlMe (**8**), and (L_4H)$_2$AlMe (**9**)) that were characterized by NMR spectroscopy (**1**−**9**) and single-crystal X-ray diffraction (**4** and **8**). These compounds were tested as catalysts for the fixation of carbon dioxide with epoxides to give cyclic carbonates, using tetrabutylammonium iodide (TBAI) as cocatalyst. The reactions were performed under solvent-free conditions at 70 °C and 1 bar CO_2 pressure. Complexes **1**−**9** were more active than their respective free guanidines under the same experimental conditions for the synthesis of styrene carbonate (**11a**). The dinuclear complex **6** was the most efficient and active catalyst for the synthesis of several monosubstituted carbonates (**11a**−**l**) with excellent conversions and selectivities. Furthermore, the formation of some disubstituted cyclic carbonates (**13a**−**c**) using this dinuclear aluminum catalyst was also studied.



INTRODUCTION

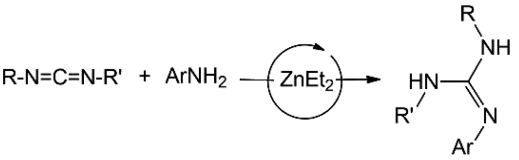
The search for new coordination and organometallic complexes involved as catalysts in synthetic processes requires the design of new and ever more complex ligands. Alternatively, there are some simple organic molecules with donor atoms that can act as auxiliary ligands for a wide variety of metals. Guanidinato monoanions of general formula $[(RN)_2CNR_2]^-$ are related to the widely used amidinato ligands, bearing an extra amino (R_2N) moiety attached to the ligands' central carbon, which confers them higher steric and electronic tunability (Scheme 1).[1−4]

Scheme 1. Main Resonance Forms of Guanidinato Ligands



Although there are stoichiometric synthetic routes, the catalytic hydroamination of carbodiimides is a 100% atom-economic procedure that allows the easy preparation of trisubstituted guanidines.[5,6] This offers the steric and electronic properties of the ligands to be modulated by means of an appropriate choice of starting reagents in the production of guanidine derivatives. Since 2010, our group has been investigating the preparation of substituted guanidines using cheap $ZnEt_2$ as catalyst (Scheme 2),[7] as well as their use as ligands in guanidinato compounds with early and late transition metals, as well as with elements from the s and p blocks.[8−13] This allows the formation of complexes with chelate ligands asymmetrically coordinated to the metal center, regardless of the metals used. Additionally, the presence of two N−H moieties in the guanidine compounds would allow further reactivity for these ligands.

Scheme 2. Catalytic Synthesis of Trisubstituted Guanidines



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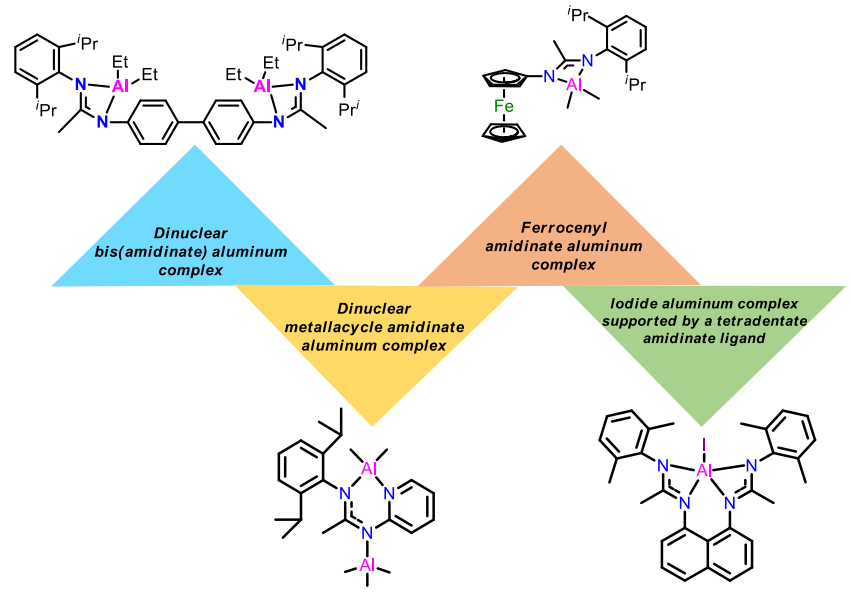

Figure 1. Previous aluminum amidinates employed as catalysts for the synthesis of cyclic carbonates from terminal epoxides and CO_2.[39−42]

Recent years have seen a renaissance of metal-based catalysts of the main group, looking for less expensive and more environmentally benign catalytic systems than traditional transition metal-based ones. For instance, coordination and organometallic complexes of group 13 metals have been widely used in homogeneous catalysis to carry out transformations of organic compounds, most of which require Lewis acids and involve polar substrates.[14] Aluminum compounds with a well-defined structure are among the most interesting for that purpose, because of their higher Lewis acidity and the greater availability of this metal.[15,16]

On the other hand, as atmospheric levels of carbon dioxide (CO_2) continue to increase daily, it is necessary to make progress in their reduction and containment. The use of this dioxide as a raw material to obtain organic compounds means generating an added value that could participate in subsidizing the costs of capturing and storing this CO_2.[17−21] In addition, it could be an alternative to alleviate our current needs for chemicals that depend heavily on the availability of fossil fuels. Among the different described processes, the formation of cyclic carbonates through the coupling of CO_2 to epoxides has attracted great attention,[22−26] as cyclic carbonates are used in industry as solvents in electrolyte solutions for Li-ion batteries,[27,28] or as polar aprotic solvents.[29] This synthesis is proposed as an industrial alternative to the condensation of the very poisonous phosgene and diols. Binary catalytic systems, which include a Lewis acid and a nucleophile, are necessary to promote the coupling between CO_2 and the epoxide. The Lewis acid activates the epoxide, allowing ring opening by the nucleophile attacking to the least substituted carbon atom. This reaction is followed by an insertion of CO_2 into the alkoxide resulting from the previous attack, leading to an alkyl carbonate which closes to form a new five-membered ring, via a backbiting mechanism, producing the cyclic carbonate and releasing the nucleophilic cocatalyst. Among the different homogeneous catalysts described for this synthesis of cyclic carbonates, the use of aluminum-based compounds should be highlighted given that they display some of the best catalytic performances reported to date.[30−38]

In this context, as a precedent to this work, some of us have described the use of mono- and dinuclear aluminum amidinates as efficient catalysts for this coupling process, from terminal epoxides, at 1 bar of CO_2, using Bu_4NI or Bu_4NBr as cocatalysts, under solvent-free and mild temperature conditions (Figure 1).[39−42]

