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Introduction

Nowadays, a great variety of coordination complexes using amidinate ligands are synthesized, due to their outstanding use for the preparation of thin films by atomic layer deposition (ALD) and chemical vapor deposition (CVD).¹ Amidinate ligands [$R_1NC(R_2)NR_1$] (R_1 and R_2 = alkyl, aryl or cyclopentadienyl) have proved to be highly versatile because their steric and electronic properties can be readily modified by the introduction of various R_1 and R_2 substituents.²

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Aluminum complexes with new non-symmetric ferrocenyl amidine ligands and their application in CO₂ transformation into cyclic carbonates†

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A set of alkyl aluminum complexes supported by non-symmetric ferrocenyl amidine ligands were used as catalysts for the preparation of cyclic carbonates from epoxides and carbon dioxide using Bu_4NI as a co-catalyst. A modified method for the synthesis of aminoferrocene allowed us to obtain this precursor in quantitative yield. Treatment of aminoferrocene with the corresponding acetimidoyl chloride afforded the desired ferrocenyl amidine ligands L_1H , (*E*)-*N*-(2,6-diisopropylphenyl)-*N'*-(ferrocenyl)acetimidamide, and L_2H , (*E*)-*N*-(2,6-dimethylphenyl)-*N'*-(ferrocenyl)acetimidamide. The reaction of these ligands with 1.0 or 0.5 equiv. of AlMe₃ led to the synthesis of aminoferrocene based aluminum complexes ((L_1)AlMe₂ (1), (L_2) AlMe₂ (2), (L_1)₂AlMe (3), and (L_2)₂AlMe (4)) in excellent yields, which were characterized by spectroscopic and X-ray diffraction methods. In addition, we have studied their electrochemical properties and complex 1 was found to be the most active catalyst for the formation of cyclic carbonates 6a-j from their corresponding epoxides 5a-j and CO₂.

Recently, aluminum amidinate complexes have also drawn attention as catalytic precursors in ring-opening polymerization $(\text{ROP})^3$ and in the transformation of CO₂ into cyclic carbonates.⁴

On the other hand, ferrocene is an interesting and useful backbone and has been employed in the design of a large variety of ligands. Thanks to its electronic and steric properties, numerous ferrocenyl ligands are used as components in different catalytic applications.⁵ Despite the easy synthesis of symmetric amidinate ligands, it is surprising that only a few examples containing an ubiquitous ferrocenyl fragment are reported in the literature (Fig. 1).⁶

Symmetric ferrocenyl amidinate ligands containing bulky substituents have been prepared by a direct reaction between ferrocenyllithium and the respective carbodiimide,^{6a,c} and behave as typical bidentate [N,N]-donor ligands coordinating to metals such as lithium,^{6a} iron,^{6d} cobalt,^{6d} rhodium,^{6c,d} iridium,^{6c} titanium,^{6e} zirconium,^{6e} and lanthanides.^{6f} These complexes have revealed interesting reactivities, giving place to CO insertion, *ortho*-metalation reaction on the ferrocene backbone and other interesting transformations such as redox tuneable olefin polymerization.⁶

It is important to note that there has been just one example of non-symmetric ferrocenyl amidinate ligand reported to date which has been obtained by treating lithium anilide [Li{N(SiMe₃)(ferrocenyl)}(TMEDA)] with benzonitrile.^{6e} This



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Fig. 1 Examples of reported ferrocenyl amidines.⁶

shows that access to non-symmetric or chiral ferrocene amidine⁷ ligands strongly depends on the synthetic methods to obtain the elusive aminoferrocene, and this is probably the reason for the low number of applications of this kind of ligand.

Carbon dioxide (CO_2) , which is the principal cause of the greenhouse effect, is generally recognized as responsible for global warming. Moreover, the accumulation of CO₂ in the atmosphere as a result of polluting emissions is triggering a negative impact on the Earth's climate. Consequently, the utilization of CO₂ as a renewable feedstock is highly recommended to avoid these problems, although its fixation into high value-added chemical products is still an important challenge for the scientific community.⁸ Furthermore, CO₂ has recently received much attention since it is an abundant, nontoxic and non-flammable source,⁹ and as a result, a large number of researchers have been focusing their attention on studying effective catalytic systems for the transformation of CO₂ into different products.¹⁰ In this context, the formation of five membered cyclic carbonates from epoxides and CO2 has been one of the most investigated CO2 fixations in recent years¹¹ (Scheme 1), as cyclic carbonates show possible industrial applications such as electrolytes for Li-ion batteries¹² and polar aprotic solvents.13

As aforementioned, despite the development of a significant variety of catalytic systems for this catalytic transformation,^{10,11} there is still a great deal of attention being paid to the preparation of new complexes using abundant metals such as aluminum for the synthesis of cyclic carbonates.¹⁴



Scheme 1 Synthesis of cyclic carbonates by the reaction of epoxides with CO₂.

As part of our ongoing interest in the design of novel ferrocenyl ligands for their application in catalysis¹⁵ and synthesis of aluminum amidinates,^{3a,4} herein we report the synthesis and structural characterization of novel alkyl aluminum complexes containing non-symmetric ferrocenyl amidine ligands which display an excellent catalytic activity for cyclic carbonate formation from epoxides and CO₂. In addition, the electrochemical properties of these ferrocenyl amidine ligands and their aluminum complexes are included.

Results and discussion

Synthesis of aminoferrocene

As mentioned before, we focused our attention on developing a methodology to obtain a new set of alkyl aluminum complexes based on non-symmetric ferrocenyl amidine ligands and probing their catalytic performance in CO_2 fixation into cyclic carbonates. Thus, the incorporation of the ferrocenyl backbone into non-symmetric amidine ligands can be accomplished using imidoyl chlorides as intermediates to react with aminoferrocene; a similar synthetic strategy has been used to access different bulky *N*,*N*'-disubstituted amidines.¹⁶

Although over the past few decades different synthetic methods have been reported for the preparation of aminoferrocene,¹⁷ these involve several synthetically challenging steps generally with low yields or requiring the synthesis of potentially explosive intermediates.¹⁸

Herein, aminoferrocene is synthesized by following the methodology proposed by Montserrat *et al.* in 1995.¹⁹ However, we have modified the preparation method of the first precursor, ferroceneboronic acid²⁰ and each step of the global reaction has been extensively optimized. The synthetic procedure is outlined in Scheme 2 (see the Experimental section for further details). Thus, aminoferrocene was obtained in 42% global yield, starting from ferrocene.

