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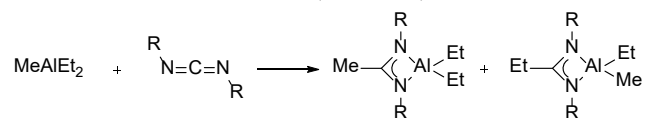
Aluminium Amidinate and Carboxylate Formation *via* Insertion of E=C=E Bonds

Stephanie J. Urwin,^{*1,2} Gary S. Nichol¹ and Michael J. Cowley^{*1}

¹EaSTCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, United Kingdom; Email: michael.cowley@ed.ac.uk. ² Current Address: Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford, OX1 3TA, United Kingdom; Email: stephanie.urwin@chem.ox.ac.uk

ABSTRACT: Selective insertion of dicyclohexylcarbodiimide or diisopropylcarbodiimide into the Al-Cp* bond of a 1,4-dialuminacyclohexadiene derivative results in unusual amidinate ligands with a 1,2,3,4,5-pentamethyl cyclopentadiene backbone whilst retaining the central Al₂C₄ functionality. An analogous reaction with carbon dioxide gives a molecular metal carboxylate, the formation of which is supported by ¹H NMR and IR spectroscopy and high resolution mass spectrometry.

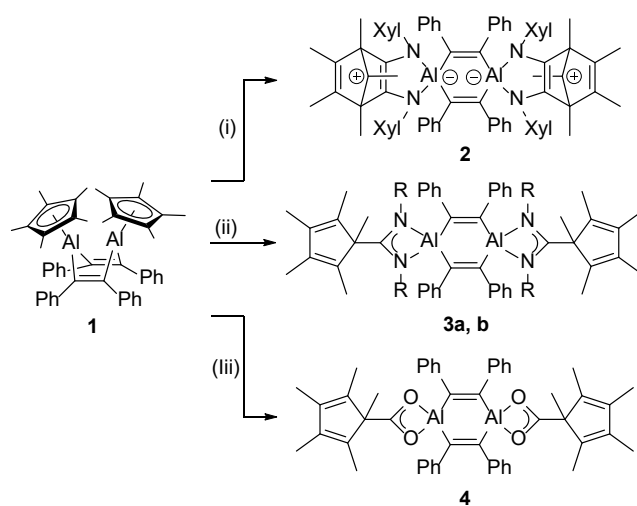
Organoaluminium centres supported by bidentate ligands such as amidinates have many applications in catalysis and polymer chemistry.¹⁻³ The insertion of unsaturated bonds into Al-C bonds is an established atom-efficient route to such ligand-supported aluminium centres.⁴⁻⁸ In the case of carbodiimide insertion into Al-C bonds, initial Lewis base coordination at Al is followed by insertion of the nitroalkene to form a new amidinate moiety.⁵ The newly formed amidinate aluminium complexes are typically very reactive, which can impede selective product isolation; further reaction and/or rearrangement of the initial products produce thermodynamic products with multiple amidinate ligands.⁹ Reaction of diisopropylcarbodiimide (DIC) with MeAlEt₂ results in a mixture of products, demonstrating the lack of selective insertion (Scheme 1).⁶



Scheme 1. Unselective insertion of carbodiimide to mixed amidinate aluminium products. R = CH(CH₃)₂

Previously, we reported that the reaction of 1,4-dialuminacyclohexadiene derivative **1** with four equivalents of isonitrile results in insertion and C-C coupling, creating a zwitterionic diamide ligand with a carbocationic backbone **2**.¹⁰ We questioned if this insertion chemistry could be extended to include other unsaturated carbon-heteroatom bonds to create novel ligand structures. Here, we report the preparation of amidinate and carboxylate aluminium centres through the reaction of **1** with carbodiimides and carbon dioxide respectively.