Several aluminum complexes with related guanidinato ligands can be obtained through various reaction pathways: (i) carbodiimide insertion in Al−N bonds,[43−49] (ii) salt metathesis reactions between Al-X (X = halide) and lithium guanidinates,[50−55] and (iii) protonolysis of Al−Y bonds (Y = alkyl or amide) and a neutral guanidine.[55−60]

It should be noted that only in very few cases has their use as catalysts it been reported, in aldehyde reduction processes,[49,54,59] ring-opening polymerization,[60] or, curiously, guanylation of aromatic amines,[47,50] but never as catalysts for the formation of cyclic carbonates. Continuing our interest in the chemistry of guanidines and their derivatives, some of us have studied the reaction of trimethylaluminum ($AlMe_3$) with *N*-phosphinoguanidine ligands, which yields stable phosphinimine-amidinato compounds, after the rearrangement of the *N*-phosphinoguanidinato intermediates initially detected.[61,62] Very recently, we have also described the use of aromatic guanidines such as those depicted in Scheme 2, as catalysts for the preparation of cyclic carbonates. In these compounds, the presence of two N−H groups represented a substantial improvement in the activity, as hydrogen-bond donor systems, compared to what was previously found with other types of guanidines.[63]

This all prompted us to explore the reactivity of catalytically obtained trisubstituted guanidines, namely $(^iPrHN)_2CNR$ (R = Ph, 2,4,6-$Me_3C_6H_2$, p-BrC_6H_4, Fc), toward $AlMe_3$. As a result of this study, we report herein the preparation of a family of aluminum guanidinato complexes with different nuclearities and coordination modes. The catalytic behavior of some of these complexes in the synthesis of cyclic carbonates is also discussed and compared with the previous results obtained with the free ligands as catalysts.

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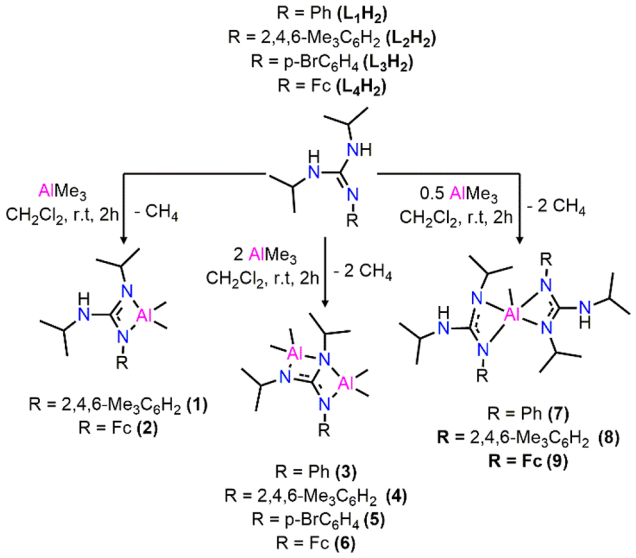
RESULTS AND DISCUSSION

Synthesis and Structural Characterization of Complexes 1−9. Guanidine ligands L_1H_2−L_4H_2 (Scheme 3) were

Scheme 3. General Pathway for the Preparation of Complexes 1−9



synthesized via guanylation of the respective amine with *N*,*N*′-diisopropylcarbodiimide in the presence of $ZnEt_2$ as catalyst, as previously reported (see Experimental Section).[7,10]

On the basis of our previous work[39−41] and acknowledging that the presence of two N−H groups in the guanidine ligand precursor will allow us to obtain mononuclear or dinuclear complexes, the latter reported to be more active in the formation of cyclic carbonates from epoxides and CO_2,[35,39,40] we performed the synthesis of the new alkyl aluminum guanidinato complexes **1**−**9** via protonolysis reaction between the respective guanidine ligands (L_1H_2−L_4H_2) with 1.0, 2.0, or 0.5 equiv of $AlMe_3$ to produce the corresponding mono- (**1** and **2**) or dinuclear (**3**−**6**) tetracoordinate aluminum complexes and the respective mononuclear pentacoordinate compounds (**7**−**9**) (Scheme 3). The reactions were carried out in dry CH_2Cl_2 for 2 h at room temperature. After the appropriate workup, complexes **1**−**9** were obtained in high yields (≥95%) as white (**1**, **3**−**5**, **7**, **8**) or reddish-brown (**9**) solids, and reddish-brown (**2** and **6**) oils. Of all the latter species, tetracoordinated complexes proved to be unstable under air, while the pentacoordinated ones remained unchanged for several hours of exposure to the atmosphere.

The structural characterization of these mono- and dinuclear compounds **1**−**9** was accomplished using standard 1D and 2D NMR characterization techniques and X-ray diffraction for **4** and **8** (see Experimental Section and Supporting Information).

The ^{1}H NMR spectra of mononuclear complexes **1** and **2**, in $CDCl_3$ and C_6D_6, respectively, supported the nuclearity of these compounds due to the signal attributed to one N−H proton of the guanidinate fragment at 3.88 ppm for **1** and 4.54 ppm for **2** together with a singlet at −0.71 and −0.12 ppm, respectively, corresponding to 6 protons of the $AlMe_2$ moiety (see Figure 2a for complex **2**). On the other hand, in the ^{1}H NMR spectra for complexes **3**−**6**, the signal ascribed to the two N−H protons of the guanidine ligand precursor was missing, therefore supporting the formation of the binuclear

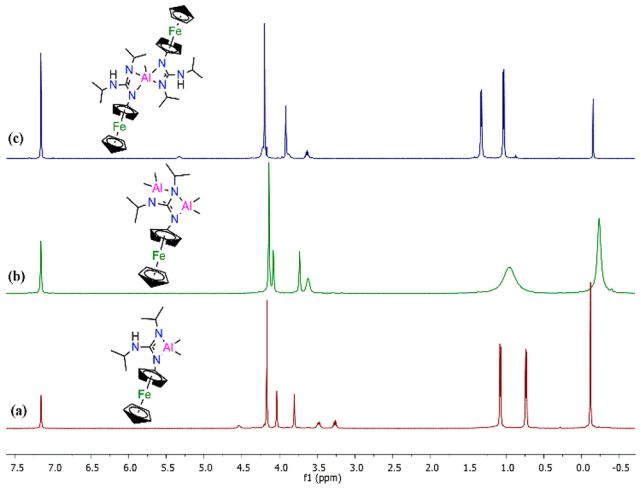


Figure 2. ^{1}H NMR spectra in C_6D_6 of (a) mononuclear complex **2**, (b) dinuclear complex **6**, and (c) mononuclear complex **9**.

aluminum complexes. Furthermore, these compounds show a characteristic singlet resonance for the two $AlMe_2$ groups at −0.94, −0.60, −0.93, and −0.23 ppm, respectively (complexes **3** and **4** in $CDCl_3$, while **5** and **6** in C_6D_6), all signals integrating for 12 protons (Figure 2b for complex **6**). The ^{1}H NMR spectra, in C_6D_6, for complexes **7**−**9**, exhibit a resonance corresponding to the N−H protons of each guanidine moiety at 3.48, 3.54, and 5.32 ppm, respectively, jointly with a singlet at −0.21, 0.09, and −0.15, respectively, attributed to the AlMe moiety (Figure 2c for complex **9**).