The preparation of ferroceneboronic acid was carried out from commercially available ferrocene which was monolithiated in the presence of *t*-BuLi in THF and the resulting *in situ*-generated ferrocenyllithium was subsequently treated



 $\mbox{Scheme 2}$ Preparation of aminoferrocene by a modified synthetic method. 19

with tri-isopropyl borate which was added slowly, and posterior hydrolysis by alkali treatment afforded the desired ferroceneboronic acid precursor. Other modifications were made in terms of optimizing the yield of each reaction step and these include the use of different polar solvents and reaction times.

Synthesis and structural characterization of the ferrocenyl amidine ligands L_1H and L_2H

The novel non-symmetric ferrocenyl amidine ligands (*E*)-*N*-(2,6-diisopropylphenyl)-*N*'-(ferrocenyl)acetimidamide (**L**₁**H**) and (*E*)-*N*-(2,6-dimethylphenyl)-*N*'-(ferrocenyl)acetimidamide (**L**₂**H**) were prepared by the reaction of aminoferrocene in THF at 0 °C in the presence of Et₃N with stoichiometric amounts of (*E*)-*N*-(2,6-diisopropylphenyl)acetimidoyl chloride¹⁶ and (*E*)-*N*-(2,6-dimethylphenyl)acetimidoyl chloride,²¹ respectively. After the appropriate workup, ligands **L**₁**H** and **L**₂**H** were isolated as orange solids in very good yields, 83 and 71%, respectively (Scheme 3).

The structural characterization of these ligands was carried out by employing one- and two-dimensional NMR techniques (¹H NMR, ¹³C{¹H} NMR, ¹H NOESY-1D and ¹H-¹³C heteronuclear correlation (g-HSQC)), and mass spectroscopy. The ¹H NMR spectra of these ligands show a broad singlet at 8.20 (L_1H) and 8.15 ppm (L_2H) , respectively (see the Experimental section), corresponding to the N-H group of the amidine moiety, which are in good agreement with the signals reported for other ferrocenyl amidines.^{6c} The protons of the monofunctionalized ferrocenyl units appear in the region between 4.76 and 3.91 ppm while the singlet belonging to the CH₃ group of the acetimidamide moiety appears at 1.58 ppm for L1H and at 1.56 ppm for L₂H. Particularly, L₁H shows resonances corresponding to the isopropyl fragment around 3.0 and 1.13 ppm, whereas the spectrum of L2H shows a signal for the methyl group at 2.04 ppm. Two dimensional experiments were carried out to confirm the assignment of most ¹H NMR resonances and ¹H-¹³C heteronuclear correlation (g-HSQC) experiments were performed to assign the signals of the corresponding carbon atoms (see the ESI⁺). Mass spectra (ESI) show the corresponding molecular ions $[M + H]^+$ at m/z 403.2 (L₁H) and 346.5 (L₂H), with agreement between the experimental and calculated patterns.

Synthesis and structural characterization of complexes 1-4

Based on our previous work in which we performed the synthesis of tetra- and pentacoordinate amidinate aluminum complexes,^{3a,4} heterometallic alkyl aluminum complexes



Scheme 3 Synthesis of L1H and L2H ferrocenyl amidine ligands.



Scheme 4 Synthesis of complexes 1–4.

(L₁)AlMe₂ (1), (L₂)AlMe₂ (2), (L₁)₂AlMe (3) and (L₂)₂AlMe (4) were prepared *via* protonolysis reaction between the ferrocenyl amidine ligand L₁H or L₂H and 1.0 or 0.5 equivalents of AlMe₃ to generate the corresponding tetracoordinate (1 and 2) or pentacoordinate (3 and 4) aluminum complexes, respectively (Scheme 4). The reactions were carried out in dry CH₂Cl₂ for 2 h at room temperature. Complexes 1–4 were obtained in high yields (\geq 85%) and were isolated as orange solids (1 and 2) and light orange solids (3 and 4).

The structural characterization of these heterobimetallic complexes was performed by multinuclear (¹H and ¹³C) NMR spectroscopy, X-ray diffraction and mass spectroscopy. Focusing on the ¹H NMR spectra of these complexes, the most relevant facts that confirmed the formation of these ferrocenyl aluminum complexes were the disappearance of the signal corresponding to the N-H proton of the ferrocenyl amidine ligands together with the appearance of their respective singlets belonging to the AlMe_n (n = 1 or 2) moieties (see the Experimental section and ESI[†]). The tetracoordinate species showed a singlet corresponding to the AlMe₂ moiety at -0.11 ppm (1) and -0.16 ppm (2), respectively, both integrating for six protons while the pentacoordinate species exhibited a singlet belonging to the AlMe moiety at 0.23 ppm (3) and 0.07 ppm (4), each one integrating for three protons. For the unequivocal assignment of most of the resonances, ¹³C¹H NMR and two-dimensional NMR experiments were accomplished for 1-4. The ¹³C NMR spectra showed as a main feature of the alkyl aluminum complexes the appearance of a signal belonging to the AlMe_n (n = 1 or 2) moieties located around -8.49 and -9.42 ppm for all complexes. Furthermore, mass spectrometry analysis of 1-4 supported the proposed heterometallic structures of these compounds (see the Experimental section).

The spectroscopic data together with X-ray single-crystal studies supported the tetrahedral coordination geometries of complexes **1** and **2**, in which the ferrocenyl amidine ligands were bonded to the aluminum atom in a κ^2 -NN coordination mode, similarly to the previously reported alkyl amidinate aluminum complexes^{3,4b,22} while the heterometallic complexes **3** and **4** showed a pentacoordination environment around the aluminum atom.