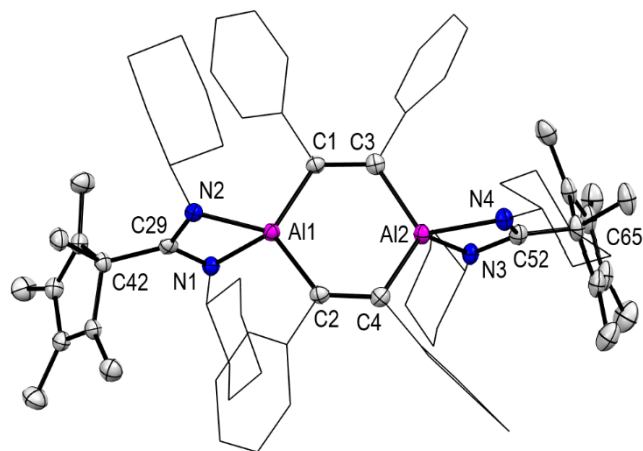
The low temperature addition of dicyclohexylcarbodiimide (DCC) to a solution of 1,4-dialuminacyclohexadiene **1** results in near-quantitative formation of **3a** as the mixture reaches room temperature (Scheme 2). The formation of a novel product was immediately evident by ¹H NMR spectroscopy of the crude mixture. Due to the high hapticity and rapid rotation of the ligand, the Cp* methyl groups in **1** appear as a singlet signal at $\delta = 1.55$. Now inequivalent in **3a**, they give three singlet signals at $\delta = 1.55$, 1.51 and 1.47 with a relative ratio of 2:1:2.



Scheme 2. Reactions of 1,4-dialuminacyclohexadiene with dicyclohexylcarbodiimide, diisopropylcarbodiimide, and carbon dioxide. (i) Previous work, 4 XylINC¹⁰ (ii) 2 RN=C=NR, **3a** R = cyclohexyl, **3b** R = isopropyl; (iii) CO₂

Looking to the aromatic region confirms that only one compound is present. The phenyl groups give three multiplet signals at $\delta = 7.37-7.30$, 7.12-7.07 and 6.92- 6.86, with a relative ratio of 2:2:1 (*ortho:meta:para*). Multiple overlapping resonances were identified for the four cyclohexyl groups in **3a**, making the alkyl region of the ¹H NMR spectrum very complex. A low field signal in the ¹³C NMR spectrum of **3a** at $\delta = 174.86$ corresponding to the central carbon in the newly formed amidinate moiety further gives evidence of selective DCC insertion. No signal was observed in the ²⁷Al NMR spectrum.

Crystals of **3a** suitable for X-ray diffraction were grown from a saturated hexane solution and the resulting solid-state structure is shown in Figure 1. The central Al₂C₄ bimetallic ring remains unreacted and is now planar as a result of the newly adopted approximately tetrahedral geometry at aluminium. The C=C



bond lengths are virtually identical to our reported isonitrile coupling product **2** (**3a**: 1.367(3) and 1.366(3); **2**: 1.368(10) Å

Figure 1. Single crystal X-ray structure of **3a**. Hydrogen atoms and 2 molecules of co-crystallised hexane are omitted for clarity. Selected Organic substituents are wireframe. Ellipsoids shown at 50 % probability. Selected bond lengths (Å) = Al1-Al2 3.424, C1-C3 1.367(3), C2-C4 1.366(3), Al1-C1 1.980(2), Al1-C2 1.986(2), Al1-N1 1.9213(17), Al1-N2 1.9162(17), C29-N1 1.336(3), C29-N2 1.351(3), C29-C42 1.540(3). Selected bond angles (°) = N1-C29-N2 107.97(16), C42-C29-N2 128.45(18), C42-C29-N1 123.47(16), C1-Al1-C2 116.12(9), N1-Al1-N2 68.98(7), N1-Al1-C2 118.95(8), N2-Al1-C1 114.56(8).

and 1.367 (10) Å).¹⁰ Delocalisation across the amidine N-C-N unit was confirmed by the sums of angles around C29 and C52 (each being 359.9(30)°), indicating an sp² hybridised central carbon. The relatively short C-N bond lengths had a range of 1.336(3) Å to 1.351(3) Å, and are comparable with the analogous bond lengths in similar aluminium amidinate compound {^tBuC(NCy)₂}Al(CH₂-CMe₃)₂ (1.343(2) Å to 1.346(2) Å)⁴. The Al-N bond lengths are also comparable with this literature complex (**3a**: 1.9162(17) Å and 1.9213(17) Å; {^tBuC(NCy)₂}Al(CH₂-CMe₃)₂: 1.9276(14) Å and 1.939(2) Å). The aluminium atoms in **3a** are in a distorted tetrahedral geometry, with angles of C1-Al1-C2 116.12(9)° and N1-Al1-N2 68.98(7)° being far from the ideal 109.5°.