The ^{13}C NMR spectra of compounds **1**−**9** evidence the presence of the diagnostic peak of the central carbon in the guanidine moiety located around 150 or 160 ppm for all complexes. Moreover, a characteristic peak for the $AlMe_2$ moiety in complexes **1**−**6** and the AlMe fragment in complexes **7**−**9** was detected around −4 or −10 ppm.

Two-dimensional experiments were carried out to assign the majority of ^{1}H NMR signals and ^{1}H−^{13}C g-HSQC experiments to locate resonances from carbon atoms. The equivalence of the substituents on the guanidinate ligands and the equivalence of the alkyl aluminum moieties allowed us to propose a tetrahedral environment around one or two aluminum atoms (compounds **1**−**2** and **3**−**6**, respectively) in which the guanidinato monoanion acts as bidentate or tridentate ligand in a κ^2-*N*,*N*′ or a μ-κ^2-*N*,*N*′-κ^2-*N*′,*N*″ coordination mode, respectively. Mononuclear complexes **7**−**9** reveal a pentacoordination geometry around the aluminum atom.

The structures of the binuclear complex **4** and the mononuclear complex **8** were determined by X-ray single crystal diffraction. Single crystals of complexes **4** and **8** were obtained by slow evaporation in cold pentane at −30 °C. Molecular structures of complexes **4** and **8** are illustrated in Figures 3 and 4, respectively. A summary of the crystallographic data and data collection parameters is incorporated in Tables S1 and S2 in the Supporting Information.

The solid-state structure of complex **4** is shown in Figure 3. The diffractometric analysis of this compound confirmed the monomeric structure with two coordinated aluminum centers. Both aluminum centers present a distorted tetrahedral geometry and are bridged by the N2 atom which is common for the two chelating guanidinato units in where each unit presents a κ^2-*N*,*N* coordination mode. The amidinate bite

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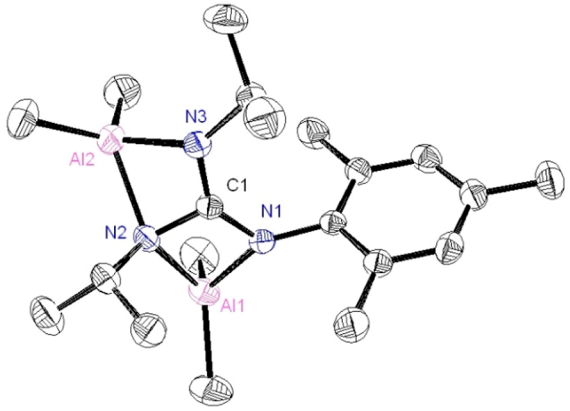

Figure 3. Molecular structure of **4**. Thermal ellipsoids are shown with 30% probability, and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N1−Al1 1.946(3), N2−Al1 1.982(3), N2−Al2 2.023(4), N3−Al2 1.945(4), C1−N3 1.315(4), C1−N1 1.320(4), C1−N2 1.449(4), Al1−C11 1.498(4); N1−Al1−N2 70.6(1), N2−Al2−N3 69.9(1), Al1−N1−C1 91.5(2), Al2−N3−C1 90.1(2), N2−C1−N1 110.0(3), N2−C1−N3 110.6(3).

angles N1−Al1−N2 70.6(1)° and N2−Al2−N3 69.9(1)° together with the C11−Al1−C12 113.3(2)° and C13−Al2−C14 114.9(2)° angles are far away from the ideal tetrahedral angle of 109.5°. The C1−N1 and C1−N3 bond distances of 1.320(4) and 1.315(4) Å supported a high degree of electron delocalization within the guanidinate backbone, like those previously reported for related Al guanidinato complexes.[43,44] The Al1−C bond lengths (range 1.945(6)−1.956(4) Å) of the Al-bound methyl moieties are according with the expected values for Al alkyl complexes.[51,58]

The molecular structure of complex **8** is depicted in Figure 4. The X-ray diffraction study indicated that compound **8** crystallized in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit. Only one molecule (molecule "A") is discussed, as both molecules show similar structural parameters.

The aluminum metal center presents the expected pentacoordinated environment. Therefore, the τ value[64,65] was calculated to determine how closely this compound approaches either a perfectly square pyramidal (τ = 0) or a perfectly trigonal bipyramidal geometry (τ = 1). A value of 0.15 for this parameter confirmed a slight distorted square-pyramidal structure in which four N atoms belonging to the two identical guanidinato units occupy the equatorial positions, while the apical position is occupied by the methyl group. It should be noted that the few pentacoordinated guanidinate aluminum complexes that have been published to date exhibit distorted trigonal bipyramidal geometries,[49,52] whereas complex **8** displayed a distorted square-pyramidal geometry probably favored by the steric and electronic properties of the asymmetric guanidine ligand employed. The acute bite angles (66.90°) produce a minor increase of the respective N1−Al1−N5 (98.4(6)°) and N2−Al1−N4 (99.0(6)°) angles and a notable increase of the N1−Al1−C8 (115.0(8)°) angle from the ideal square pyramidal angle of 90°. Furthermore, a significant decrease of the N1−Al1−N4 (134.7(7)°) and N2−Al1−N5 (143.6(7)°) angles from the ideal angle of 180° is also noted. Charge delocalization in the NCN fragments is supported by the respective C−N bond lengths, which present values between 1.331(2) and 1.338(2) Å and are comparable to those C−N distances of other metal guanidinato complexes.[45,49] Furthermore, the Al1−C8 distance 1.972(2) Å is consistent with values previously reported.[51]

Catalytic Studies for the Synthesis of Cyclic Carbonates. As mentioned before, we reported the use of aromatic mono- and bisguanidines as very active binary catalyst systems for the preparation of cyclic carbonates from epoxides and CO_2.[63] Thus, having prepared the asymmetric aluminum guanidinato complexes **1**−**9**, which present different nuclearities and coordination modes, we decided to test them as