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The molecular geometries in the solid state of the heterometallic complexes 1, 3 and 4 were unequivocally determined through X-ray diffraction analysis. Thus, single crystals of complex 1 were obtained from cold hexane at -30 °C whereas single crystals of 3 and 4 were grown by slow evaporation in CH₂Cl₂ at room temperature. The X-ray crystal structures of complexes 1, 3 and 4 are shown in Fig. 2, 3 and 4, respectively. The crystallographic data and selected bond angles and distances are given in Tables S1–S4 in the ESI.†



Fig. 2 Crystal structure of complex 1. Thermals ellipsoids are shown with 15% probability. Hydrogen atoms are omitted for clarity.



Fig. 3 Crystal structure of complex **3**. Thermals ellipsoids are shown with 15% probability. Hydrogen atoms are omitted for clarity. Only one molecule (molecule "A") of two found in the asymmetric unit is shown.



Fig. 4 Crystal structure of complex 4. Thermals ellipsoids are shown with 30% probability. Hydrogen atoms are omitted for clarity.

As can be seen in Fig. 2, complex 1 displays a four-membered metallacycle where the aluminum center has a highly distorted tetrahedral geometry, with an amidinate bite angle N2-Al1-N1 of 68.3(1)° while the C4-Al1-C3 angle is 119.6(2)°, which are rather far from the ideal tetrahedral angle of 109.5°. It is further observed that the plane formed by the metallacycle is located perpendicularly (89.3°) to the aromatic ring substituted with the isopropyl fragment while the ferrocenyl-Cp plane is tilted with respect to the amidine NCN plane by 19.4°. The indistinguishable bond distances N2-C1 (1.335(3) Å) and N1-C1 (1.332(3) Å) in the NCN unit and the almost equal bond distances N2-Al1 (1.936(2) Å) and N1-Al1 (1.941(2) Å) proved the formation of a delocalized system and also supported the κ^2 -NN coordination mode of the ferrocenyl amidinate ligand to the aluminum centre. The distance measured for C4-Al1 (1.950(3) Å) coincides with the values previously found for this type of complex.3b,22

Heterotrimetallic complex 3 crystallizes in the monoclinic space group $P2_1/n$ with two independent molecules in the asymmetric unit, while the complex 4 crystallizes with one molecule in the monoclinic space group C2/c. For compound 3 only one molecule (molecule "A") is discussed, as both molecules present similar geometrical parameters. Both complexes display the expected pentacoordination environment in the aluminum metal center. However, the angular structural parameter (τ value)²³ was calculated for 3 and 4 in order to determine how closely these complexes could adopt either a perfectly square pyramidal ($\tau = 0$) or a perfectly trigonal bipyramidal geometry ($\tau = 1$).

From the τ values of complexes 3 and 4 (0.42 and 0.48) we can appreciate that both complexes show highly distorted square pyramidal geometries. In addition, equally bidentate ferrocenyl amidinate ligands (L_1 and L_2) occupy the equatorial positions while the apical position is occupied by the methyl group. The acute amidinate bite angles 66.4° (average) in 3 and 66.7° (average) in 4 generate a small increase of the respective N1–Al1–N4 [98.4(2)° for 3 and 99.6(1)° for 4] and N2–Al1–N3 [100.3(2)° for 3 and 99.1(1)° for 4] angles and a significant increase of the N2–Al1–C5 [117.9(2)° for 3 and 119.8(1)° for 4] angles from the ideal square pyramidal angle of 90°. In addition, a significant decrease of the N2–Al1–N4 [125.2(2)° for 3 and 123.1(1)° for 4] and N1–Al1–N3 [150.4(2)° for 3 and 151.6(1)° for 4] angles from the ideal angle of 180° is observed.

In complexes 3 (Fig. 3) and 4 (Fig. 4), the bond distances corresponding to the nitrogen atoms substituted with ferrocenyl fragments N1–Al1 and N3–Al1 are longer (*ca.* 0.1 Å) than the other two N2–Al1 and N4–Al1 bond lengths, probably due to the stronger electron donation of these ferrocenyl fragments in comparison with the aryl substituted rings. The Al1–C5 distances 1.982(5) Å in 3 and 1.964(3) Å in 4 are close to those of five-coordinate alkyl aluminum compounds reported in the literature.^{4b,24} Charge delocalization in the amidinate NCN backbone is demonstrated in 3 and 4 by using the C–N bond lengths, which show the values between 1.329(6) and 1.343(4) Å.

In both structures, as a result of minimizing the steric interactions between the two bulky substituted groups in the amidi-

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nate moiety, the plane formed by the cyclopentadienyl ring directly bonded to the nitrogen atoms (N1 and N3) is perpendicular to the respective bulky aryl groups, therefore in complex 3, one ferrocenyl moiety is oriented *syn* with respect to the other while in complex 4 they are located in the *anti* position.

Electrochemical behavior of ferrocenyl amidine ligands and heterometallic aluminum ferrocenyl amidinate complexes

The anodic electrochemistry of the ferrocenyl amidine ligands L_1H and L_2H and of the corresponding aluminum complexes 1–4 was examined by cyclic voltammetry (CV), using dichloromethane as the solvent, tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆) as the supporting electrolyte and ferrocene as the internal standard. The recorded voltammetric potential data are given in Table 1.

Fig. 5 shows the comparison of the CV responses, in the potential region between -1.1 and +0.5 V, of ferrocenyl amidine L_1H with respect to the corresponding heterobimetallic complex 1 (Fe/Al) and trimetallic (2Fe/Al) complex 3. The anodic electrochemical behavior of ferrocenyl amidine compounds L_1H and L_2H and 1-4 is dominated by the presence of the wave corresponding to the ferrocene/ferrocenium redox couple.

From the results shown in Fig. 5 and in Table 1, it becomes patently obvious that amidines L_1H and L_2H exhibit a distinctive voltammetric behavior. Clearly, the direct attachment of the amidine group to the cyclopentadienyl ring increases the electronic density of the ferrocene moiety, causing a striking effect on the observed half-wave redox potential ($E_{1/2}$). The higher electron rich nature of these ferrocenyl amidines results in low half-wave potentials $E_{1/2} = -0.253$ and -0.271 V *versus* ferrocene/ferrocenium, indicating that the oxidation of the ferrocene moiety becomes thermodynamically facilitated. However, the oxidation of the ferrocenyl moiety in these amidines L_1H and L_2H is slightly more difficult than that in the 1-aminoferrocene precursor FcNH₂ ($E_{1/2} = -0.335$ V *versus* ferrocene/ferrocenium in CH₂Cl₂/*n*-Bu₄NPF₆).