The conversion of **1** to **3a** was near-quantitative when measured by NMR spectroscopy. However, isolated yields were lower when **3a** was synthesized on a preparative scale, and pure samples were challenging to obtain. To aid isolation, reaction of **1** with DIC was investigated. Using analogous conditions to the formation of **3a**, DIC insertion product **3b** was isolated (Scheme 2). Exchanging the conformationally flexible cyclohexyl groups for isopropyl groups resulted in a simplified ¹H NMR spectrum, but even so noteworthy features were identified. Four doublet signals corresponding to inequivalent isopropyl methyl groups were seen at δ = 1.01 (¹J_{H-H} = 6.3 Hz), 1.07 (¹J_{H-H} = 6.1 Hz), 1.16 (¹J_{H-H} = 6.4 Hz), 1.26 (¹J_{H-H} = 6.1 Hz), which each couple to one of four septet signals (δ = 3.21 (¹J_{H-H} = 6.3 Hz), 3.28 (¹J_{H-H} = 6.3 Hz), 3.99 (¹J_{H-H} = 6.2 Hz), 4.09 (¹J_{H-H} = 6.1 Hz)) in the ¹H-¹H COSY spectrum (Figure S5). This implies hindered rotation around the central isopropyl carbon, and the methyl groups are locked into a single configuration.

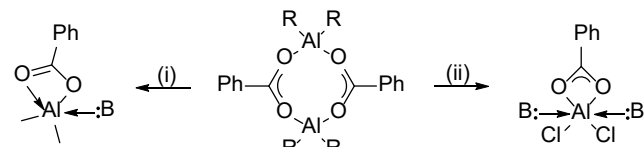
The signal for the Cp* methyl groups was assigned to the only remaining signal in the high field region of the ¹H NMR spectrum of **3b**, where overlapping signals around δ = 1.51-1.47 loosely resembled a triplet. However, when integrated this signal did not account for all thirty of the Cp*-based protons.

Variable temperature ¹H NMR experiments revealed two other signals at 333 K, δ = 1.23 and 1.21, attributed to the “missing” methyl groups, which are concealed by one of the ⁱPr doublets at 300 K. Increasing the temperature further to 363 K allowed for distinct signals corresponding to five inequivalent methyl environments to be observed (Figure S6). We propose that this behaviour is the result of thermally-induced chemical shift changes, rather than through intramolecular dynamic processes. Consistent with compounds **1** and **3a**, no signal was observed in the ²⁷Al NMR spectrum. Despite efforts, single crystals of **3b** suitable for X-ray diffraction to confirm the solid-state structure were not obtained. Both amidinate complexes **3a** and **3b** are stable in the solid state for several months when stored in an inert atmosphere.

Unlike molecular amidinates, aluminium carboxylate complexes typically aggregate to form polyoxometalate clusters because no substituent can be placed at the O atom to sterically shield the aluminium centre. Due to the significant ring strain associated with an AlO₂C ring, symmetrical aluminium mono-carboxylates are particularly challenging to isolate from organoaluminium starting materials. The presence of an external Lewis base was required to isolate a κ² mono-carboxylate product via a ring contraction (Scheme 3).^{11,12} As carbodiimides are isoelectronic with carbon dioxide, it was expected that reactions of 1,4-dialuminacyclohexadiene derivative **1** with CO₂ would proceed in a similar fashion to that of the formation of amidinate complexes **3a** and **3b** to form an aluminium κ² carboxylate. Whilst intramolecular bridging carboxylates are more typical products of such a reaction,¹³ we hypothesized that CO₂ would selectively insert into the Cp*-Al bonds of **1** with the central Al₂C₄ ring remaining intact, thus forcing κ² mono-carboxylate formation.