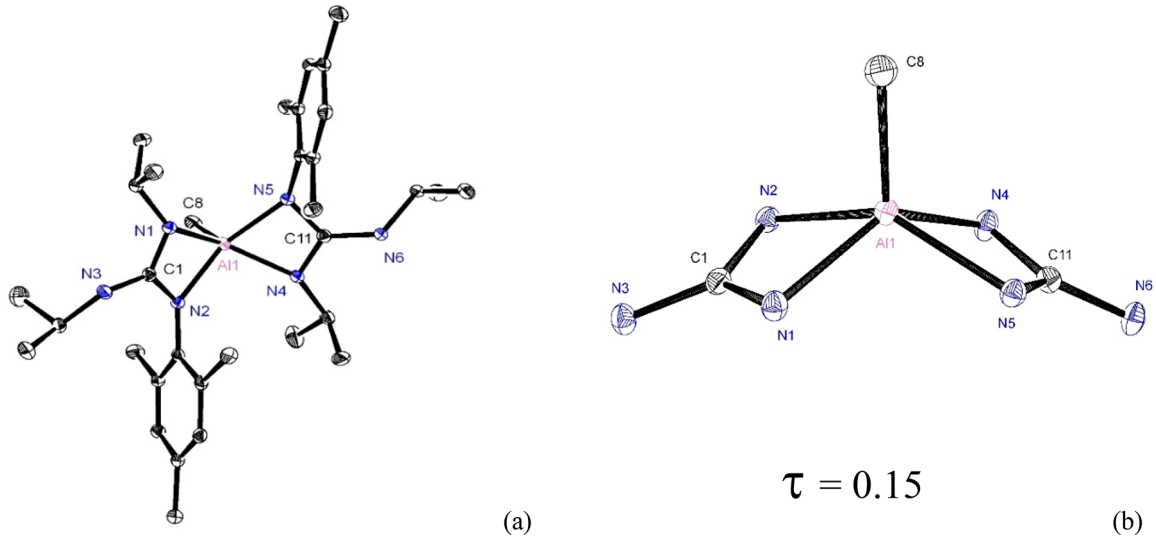

Figure 4. (a) Molecular structure of **8**. Thermal ellipsoids are shown with 30% probability, and hydrogen atoms have been omitted for clarity. Only one of the two molecules (molecule "A") found in the asymmetric unit is shown. Selected bond distances (Å) and angles (deg): N1−Al1 1.971(2), N2−Al1 2.011(2), N5−Al1 2.003(2), N4−Al1 1.984(2), C1−N1 1.337(2), C11−N5 1.336(2), Al1−C8 1.972(2), C1−N3 1.363(2); N1−Al1−N2 66.9(6), N4−Al1−N5 66.9(6), N1−Al1−C8 115.0(8), N1−Al1−N4 134.7(7), N1−Al1−N5 98.4(6), N5−C11−N6 124.8(2). (b) Geometry around Al.

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catalysts for this catalytic application and compare their activity with the respective free ligands L_1H_2−L_4H_2.

Therefore, the transformation of styrene oxide **10a** into styrene carbonate **11a** was initially performed with complexes **1**, **2**, **4**, **6**, **8**, and **9**, which have the same ligands and different nuclearity, under the same catalytic conditions employed with the free guanidines,[63] and we proceeded to compare their catalytic activity.

The reactions were performed at 70 °C and 1 bar of CO_2 pressure (balloon) for 24 h under solvent-free conditions using 2.0 mol % of free guanidines (L_1H_2−L_4H_2), 2.0 mol % of mononuclear complexes **1**, **2**, **8**, and **9**, and 1.0 mol % of dinuclear complexes **4** and **6**, with the aluminum concentration kept constant at 2.0 mol % and using tetrabutylammonium iodide (TBAI) as cocatalyst. These results are shown in Table 1.

Table 1. Synthesis of Styrene Carbonate 11a Employing Guanidine Ligands L_1H_2−L_4H_2 and Catalysts 1, 2, 4, 6, 8, and 9[a]

entry	cat.	cat. (mol %)	conversion[b] (%)
1	L_1H_2	2.0	70[c]
2	L_2H_2	2.0	54[c]
3	L_3H_2	2.0	74
4	L_4H_2	2.0	93[c]
5	**1**	2.0	100
6	**2**	2.0	100
7	**4**	1.0	100
8	**6**	1.0	100
9	**8**	2.0	100
10	**9**	2.0	100

[a]Reactions were carried out at 70 °C and 1 bar of CO_2 pressure for 24 h using 2.0 mol % of TBAI and under solvent-free conditions. [b]Conversion was determined by ^{1}H NMR spectroscopy of the reaction mixture relative to starting epoxide. [c]Conversion reported by Rojas et al.[63]

It is notable that both, mono- and dinuclear aluminum complexes (Table 1, entries 5−10), presented excellent conversions (100%) for the preparation of styrene carbonate **11a** compared with the high to moderate conversions (54−93%) exhibited by the free guanidines (Table 1, entries 1−4). Therefore, these aluminum guanidinato complexes allowed a significant improvement in the catalytic activity and turned to be more active and efficient catalytic systems than free guanidines This could be explained through the fact that the Lewis acidity of the Al(III) metal center is more efficient than the hydrogen-bonding interaction approach ascribed to free guanidines for the activation of the epoxide. Thus, the Al(III)−O interaction should facilitate further the epoxide ring opening.

Furthermore, we focused our attention on the catalytic behavior of complexes **1**−**9** for the preparation of styrene carbonate **11a**. For that reason, we opted for decreasing by half the loadings of the previously studied catalysts. The catalytic results are illustrated in Table 2.