This behavior contrasts with the extremely high electron rich nature of ferrocenyl guanidine²⁵ which exhibits a very low half-wave potential $E_{1/2} = -0.404$ V *versus* ferrocene/ferrocenium, indicating that the oxidation of the ferrocene moiety is thermodynamically more facilitated. In this particular case,



Fig. 5 Comparison of the CV responses of the ferrocenyl amidine ligand L_1H , heterometallic Fe/Al complex 1 and 2Fe/Al complex 3 in a 0.2 M solution of n-Bu₄NPF₆ in CH₂Cl₂. Scan rate: 0.1 V s⁻¹.

the oxidation of the ferrocenyl moiety in guanidine 25 is easier than that in the 1-aminoferrocene precursor.

Fig. 5 also shows that, compared to the free neutral ferrocenyl amidines L_1H and L_2H , in heterobimetallic Fe/Al complexes 1 and 2 the oxidation of the ferrocenyl moiety shifts to more positive values to a remarkable extent by 0.103 and 0.175 V for complexes 1 and 2 respectively, while the quasi reversibility of the redox processes is maintained. Therefore, the coordination of the nitrogen-donor ligands L_1H and L_2H to the aluminum atom significantly reduces the electron density of the ferrocenyl moiety and, consequently, it is more difficult to oxidize.

Complexes 3 and 4 showed two quasi-reversible oxidation waves, at $E_{1/2} = -0.221$ and -0.368 V for 3 and $E_{1/2} = -0.213$ and -0.339 V for 4, which is attributed to the two Fe²⁺/Fe³⁺ redox systems. This fact reveals that the two ferrocenyl units in compounds 3 and 4 seem to behave as connected redox moieties.²⁶ Consequently, in these trimetallic molecules, the two ferrocenyl amidine moieties are spatially well separated but the aluminum center permits electronic communication between the two ferrocene units.²⁶ The first oxidation waves in 3 and 4 are 0.218 and 0.243 V lower than those in complexes 1 and 2, respectively, indicating that the presence of a second amidine fragment coordinated to the aluminum center produces an increment in the electronic density of the ferrocene unit. On the other hand, the second oxidation waves in 3 and

Table 1 Electrochemical data obtained for ferrocenyl amidines $(L_1H - L_2H)$ and their aluminum complexes (1-4)

Comp.	$E_{1/2}^{a}$ (V)	$E_{\mathrm{pa}}\left(\mathrm{V}\right)$	$E_{\rm pc}$ (V)	$\Delta E_{\mathrm{p}} \left(\mathrm{mV}\right)$	$i_{ m pc}/i_{ m pa}$	
L ₁ H	-0.253	-0.182	-0.324	142	0.94	
L_2H	-0.271	-0.202	-0.340	138	0.95	
1	-0.150	-0.074	-0.226	152	0.85	
2	-0.096	-0.010	-0.182	172	0.77	
3	-0.221, -0.368	-0.162, -0.302	-0.280, -0.434	118, 132	0.95, 0.76	
4	-0.213, -0.339	-0.156, -0.272	-0.270, -0.406	114, 134	0.82, 0.65	
FcNH ₂	-0.335	-0.236	-0.434	198	0.75	

^{*a*} Half-wave potentials measured in CH₂Cl₂. Scan rate: 0.1 V s⁻¹ in CH₂Cl₂/0.2 M *n*-Bu₄NPF₆. Ferrocene was used as an internal reference ($E_{1/2}$ (FeCp₂^{0/+}) = 0 V).

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4 (3⁺ to 3²⁺ or 4⁺ to 4²⁺) at -0.221 and -0.213 V seem to indicate that the electronic density contributed by the second amidine fragment of the ferrocene unit is partially removed in the first oxidation wave.

Catalytic studies for the synthesis of cyclic carbonates

Having prepared the aluminum complexes 1–4, we decided to focus our attention on exploring their use as catalysts for the formation of cyclic carbonates. Firstly, styrene oxide **5a** was selected as a model substrate to study the catalytic activity of these complexes. The reactions were performed at 80 °C and 1 bar of CO₂ pressure (balloon) for 6–24 h under solvent-free conditions using 1.0–1.7 mol% of catalysts 1–4 and 1.0–1.7 mol% of tetrabutylammonium iodide (Bu₄NI) as a co-catalyst, based on our previous work^{4,27} in which the ammonium salt was found to be the best nucleophile. The catalytic results are shown in Table 2.

It is remarkable that tetracoordinate aluminum complexes 1 and 2 (Table 2, entries 1 and 2) displayed higher catalytic activity than their analogous pentacoordinate complexes 3 and 4 (Table 2, entries 3 and 4) probably due to the greater steric hindrance of the latter ones, which makes the interaction between the epoxide and the aluminum center more difficult. Moreover, the lower Lewis acidity of the Al(m) center of pentacoordinate complexes 3 and 4 *versus* tetracoordinate compounds 1 and 2 could be another possible cause of the obtained results.

As can be seen in Table 2, complex 1, which achieved the highest value of TOF ($3.58 h^{-1}$), was selected as the most active catalyst for styrene carbonate preparation. In order to obtain quantitative conversions, we opted to increase the catalyst and co-catalyst loadings to 1.7 mol% and 100% conversion was obtained after 24 h (Table 2, entry 5). After that, to study the impact of the reaction time under these conditions, we monitored the formation of **6a** after 6, 10 and 16 h (Table 2, entries 6–8). It is important to note that although the highest value of

Table 2 Synthesis of styrene carbonate 6a using heterometallic aluminum complexes $1-4^a$

Entry	Cat. (mol%)	Co-catalyst (mol%)	Time (h)	Conversion ^b (%)	TOF^{\prime} (h^{-1})
1	1 (1.0)	1.0	24	86	3.58
2	2(1.0)	1.0	24	76	3.17
3	3 (1.0)	1.0	24	67	2.79
4	4(1.0)	1.0	24	70	2.91
5	1 (1.7)	1.7	24	100	2.45
6	1 (1.7)	1.7	16	89	3.27
7	1 (1.7)	1.7	10	68	4.00
8	1 (1.7)	1.7	6	45	4.41
9^d	1 (1.7)	—	24	0	0
10^e	_	1.7	24	9	0.22

^{*a*} Reactions were carried out at 80 °C and 1 bar of CO₂ pressure (balloon) for 6–24 h using 1.0–1.7 mol% of Bu₄NI under solvent free conditions unless specified otherwise. ^{*b*} Conversion was achieved by ¹H NMR spectroscopy of the reaction mixture relative to starting epoxide. ^{*c*} TOF = moles of product/(moles of catalyst × time). ^{*d*} No Bu₄NI was added. ^{*e*} No complex 1 was added.

TOF (4.41 h⁻¹) was achieved after 6 h (Table 2, entry 8), we decided to choose 24 h as the optimal reaction time (Table 2, entry 5) in order to obtain quantitative conversions in cyclic carbonate formation. Control experiments showed that complex 1 and Bu_4NI are indispensable components to achieve excellent conversions since low conversions were obtained when both components of the catalyst system (1/ Bu_4NI) were employed in the absence of the other (Table 2, entries 9 and 10).

Once we selected the optimal reaction conditions for the preparation of styrene carbonate 6a as 1.7 mol% of complex 1 and Bu₄NI at 80 °C and 1 bar of CO₂ pressure (balloon) for 24 h, we subsequently studied the reaction of a range of monosubstituted epoxides with CO₂ for the synthesis of the following cyclic carbonates 6a-j (Fig. 6) in order to study the reproducibility of the aforementioned catalytic system. Related to this we decided to select various substrates with different functional groups such as alkyl (5b-d), alcohol (5e), ether (5f) and halide (5g and 5h) with the principal objective to investigate how the steric and electronic properties of these epoxides could affect the effectiveness of the used catalytic system. Furthermore, we decided to incorporate highly fluorinated epoxides (5i and 5j) owing to the fact that their corresponding cyclic carbonates (6i and 6j) can be applied as electrolytes in lithium-ion batteries.28

Generally, good to excellent isolated yields (70–98%) with selectivities towards cyclic carbonates up to >99% were obtained under the aforementioned reaction conditions, nevertheless volatility limitations were observed for the synthesis of cyclic carbonates **6b** and **6c**. consequently the preparation of these compounds was accomplished at 25 °C for 48 h. It is relevant to point out the importance of steric hin-



$$\begin{split} \textbf{5,6:} \ \mathsf{R} &= \mathsf{Ph} \ (\textbf{a})^{a}; \ \mathsf{Me} \ (\textbf{b})^{b}; \ \mathsf{Et} \ (\textbf{c})^{b}, \ ^{\mathsf{n}}\mathsf{Bu} \ (\textbf{d})^{a}; \ \mathsf{CH}_2\mathsf{OH} \ (\textbf{e})^{a}; \ \mathsf{CH}_2\mathsf{OPh} \ (\textbf{f})^{a}; \ \mathsf{CH}_2\mathsf{CI} \ (\textbf{g})^{a}; \\ & 4\text{-}\mathsf{Br}\text{-}\mathsf{C}_6\mathsf{H}_4 \ (\textbf{h})^{a}; \ \mathsf{CHF}_2\mathsf{CF}_2\mathsf{CH}_2\mathsf{OCH}_2 \ (i)^{a}; \ \mathsf{CHF}_2(\mathsf{CF}_2)_3\mathsf{CH}_2\mathsf{OCH}_2 \ (j)^{a} \end{split}$$



Fig. 6 Cyclic carbonates **6a–j** catalyzed by **1**. ^aReaction carried out at 80 °C for 24 h. ^bReaction carried out at 25 °C for 48 h. ^cIsolated yield from purified cyclic carbonate.

drance for the preparation of alkyl cyclic carbonates (6b-d) in which the isolated yield of 6d (70%) is significantly lower than those of its analogues 6b and 6c, even though 6d was prepared at higher temperature. It is also notable that due to the influence of the electronic effect in 6h, it was obtained with a smaller yield than styrene carbonate, 6a. Finally, fluorinated cyclic carbonates 6i and 6j were afforded almost in quantitative vields. Although the catalyst system (1/Bu₄NI) was perfectly soluble under the reaction conditions used, probably another important factor to explain these catalytic results could be different solubilities of the catalyst system in the epoxides employed as we have carried out these experiments under solvent-free conditions. In conclusion, the combination of complex 1 and Bu₄NI was able to produce a large variety of cyclic carbonates from aryl and alkyl epoxides and others with functional groups such as ether, halide, and alcohol. These results confirmed that this catalyst system exhibits catalytic potential for the preparation of cyclic carbonates.

Conclusions

New non-symmetric ferrocenyl amidine ligands $(L_1H \text{ and } L_2H)$ were prepared via a reaction between aminoferrocene and the respective acetimidovl chloride. A modified synthetic method for ferrocenylamine allowed us to obtain this precursor in quantitative yield. By using these ferrocenyl ligands we were able to prepare their alkyl aluminum complexes (1-4) via protonolysis reaction with AlMe₃. NMR spectroscopy and singlecrystal X-ray diffraction studies uphold the expected κ^2 -NN coordination mode for heterobimetallic complexes 1 and 2 while heterotrimetallic complexes 3 and 4 show a pentacoordinated aluminum center with a highly distorted square pyramidal geometry. Electrochemical studies revealed quasi-reversible oxidation and reduction waves for the ferrocene/ferrocenium couple for ligands L1H and L2H and for complexes 1 and 2 whilst heterotrimetallic complexes 3 and 4 showed two quasireversible oxidation waves indicating a significant electronic communication between the two ferrocenyl redox centers.