As can be seen, dinuclear complexes **3**−**6** (Table 2, entries 3−6) displayed higher catalytic activity than their tetracoordinate (**1**−**2**, Table 2, entries 1 and 2) and pentacoordinate (**8** and **9**, Table 2, entries 8 and 9) mononuclear counterparts. These results support the importance of the catalyst design and are in good agreement with previous reports on binuclear

Table 2. Synthesis of Styrene Carbonate 11a Employing Catalysts 1−9[a]

entry	cat.	cat. (mol %)	conversion[b] (%)
1	**1**	1.0	70
2	**2**	1.0	75
3	**3**	0.5	90
4	**4**	0.5	91
5	**5**	0.5	81
6	**6**	0.5	92
7	**7**	1.0	82
8	**8**	1.0	87
9	**9**	1.0	88
10	**6**	0.5	0[c]
11			8[d]

[a]Reactions were carried out at 70 °C and 1 bar of CO_2 pressure for 24 h using 1.0 mol % of TBAI and under solvent-free conditions. [b]Conversion was determined by ^{1}H NMR spectroscopy of the reaction mixture relative to starting epoxide. [c]No TBAI was added. [d]No catalyst was added.

compounds, which show higher catalytic activities probably due to cooperative effects between the two metal centers.[39,40] Focusing on the dinuclear complexes, it is noteworthy to see the electronic influence of the aromatic ring in the catalytic activity of these systems, as the presence of electron withdrawing groups (EWGs) such as *p*-BrC_6H_4 in **5** resulted in a slight decrease in the activity (Table 2, entry 5) vs the unsubstituted phenyl ring in **3** (Table 2, entry 3), whereas strong electron donating groups (EDGs) such as Fc in **6** and 2,4,6-$Me_3C_6H_3$ in **4** (Table 2, entries 4 and 6) caused an increase in the catalytic activity. Nevertheless, the higher solubility of these complexes in the reagent mixture cannot be excluded as responsible for this behavior. Out of all the catalysts tested, dinuclear complex **6** showed the highest activity toward the preparation of styrene carbonate **11a**. For this reason, control experiments were carried out to determine that neither complex **6** nor TBAI exhibited significant activity on their own (Table 2, entries 10 and 11).

With the optimized reactions conditions for the preparation of **11a** with catalyst **6** at hand (see entry 6 in Table 2), we decided to attempt the synthesis of 12 monosubstituted cyclic carbonates **11a**−**l** from their respective terminal epoxide (**10a**−**l**) and carbon dioxide (Figure 5). In general, the catalytic system (**6**/TBAI) afforded remarkable results with selectivities > 99% toward cyclic carbonates bearing different functional groups such as aryl, alkyl, alcohol, halide, and ether groups under the conditions described about. Particularly, the alkyl cyclic carbonates (**11b**−**d**) together with those bearing phenyl, ether, and halide groups in their structure (**11a**, **11f**−**g**, and **11l**) were accomplished in notable yields (82−96%), while the functionalized aromatic cyclic carbonates (**11i**−**j**) were obtained in good yields (71−77%). A remarkable result was found for glycerol carbonate (**11e**), which was obtained in exceptional yield (93%) despite the tendency of glycidol epoxide to generate polymer products.[66,67] Additionally, the highly fluorinated cyclic carbonate **11k** was prepared in outstanding yield (85%), this being a cyclic carbonate that presents a potential application as electrolyte in lithium-ion batteries.[28,68] These results indicate that **6**/TBAI is an efficient system for the synthesis of monosubstituted cyclic carbonates.

As a result of the high activity presented by the catalytic system (**6**/TBAI) for the preparation of terminal cyclic

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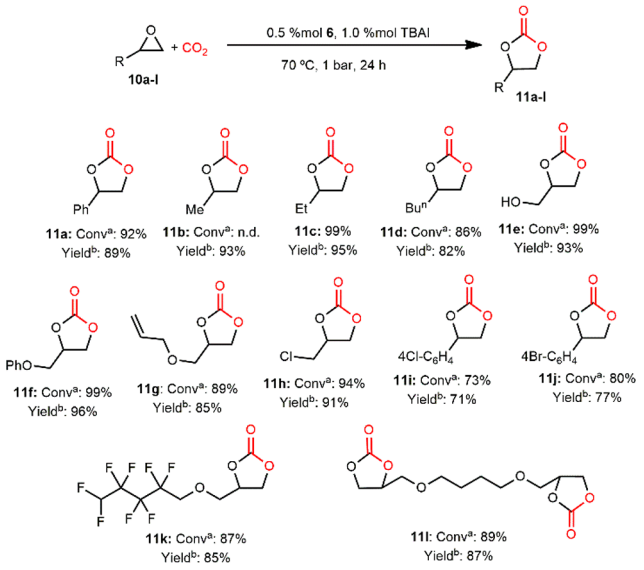
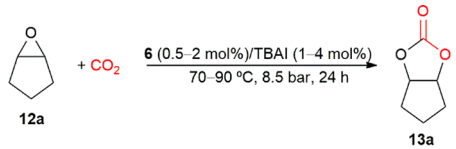


Figure 5. Cyclic carbonates **11a–l** were obtained by the catalyst system **6**/TBAI in a molar ratio of 0.5:1.0. Reactions were performed at 70 °C and 1 bar of CO_2 pressure in the absence of solvent. [a]Conversion was determined using ^{1}H NMR spectroscopy of the crude reaction mixture. [b]Isolated yield obtained from purified cyclic carbonate.

carbonates, we decided to expand the substrate scope by studying the use of internal or disubstituted epoxides. Initially, we employed cyclopentene oxide **12a** as a model substrate under 8.5 bar of CO_2 due to the lower reactivity of these internal epoxides. These results are shown in Table 3.

Table 3. Synthesis of Cyclopentane Carbonate 13a Catalyzed by Complex 6[a]



entry	cat. (mol %)	TBAI (mol %)	T (° C)	conversion[b] (%)
1	0.5	1.0	70	0
2	1.5	3.0	70	15
3	2.0	4.0	70	20
4	0.5	1.0	90	32
5	1.5	3.0	90	64
6	2.0	4.0	90	96
7	2.0	0	90	0
8	0	4.0	90	2

[a]Reactions were carried out at 70–90 °C and 8.5 bar of CO_2 pressure for 24 h using 0.5–2 mol % of complex **6** and 1–4 mol % of TBAI and under solvent-free conditions. [b]Conversion was determined by ^{1}H NMR spectroscopy of the reaction mixture relative to starting epoxide.

As may be noted, none or low conversion to cyclopentene carbonate **13a** was obtained at 70 °C employing different loadings of catalyst with cocatalyst (**6**/TBAI) keeping constant the molar ratio at 1:2 (Table 3, entries 1–3). With the aim to improve the catalytic activity, we decided to increase the temperature to 90 °C, and the highest conversion to cyclopentene carbonate **13a** (96%) was achieved by using 2.0 mol % of complex **6** and 4.0 mol % of TBAI at 8.5 bar of CO_2 (Table 3, entry 6).

Having optimized the reaction conditions for the synthesis of cyclopentene oxide **13a**, a series of internal epoxides (**12a–c**) and CO_2 were employed under the same experimental conditions to prepare other disubstituted cyclic carbonates (Figure 6).