These complexes are shown to be efficient catalysts for the transformation of CO_2 into cyclic carbonates from terminal epoxides in the presence of Bu_4NI as a co-catalyst, where the tetracoordinate aluminum complexes 1 and 2 displayed higher catalytic activity than their analogous pentacoordinate complexes 3 and 4, probably due to the lower Lewis acidity of the Al(m) centre together with the higher steric hindrance of the latter ones, which decreases and hampers the interaction between the aluminum metal center and the terminal epoxide. Among them, the heterobimetallic complex 1 showed the highest catalytic activity at 25–80 °C and 1 bar of CO_2 pressure for 24–48 h in the absence of the solvent. This catalyst system was able to synthesize several cyclic carbonates from different functionalized terminal epoxides such as alkyl, aryl, ether, alcohol, and halide in good to excellent yields.

It is important to highlight that these complexes are some of the first ferrocenyl amidinate aluminum complexes that have been used in the synthesis of cyclic carbonates from terminal epoxides and CO_2 . Further research will be directed toward the development of these complexes in their oxidized form with the aim to design a redox switchable strategy that can be applied in the CO_2 conversion with epoxides for generating cyclic carbonates or polycarbonates.

Experimental

General procedures and equipment

All manipulations were performed under an inert atmosphere using a standard glovebox and Schlenk-line techniques. Reagent-grade solvents were obtained from E. Merck. Toluene, dichloromethane, diethyl ether, tetrahydrofuran (THF) and hexane were dried using an Innovative Technology Pure Solv Model PS-MD-5. Ferrocene, tri-isopropyl borate ([(CH₃)₂CHO]₃B), t-BuLi (1.7 M in pentane), NaOH, Na₂SO₄, KOH, CH₃COOH, EtOAc, hydrazine hydrate (N_2H_4 ·H₂O), EtOH, triethylamine, MeOH, trimethylaluminum (AlMe₃, TMA), epoxides, and Bu₄NI were purchased from Aldrich and used as received. Copper(II) phthalimide,¹⁹ imidoyl chloride (E)-N-(2,6diisopropylphenyl)acetimidoyl chloride,¹⁶ and (E)-N-(2,6-dimethylphenyl)acetimidoyl chloride²¹ were prepared according to published methods and ferroceneboronic acid and aminoferrocene were prepared by a modified method.^{19,20} The following instruments were used for the physical characterization of the compounds. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts and 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 ¹³C NMR analysis ranged from 0.5 to 2 K depending on the sample concentration. For ESI mass spectral characterization a Bruker Daltonics Micro Tof spectrometer was used, employing methanol as the ionizing phase, while heated electrospray ionization (HESI) mass spectra were recorded by using a high resolution mass spectrometer Exactive[™] Plus Orbitrap (ThermoFischer Scientific). Samples were prepared in dichloromethane solution. Cyclic voltammetry measurements were carried out with a "portable Bipotentiostat/Galvanostat µSTAT400" from Dropsens under drv nitrogen using dichloromethane as the solvent. Tetrabutylammonium hexafluorophosphate (0.2 mol dm⁻³) was prepared by a described procedure²⁹ and was used as the electrolyte support. A two-platinum-silver electrode cell with ferrocene as an internal reference was used in a glove box. For X-ray crystal structure analysis, datasets were collected by Dr Constantin G. Daniliuc with a Bruker APEX II CCD diffractometer and a Nonius Kappa CCD diffractometer, respectively. CCDC 1923169 (1), 1923170 (3) and 1923171 (4) contain the supplementary crystallographic data of this paper.†

Synthesis of aminoferrocene. Aminoferrocene was synthesized by modifying the first step and optimizing the methodology given by Montserrat.¹⁹ This synthesis begins with ferroceneboronic acid, which was obtained by the reaction

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between mono-lithioferrocene and tri-isopropyl borate, in which ferrocene (1.0 g, 5.4 mmol) was dissolved in 7 mL of THF under an inert atmosphere and cooled at 0 °C for 15 minutes. t-BuLi was slowly added (4.76 mL, 8.1 mmol, 1.7 M t-BuLi in pentane) and the reaction mixture was stirred over 15 minutes and allowed to warm to room temperature for 20 minutes. The system was cooled to -78 °C followed by the dropwise addition of 2.48 mL of tri-isopropyl borate (10.1 mol, $\rho = 0.815 \text{ g mL}^{-1}$), which was previously dissolved in 2.5 mL of THF. The reaction mixture was stirred at -40 °C for16 h. The reaction product was taken up in 30 mL of NaOH 2.0 M and washed twice with 30 mL of NaOH 2.0 M. The combined fractions were dried (Na₂SO₄) and filtered, and the solvent was removed in vacuo giving the intermediate product, ferroceneboronic acid, as an orange solid (0.75 g, 60%). ¹H NMR (400 MHz, CD₃OD, 298 K): δ /ppm = 4.44-4.32 (m, 4H, C₅H₄), 4.13 (m, 5H, C₅H₅). Ferroceneboronic acid (0.25 g, 1.1 mmol) and copper(II) phthalimide¹⁹ (0.75 g, 3.6 mmol) were added under a nitrogen atmosphere to a 20 mL mixture of MeOH/ $H_2O(8:2)$ and stirred for 24 h at room temperature. The mixture was diluted with 50 mL of Et₂O and filtered. The final solution was treated with 50 mL of (1) KOH 10%, (2) H_2O_2 , (3) CH₃COOH 10%, and (4) H₂O. The organic fractions were dried (Na₂SO₄) and filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography using silica gel and hexane/EtOAc (100:0 to 98:2) and further obtained as an orange solid (0.255 g, 70%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ /ppm = 7.86 (m, 2H, C₆H₄), 7.75 (m, 2H, C₆H₄), 5.00 (m, 2H, C₅H₄), 4.21 (m, 5H, C₅H₅), 4.19 (m, 2H, C₅H₄). Phthalimidoferrocene (0.50 g, 1.5 mmol) and hydrazine hydrate (0.54 mL, 11.0 mmol, $\rho = 1.03 \text{ g mL}^{-1}$) were heated under reflux in EtOH (20 mL) under N₂ for 2 h. The mixture was cooled, added 20 mL of H2O and extracted with Et_2O (3 × 20 mL). The organic fractions were dried (Na₂SO₄) and filtered, and the solvent was removed in vacuo. The final product was obtained as an yellow solid (0.30 g, 99%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ/ppm = 4.10 (m, 5H, C₅H₅), 4.00 (m, 2H, C₅H₄), 3.84 (m, 2H, C₅H₄), 2.58 (br. s, 2H, NH).

Synthesis of (E)-N-(2,6-diisopropylphenyl)-N'-(ferrocenyl) acetimidamide (L1H). Aminoferrocene (325 mg, 1.62 mmol) was dissolved in 15 mL of THF under an inert atmosphere and cooled at 0 °C for 15 minutes. Triethylamine (0.23 mL, 1.62 mmol) was added followed by the dropwise addition of (E)-N-(2,6-diisopropylphenyl)acetimidoylchloride¹⁶ (385 mg, 1.62 mmol) over 2 minutes, and the reaction mixture was stirred and was allowed to warm to room temperature over 4 h. The reaction mixture was taken up in 30 mL of diethyl ether and washed twice with 15 mL of water. The combined organic fractions were dried (Na₂SO₄) and filtered, and the solvent was removed *in vacuo* giving L_1H as a viscous brown orange liquid. The product was recrystallized with methanol at -20 °C to give an orange crystalline material (541.16 mg, 83%). ¹H NMR (400 MHz, DMSO-d₆, 298 K): δ /ppm = 8.20 (br. s, 1H, NH), 7.04 $(d, J = 7.6 Hz, 2H, H_9), 6.91 (t, J = 6.9 Hz, 1H, H_{10}), 4.76 (br. s,$ 2H, H₂), 4.10 (br. s, 5H, H₄), 3.91 (br. s, 2H, H₃), 3.00 (m, 2H, H_{11}), 1.58 (s, 3H, H_6), 1.13 (dd, J = 11.1, 6.9 Hz, 12H, $H_{12,13}$).

¹³C{¹H} **NMR** (100 MHz, DMSO-d₆, 298 K): δ /ppm = 151.91 (C₅), 146.49 (C₇), 137.66 (C₈), 122.45 (C₉), 121.65 (C₁₀), 99.32 (C₁), 68.45 (C₄), 62.98 (C₃), 59.38 (C₂), 27.38 (C₁₁) 23.61 (C₁₃), 22.91 (C₁₂), 17.69 (C₆). **MS** (**ESI**) C₂₄H₃₀N₂Fe [M + H]⁺: *m/z* calcd: 403.3; found: 403.2.

Synthesis of (E)-N-(2,6-dimethylphenyl)-N'-(ferrocenyl)acetimidamide (L₂H). Aminoferrocene (1.0 g, 5.0 mmol) was dissolved in 30 mL of THF under an inert atmosphere and cooled at 0 °C during 15 minutes. Triethylamine (0.7 mL, 5.0 mmol) was added followed by the dropwise addition of (E)-N-(2,6-dimethylphenyl)acetimidoylchloride²¹ (0.9 g, 5.0 mmol) over 2 minutes, and the reaction mixture was stirred and was allowed to warm to room temperature over 4 hours. The reaction mixture was taken up in 40 mL of diethyl ether and washed twice with 20 mL of water. The combined organic fractions were dried (Na₂SO₄) and filtered, and the solvent was removed in vacuo giving L_2H as a viscous brown orange liquid. The product was recrystallized with methanol at -20 °C to give a brown crystalline material (1.22 g, 71%). ¹H NMR (400 MHz, DMSO-d₆, 298 K): δ/ppm = 8.15 (br. s, 1H, NH), 6.98 (d, J = 7.5 Hz, 2H, H₉), 6.75 (t, J = 7.4 Hz, 1H, H₁₀), 4.75 (br. s, 2H, H₂), 4.12 (br. s, 5H, H₄), 3.91 (br. s, 2H, H₃), 2.04 (s, 6H, H₁₁), 1.56 (s, 3H, H₆). ¹³C{¹H} NMR (100 MHz, DMSO-d₆, 298 K): δ /ppm = 151.96 (C₅), 149.35 (C₈), 127.49 (C₉), 127.38 (C₇), 120.84 (C₁₀), 99.14 (C1), 68.52 (C4), 63.01 (C3), 59.74 (C2), 18.04 (C11), 17.45 (C₆). **MS (ESI)** C₂₄H₃₀N₂Fe $[M + H]^+$: m/z calcd: 346.2; found: 346.5.

Synthesis of $[(L_1)AlMe_2]$ (1). A solution of trimethylaluminum (TMA) (26.87 mg, 0.37 mmol) in dichloromethane was quickly added to a solution of L1H (150 mg, 0.37 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. The orange solid was recrystallized from cold hexane giving compound 1 as an orange crystalline material in 96% yield (163 mg). Single orange crystals for X-ray crystallography were grown from cold hexane at -30 °C. ¹H NMR (400 MHz, C₆D₆, 298 K): δ /ppm = 7.14 (m, 1H, H_{10}), 7.08 (d, J = 7.6 Hz, 2H, H_9), 4.13 (br. s, 5H, H₄), 4.01 (br. s, 2H, H₂), 3.83 (br. s, 2H, H₃), 3.24 (m, 2H, H₁₁), 1.58 (s, 3H, H₆), 1.18 (d, J = 6.7 Hz, 6H, H₁₂), 1.10 (d, J = 6.9Hz, 6H, H_{13}), -0.11 (s, 6H, H_{14}). ¹³C{¹H} NMR (100 MHz, C_6D_6 , 298 K): δ /ppm = 174.89 (C_5), 144.85 (C_8), 138.09 (C_7), 126.59 (C_{10}), 123.98 (C_9), 100.32 (C_1), 69.40 (C_4), 65.19 (C_3), 63.09 (C₂) 28.44 (C₁₁), 24.71 (C₁₂), 23.83 (C₁₃), 14.53 (C₆), -9.42 (C₁₄). MS (HESI) C₂₆H₃₅AlFeN₂ [M]: *m*/*z* calcd: 458.1960; found: 458.1870.