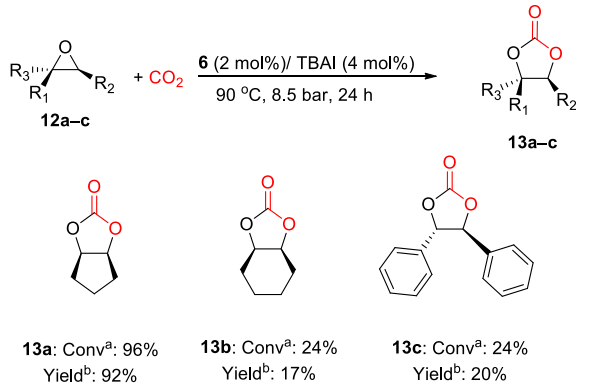


Figure 6. Synthesis of disubstituted cyclic carbonates **13a–c** using the catalytic system **6**/TBAI. [a]Conversion was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [b]Isolated yield obtained from purified cyclic carbonate. No polycarbonate was obtained from stilbene epoxide.

In general, low to high yields (17–92%) were achieved using the catalytic system **6**/TBAI for the preparation of cyclic carbonates **13a–c**. Pleasingly, the cyclic carbonate **13a** was accomplished in good yield, 92%, with 100% retention of stereochemistry and selectivity. However, for cyclohexene carbonate **13b**, not only was the formation of cyclic carbonate observed but also the corresponding polycarbonate was detected in the NMR spectra of the product, as only a 17% of yield of *cis*-cyclohexene carbonate **13b** was produced, indicating that cyclohexene oxide **12b** was not a good substrate for this catalytic system (**6**/TBAI). Finally, when stilbene epoxide **12c** was used, only a 20% yield of its respective cyclic carbonate **13c** was obtained, and no polycarbonate was found.

CONCLUSIONS

In conclusion, mono- and dinuclear aluminum guanidinato complexes **1–9** were prepared *via* protonolysis between the respective trisubstituted guanidine ligands ($\mathbf{L_1H_2}$–$\mathbf{L_4H_2}$) through different molar ratios, and $AlMe_3$. NMR spectroscopy and X-ray diffraction analysis allowed us to establish a tetrahedral environment around the mononuclear complexes **1–2** and dinuclear complexes **3–6** in which the guanidinato monoanion is coordinated to one or two $AlMe_2$ moieties, respectively, in a κ^2-*N*,*N* coordination mode, whereas mononuclear complexes **7–9** present a pentacoordinated environment around the aluminum metal center, with two guanidinato ligands chelating the metal center also in a κ^2-*N*,*N* coordination mode.

Complexes **1**, **2**, **4**, **6**, **8**, and **9** are very active catalysts for the transformation of styrene oxide and CO_2 into styrene carbonate. In all cases, the aluminum complexes were more active and efficient catalysts than their respective free guanidines ($\mathbf{L_1H_2}$–$\mathbf{L_4H_2}$) at 70 °C and 1 bar of CO_2 for 24 h employing 2.0 mol % of catalyst and 2.0 mol % of TBAI as cocatalyst. Consequently, aluminum guanidinato complexes

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provide a significant improvement in the catalytic activity compared with the respective parent guanidines.

Among complexes **1**−**9**, dinuclear complexes **4** and **6** exhibited higher catalytic activity than their mononuclear counterparts **1** and **2**, and their respective pentacoordinated analogues **8** and **9** for the preparation of styrene carbonate using 0.5 mol % of complex and 1 mol % of TBAI at 70 °C and 1 bar of CO_2 pressure for 24 h. Dinuclear complex **6** in the presence of TBAI presented the highest catalytic activity at 70 °C and 1 bar of pressure of CO_2 for 24 h and was able to produce a wide scope of terminal cyclic carbonates from different functionalized epoxides with aryl, alkyl, alcohol, ether, and halide moieties, in good to excellent yields (71−96%), while the respective internal carbonates were obtained in low to high yields (17−92%) even at higher temperatures and CO_2 pressure.

The trisubstituted guanidine pro-ligands described here are easy to prepare on a large scale and present high tunability, and equally important, the presence of two N−H groups in these species allows the future development of new complexes with different nuclearities and coordination modes that could be highly active for the preparation of cyclic carbonates.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. Reagent-grade solvents, toluene, dichloromethane, diethyl ether, pentane, tetrahydrofuran (THF), and hexane, were dried using an Innovative Technology Pure Solv Model PS-MD-5. Aminoferrocene[41,69] and guanidine ligands $\mathbf{L_1H_2}$−$\mathbf{L_3}$-$\mathbf{H_2}$[7] and $\mathbf{L_4H_2}$[10] were prepared as previously reported. All other chemical reagents and solvents were obtained from the usual commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts and coupling constants are reported in parts per million and hertz, respectively. Most of the NMR assignments were supported by additional 2D. Microanalyses of solid samples were carried out with a LECO CHNS-932 analyzer. For X-ray crystal structure analysis of complex **4**, data sets were collected by Dr. Antonio Rodríguez-Diéguez, on a Bruker D8 Venture with a photon detector equipped with monochromated MoKα radiation (λ = 0.71073 Å), and for complex **8**, data sets were collected by Dr. Constantin G. Daniliuc, with a Bruker D8 Venture Photon III Diffractometer system equipped with a micro focus tube MoKα radiation (λ = 0.71073 Å) and a mirror monochromator. CCDC 2069446 (**4**) and 2082070 (**8**) contain the supplementary crystallographic data of this paper.

Synthesis of Complex 1. A dichloromethane solution of trimethylaluminum (55.1 mg, 0.765 mmol) in was added to a dichloromethane solution of 1,3-diisopropyl-2-mesitylguanidine (200 mg, 0.765 mmol). The reaction mixture was stirred for 2 h at room temperature, and the volatiles were then removed under vacuum. The product thus obtained was dissolved in pentane and kept at −30 °C to precipitate complex **1** as a white solid (0.734 mmol, 233 mg, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm; see Supporting Information for atom assignment): δ 6.84 (s, 2H, H_9), 3.88 (d, J = 9.2 Hz, 1H, N-H, H_5), 3.45 (m, 1H, H_2), 3.29 (m, 1H, H_4), 2.27 (s, 1H, H_{11}), 2.20 (s, 2H, H_{12}), 1.19 (d, J = 6.3 Hz, 6H, H_1), 0.99 (d, J = 6.4 Hz, 6H, H_3), −0.71 (s, 12H, H_{13}). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, ppm): δ159.68 (C_6), 139.07 (C_7), 134.28 (C_8), 133.19 (C_{10}), 128.86 (C_9), 44.03 (C_2), 43.93 (C_4), 24.59 (C_1), 24.20 (C_3), 20.91 (C_{11}), 18.78 (C_{12}), −8.94 (C_{13}). Anal. Calcd. for $C_{18}H_{32}AlN_3$: C, 68.10; H, 10.16; N, 13.24. Found: C, 68.52; H, 9.94; N, 13.33.