Synthesis of $[(L_2)AIMe_2]$ (2). A solution of trimethylaluminum (TMA) (62.7 mg, 0.87 mmol) in dichloromethane was quickly added to a solution of L_2H (300 mg, 0.87 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. The orange solid was recrystallized from cold hexane giving compound 2 as an orange crystalline material in 85% yield (297.5 mg). ¹H NMR (400 MHz, C₆D₆, 298 K): δ /ppm = 6.97–6.94 (m, 3H, H_{10,9}), 4.13 (br. s, 5H, H₄), 3.99 (br. s, 2H, H₂), 3.83 (br. s, 2H, H₃), 2.08 (s, 6H, H₁₁), 1.43 (s, 3H, H₆), -0.16 (s, 6H, H₁₂). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ /ppm = 174.01 (C₅), 141.42 (C₈), 134.34 (C₇), 128.58 (C₉), 125.56 (C₁₀), 100.29 (C₁), 69.39 (C₄), 65.16 (C₃), 63.15 (C₂), 18.86 (C₁₁), 13.69 (C₆), -8.91 (C₁₂). MS (HESI) C₂₂H₂₇AlFeN₂ [M + H]⁺: *m*/*z* calcd: 403.1412; found: 403.1443.

Synthesis of $[(L_1)_2AIMe]$ (3). A solution of trimethylaluminum $(Al(CH_3)_3)$ (9 mg, 0.125 mmol) in dichloromethane was quickly added to a solution of two equivalents of L1H (100 mg, 0.25 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 3 was obtained as a reddish orange solid in 91% yield (96 mg). Single red crystals for X-ray crystallography were grown by the evaporation of dichloromethane at room temperature. ¹H NMR (400 MHz, C_6D_6 , 298 K): δ /ppm = 7.19–7.11 (m, 4H, $H_{9b,10}$), 7.00 (d, J = 7.2 Hz, 2H, H_{9a}), 4.11 (br. s, 10H, H₄), 3.73 (br. s, 2H, H_{2b}), 3.66 (br. s, 4H, H_{3a,b}), 3.63-3.58 (m, 4H, H_{2a,11b}), 3.33-3.23 (m, 2H, H_{11a}), 1.86 (s, 6H, H_6), 1.53 (d, J = 6.7 Hz, 6H, H_{12b}), 1.29 (d, J = 6.7 Hz, 6H, H_{13b}), 1.13 (d, J = 6.8 Hz, 6H, H_{12a}), 1.01 (d, J = 6.7 Hz, 6H, H_{13a}), 0.23 (s, 3H, H₁₄). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ /ppm = 172.61 (C₅), 145.49 (C_{8a}), 144.81 (C_{8b}), 139.19 (C₇), 126.31 (C₁₀), 123.82 (C_{9b}), 123.51 (C_{9a}), 101.42 (C_1), 69.13 (C_4), 64.42 (C_{3b}), 64.16 (C_{2a}), 63.15 (C_{3a}), 59.42 (C_{2b}), 28.70 (C_{11a}), 28.50 (C_{11b}), 25.18 (C_{12a}), 24.82 (C_{12b}), 24.34 (C_{13b}), 23.17 (C_{13a}), 15.63 (C₆), -9.42 (C₁₄). MS (HESI) C₄₉H₆₁AlFe₂N₄ [M]: *m/z* calcd: 844.3405; found: 844.3335.

Synthesis of $[(L_2)_2AIMe]$ (4). A solution of trimethylaluminum $(Al(CH_3)_3)$ (21 mg, 0.29 mmol) in dichloromethane was quickly added to a solution of two equivalents of L₂H (200 mg, 0.58 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 reddish orange solid in 96% yield (204 mg). Single red crystals for X-ray crystallography were grown by the evaporation of dichloromethane at room temperature. ¹H NMR (400 MHz, C_6D_6 , 298 K): δ /ppm = 7.09 (t, J = 4.6 Hz, 2H, H_{9a}), 7.01 (d, J = 5.2 Hz, 4H, H_{10.9b}), 4.03 (br. s, 10H, H₄), 3.70 (td, J = 2.5, 1.4 Hz, 2H, H_{3a}), 3.64 (td, J =2.5, 1.3 Hz, 2H, H_{2a}), 3.60 (dt, J = 2.6, 1.4 Hz, 2H, H_{2b}), 3.55 $(dt, J = 2.6, 1.3 Hz, 2H, H_{3b}), 2.35 (s, 6H, H_{11a}), 2.21 (s, 6H, H_{11a}))$ $H_{11b}), \ 1.73$ (s, 6H, $H_6), \ 0.07$ (s, 3H, $H_{12}).$ $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6 , 298 K): δ /ppm = 172.45 (C_5), 142.75 (C_7), 135.21 (C_{8b}), 134.81 (C_{8a}), 128.55 (C_{9a}), 128.35 (C_{9b}), 125.37 (C10), 101.37 (C1), 69.20 (C4), 64.55 (C3a), 64.51 (C2a), 62.40 (C_{2b}), 61.55 (C_{3b}), 19.48 (C_{11b}), 19.21 (C_{11a}), 14.09 (C₆), -8.49 (C₁₂). MS (HESI) $C_{41}H_{45}AlFe_2N_4$ [M]: m/z calcd: 732.2153; found: 732.2094.

General procedure for catalyst screening at 1 bar pressure. Styrene oxide 6a (1.7 mmol), heterometallic ferrocenyl amidinate aluminum catalysts 1–4 (17.0–28.9 μ mol) and Bu₄NI (17.0–28.9 μ mol) were added into a sample vial with a magnetic stirrer bar. The sample vial was fitted with a rubber stopper pierced by a balloon filled with CO₂. The reaction mixture was stirred at 80 °C and 1 bar of CO₂ pressure for

6-24 h, and then the conversion of styrene oxide **5a** into styrene carbonate **6a** was determined by the analysis of a sample by ¹H NMR spectroscopy relative to the starting styrene oxide compound.

Conflicts of interest

There are no conflicts to declare.

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