Synthesis of Complex 2. A dichloromethane solution of 2 equiv of trimethylaluminum (44.05 mg, 0.611 mmol) was added to a dichloromethane solution of diisopropyl ferrocenyl guanidine (200 mg, 0.611 mmol). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was dissolved with hexane. After the appropriate workup, complex **2** was obtained as a viscous orange oil. Yield: 94% (220 mg, 0.574 mmol). **^{1}H NMR** (C_6D_6, 400 MHz, ppm): δ 4.54 (d, J = 8.7 Hz, 1H, N-H, H_5), 4.17 (s, 5H, H_{10}), 4.04 (s, 2H, H_8), 3.81 (s, 2H, H_9), 3.48 (m, 1H, H_4), 3.27 (m, 1H, H_2), 1.08 (d, J = 6.2 Hz, 6H, H_1), 0.74 (d, J = 6.3 Hz, 6H, H_3), - 0.12 (s, 6H, H_{11}). **^{13}C{^{1}H} NMR** (C_6D_6, 100 MHz, ppm): δ 161.11 (C_6), 101.46 (C_7), 69.24 (C_{10}), 65.07 (C_9), 63.81 (d, J = 2.6 Hz, C_8), 44.48 (C_2), 44.17 (d, J = 11.4 Hz, C_4), 24.71 (C_1), 23.53 (d, J = 4.8 Hz, C_3), −8.62 (C_{11}). Anal. Calcd. for $C_{19}H_{30}AlFeN_3$: C, 59.54; H, 7.89; N, 10.96. Found: C, 59.72; H, 7.94; N, 11.03.

Synthesis of Complex 3. A dichloromethane solution of 2 equiv of trimethylaluminum (131.2 mg, 1.82 mmol) was added to a dichloromethane solution of 1 equiv of 1,3-diisopropyl-2-phenylguanidine (200 mg, 0.912 mmol). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was dissolved in pentane and kept at −30 °C to precipitate complex **3** as a white solid (0.894 mmol, 296 mg, 98%). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.24 (dd, J = 10.8, 5.0 Hz, 1H, H_6), 7.00 (t, J = 7.3 Hz, 2H, H_7), 6.82 (d, J = 7.6 Hz, 2H, H_5), 3.98 (s, 2H, H_2), 1.22 (d, 12H, H_1), −0.94 (s, 12H, H_8). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, ppm): δ 159.07 (C_3), 149.34 (C_4), 129.28 (C_6), 122.95 (C_7), 119.97 (C_5), 45.11 (C_2), 25.15 (C_1), −9.65 (C_8). Anal. Calcd. for $C_{17}H_{31}Al_2N_3$: C, 61.61; H, 9.43; N, 12.68. Found: C, 61.52; H, 9.64; N, 12.53.

Synthesis of Complex 4. A dichloromethane solution of 2 equiv of trimethylaluminum (110.3 mg, 1.53 mmol) was added to a dichloromethane solution of 1 equiv of 1,3-diisopropyl-2-mesitylguanidine (200 mg, 0.765 mmol. The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was dissolved in pentane and kept at −30 °C to precipitate complex **4** as a white solid (0.750 mmol, 280 mg, 98%). Single colorless crystals for X-ray crystallography were grown from cold pentane at −30 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.83 (s, 2H, H_8), 3.89 (m, 1H, H_4), 3.21 (m, 1H, H_2), 2.27 (s, 9H, $H_{10,11}$), 1.33 (d, J = 6.0 Hz, 6H, H_3), 0.85 (s, 6H, H_1), −0.60 (s, 12H, H_{12}). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, ppm): δ 161.77 (C_5), 137.11 (C_6), 135.06 (C_9), 133.48 (C_7), 128.86 (C_8), 54.32 (C_4), 44.35 (C_2), 24.76 (C_1), 22.21 (C_3), 20.88 (C_{10}), 19.59 (C_{11}), −6.98 (C_{12}). Anal. Calcd. for $C_{20}H_{37}Al_2N_3$: C, 64.32; H, 9.99; N, 11.25. Found: C, 64.44; H, 10.09; N, 11.33.

Synthesis of Complex 5. A dichloromethane solution of 2 equiv of trimethylaluminum (96.6 mg, 1.34 mmol) was added to a dichloromethane solution of 1 equiv of 2-(4-bromophenyl)-1,3-diisopropylguanidine (200 mg, 0.671 mmol). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was dissolved in pentane and kept at −30 °C to precipitate complex **5** as a white solid (0.651 mmol, 267.5 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.34 (d, J = 8.4 Hz, 2H, H_6), 6.70 (d, J = 8.3 Hz, 2H, H_5), 3.97 (m, 2H, H_2), 1.21 (d, J = 6.3 Hz, 12H, H_1), −0.93 (s, 12H, H_8). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, ppm): δ 158.84 (C_3), 148.72 (C_4), 132.29 (C_6), 121.70 (C_5), 115.68 (C_7), 45.19 (C_2), 25.12 (C_1), −9.63 (C_8). Anal. Calcd. for $C_{17}H_{30}Al_2BrN_3$: C, 49.76; H, 7.37; N, 10.24. Found: C, 49.84; H, 7.44; N, 10.32.

Synthesis of Complex 6. A dichloromethane solution of 2 equiv of trimethylaluminum (220.6 mg, 3.06 mmol) was added to a dichloromethane solution of 1 equiv of diisopropyl ferrocenyl guanidine (500 mg, 1.53 mmol). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was dissolved with hexane. After the appropriate workup, complex **6** was obtained as a viscous orange liquid. Yield: 96% (1.47 mmol, 646 mg). **^{1}H NMR** (C_6D_6, 400 MHz, ppm): δ 4.14 (s, 5H, H_9), 4.08 (s, 2H, H_7), 3.73 (s, 2H, H_8), 3.62 (m, 2H, $H_{2,4}$), 0.96 (m, 12H, $H_{1,3}$), −0.23 (s, 12H, H_{10}). **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, ppm): δ 163.95 (C_5), 99.27 (C_6), 69.51 (C_9), 65.31 ($C_{7,8}$), 53.87, 44.73 (C_4), 23.81, 22.05 (C_2), −7.58 (C_{10}). Anal. Calcd. for $C_{21}H_{35}Al_2FeN_3$: C, 57.41; H, 8.03; N, 12.28. Found: C, 57.72; H, 7.94; N, 12.43.

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Synthesis of Complex 7. A dichloromethane solution of 1 equiv of trimethylaluminum (32.87 mg, 0.456 mmol) was added to a dichloromethane solution of 2 equiv of 1,3-diisopropyl-2-phenylguanidine (200 mg, 0.912 mmol). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was washed with hexane. Complex **7** was obtained as a white solid (0.451 mmol, 178 mg, 99%). **^{1}H NMR** (C_6D_6, 400 MHz, ppm): δ7.15 (d, J = 7.2, 4H, H_8), 7.11 (d, J = 9.1, 4H, H_9), 6.83 (t, J = 6.9, 2H, H_{10}), 3.48 (d, J = 9.6 Hz, 2H, N-H), 3.32 (m, 2H, H_5), 3.13 (m, 2H, H_2), 1.11 (d, J = 21.1, 12H, H_1), 0.59 (d, J = 15.1, 8.6 Hz, 12H, H_6), −0.21 (m, 3H, H_{11}). **^{13}C{^{1}H} NMR** (C_6D_6, 100 MHz, ppm): δ 162.17 (C_3), 148.17 (C_7), 128.91 (C_{10}), 124.83 (C_9), 121.66 (C_8), 45.06 (C_2), 44.57 (C_5), 24.18 (C_1), 23.22 (C_6), −7.49 (C_{11}). Anal. Calcd. for $C_{27}H_{43}AlN_6$: C, 67.75; H, 9.05; N, 17.56. Found: C, 68.14; H, 8.74; N, 17.72.

Synthesis of Complex 8. A dichloromethane solution of 1 equiv of trimethylaluminum (27.6 mg, 0.382 mmol) was added to a dichloromethane solution of 2 equiv of 1,3-diisopropyl-2-mesitylguanidine (200 mg, 0.765 mmol). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was washed with hexane. Complex **8** was obtained as a white solid (0.378 mmol, 179 mg, 99%). **^{1}H NMR** (C_6D_6, 400 MHz, ppm): δ6.93 (d, J = 7.2 Hz, 4H, H_9), 3.54 (d, J = 9.9 Hz, 2H, N-H), 3.35 (m, 2H, H_2), 3.20 (m, 2H, H_5), 2.57 (s, 6H, H_{12a}), 2.54 (s, 6H, H_{12b}), 2.21 (s, 6H, H_{11}), 1.11 (d, J = 6.3 Hz, 6H, H_6), 0.75 (d, J = 6.3 Hz, 6H, H_1), 0.67 (d, J = 6.4 Hz, 6H, H_6), 0.62 (d, J = 6.3 Hz, 6H, H_1), 0.09 (s, 3H, H_{13}). **^{13}C{^{1}H} NMR** (C_6D_6, 100 MHz, ppm): δ 160.28 (C_4), 141.34 (C_7), 136.17 (C_{8b}), 135.80 (C_{8a}),133.13 (C_{10}), 129.23 (C_9), 129.00 (C_9), 44.53 (C_2), 43.99 (C_5), 24.51 (C_1), 24.06 (C_6), 21.09 (C_{11}), 19.97 (C_{12a}), 19.40 (C_{12b}), −4.12 (C_{13}). Anal. Calcd. for $C_{33}H_{55}AlN_6$: C, 70.42; H, 9.85; N, 14.93. Found: C, 70.74; H, 9.64; N, 15.09.

Synthesis of Complex 9. A dichloromethane solution of 1 equiv of trimethylaluminum (22.1 mg, 0.306 mmol) was added to a dichloromethane solution of 2 equiv of diisopropyl ferrocenyl guanidine (200 mg, 0.612 mmol). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under vacuum, and the product was washed with hexane. Complex **9** was obtained as an orange solid. Yield: 95% (202 mg, 0.291 mmol). Orange single crystals for X-ray crystallography were grown from cold pentane at −30 °C. **^{1}H NMR** (C_6D_6, 400 MHz, ppm): δ 5.32 (d, J = 8.1 Hz, 2H, N-H, H_4), 4.22 (m, 4H, H_8), 4.20 (s, 10H, H_{10}), 3.92 (t, J = 1.92 Hz, 4H, H_9), 3.88 (m, 2H, H_5), 3.64 (m, 2H, H_2), 1.33 (d, J = 6.3 Hz, 12H, H_1), 1.03 (d, J = 6.3 Hz, 12H, H_6), −0.15 (s, 3H, H_{11}). **^{13}C{^{1}H} NMR** (C_6D_6, 100 MHz, ppm): δ 161.75 (C_3), 104.19 (C_7), 68.96 (C_{10}), 64.31 (C_9), 62.02 (C_8), 45.42 (C_2), 45.11 (d, J = 10.1 Hz, C_5), 24.67 (C_1), 23.89 (d, J = 5.1 Hz, C_6), −6.83(C_{11}). Anal. Calcd. for $C_{35}H_{51}AlFe_2N_6$: C, 60.53; H, 7.41; N, 12.10. Found: C, 60.84; H, 7.22; N, 12.23.

General Procedure for Catalyst Screening at 1 bar Pressure. Styrene oxide **10a** (1.66 mmol), free guanidines (**L_1H_2**−**L_4H_2**) (33.2 μmol), or complexes **1**−**9** (8.3−33.2 μmol), and TBAI (16.6−33.2 μmol) were placed in a vial containing a magnetic stir bar. The vial was fitted with a rubber stopper pierced by a balloon filled with CO_2. The reaction mixture was stirred at 70 °C and 1 bar of CO_2 pressure for 24 h. Then, the conversion of styrene oxide **10a** into styrene carbonate **11a** was determined by ^{1}H NMR analysis of a sample relative to the starting styrene oxide.

General Procedure for Catalyst Screening at 8.5 bar Pressure. Cyclopentane oxide **12a** (1.66 mmol), complex **6** (8.3−33.2 μmol), and TBAI (16.6−66.4 μmol) were placed in a stainless-steel reactor with a magnetic stirrer bar, and it was pressurized to 8.5 bar. The reaction mixture was stirred at 70−90 °C for 24 h; then the conversion of cyclopentane oxide **12a** into cyclopentane carbonate **13a** was determined by analysis of a sample by ^{1}H NMR spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00319.

Supplementary figures referenced in the text, structural characterization data (^{1}H and ^{13}C NMR spectra) for all compounds including cyclic carbonates **11a**−**l**, **13a**−**d**, and X-ray crystallographic data for complexes **4** and **8** (PDF)

Accession Codes

CCDC 2069446 and 2082070 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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