Exposing a degassed benzene solution of **1** to an atmosphere of CO₂ results in the almost immediate decolourisation of the orange solution and precipitation of a white solid, identified as the CO₂ insertion product **4** (Scheme 2). The favourable formation of Al-O bonds likely provides the reaction driving force. This fixation of CO₂ was not reversible, and **4** was found to be stable under vacuum for prolonged periods. Isolated solid samples of **4** were stable for up to a month under an argon atmosphere. Structural and spectroscopic analysis of bis κ² carboxylate **4** was complicated by its low solubility (insoluble in benzene, toluene, hexane, pentane and dichloromethane) and instability in solvents in which it is soluble (THF). Nevertheless, dissolution of solid **4** in THF-d₈ allowed for rapid acquisition of ¹H and ¹³C NMR spectra before decomposition, which was entirely complete after approximately 30 minutes.

The ¹H NMR spectrum of **4** was strikingly different from that of the starting material **1**. Reminiscent of DCC insertion product **3a**, the single Cp* resonance of **1**, at δ = 1.71, was replaced with three singlet signals for the now chemically inequivalent methyl groups at δ = 1.80, 1.76 and 1.73 which when integrated gave a



ratio 2:1:2. The single set of environments for the two Cp* groups indicates symmetrical insertion of CO₂ into both Cp*-Al units. Two multiplet signals in the aromatic region complete the ¹H NMR spectrum of **4**, corresponding to the phenyl groups; a triplet signal at δ = 6.90 (¹J_{H-H} = 7.5 Hz) and a multiplet signal

Scheme 3. Literature reported addition of Lewis bases to induce Al₂O₄C₂ ring contraction. (i) addition of B = pyridine, R = methyl;¹²(ii) addition of B = pyridine, R = chloride.¹¹

around δ = 6.80 – 6.73. A characteristic signal at δ = 180.5 in the ¹³C NMR spectrum is attributed to the new carboxylate carbon in **4**, slightly downfield from the analogous carbon signals in carbodiimide products **3a** and **3b** (δ = 174.8 for both). No signal was observed in the ²⁷Al NMR spectrum.

In lieu of X-Ray quality crystals, to confirm the molecularity of **4**, mass spectrometry was carried out. High resolution EI MS identified a molecular ion mass of 769.34127 au, consistent with the molecular formula as [C₅₀H₅₀O₄Al₂]⁺ (expected accurate mass: 769.333992 au), which is consistent with the incorporation of two equivalents of CO₂ into dialuminacyclohexadiene **1**.

The low solubility of **4** precluded the growth of X-ray quality crystals. The bonding mode of the carboxylate group was probed using solid-state infrared spectroscopy (Figure S9). A strong, sharp stretch at 1425 cm⁻¹ with an adjacent weaker stretch at 1557 cm⁻¹ indicates a symmetrical carboxylate unit with a low C-O bond order. This data fits well with the bidentate AlO₂C complex reported by Lewiński and coworkers¹¹ (Scheme 3), which has IR stretching frequencies at 1451 cm⁻¹ and 1627 cm⁻¹. If an unsymmetrical bonding mode was present, a greater number of stretching frequencies would be observed, most likely at higher wavenumber.¹⁴ Several stretches are seen in the alkyl region, at 2699 cm⁻¹, 2911 cm⁻¹ and 2856 cm⁻¹, are caused by the methyl groups associated with the Cp* group.

In summary, we have shown that amidine ligands with a Cp* backbone can be created by the insertion of two equivalents of DCC or DIC into the Al-Cp* bonds of 1,4-dialuminacyclohexadiene **1**. Irreversible CO₂ fixation by **1** results in formation of aluminium carboxylate **4**, likely featuring a symmetrical chelating carboxylate ligand. Ligand supported aluminium complexes are well-established as catalysts for the formation of valuable cyclic carbonates from carbon dioxide.^{2,15} Given the unstable nature of **4**, applications of **1** into such catalytic transformations are under investigation.

ASSOCIATED CONTENT

Supporting Information

Supporting information (PDF) is available containing:

- NMR spectra of compounds **3a**, **3b** and **4**
- Infrared spectrum of **4**
- Crystal data and structure refinement data of **3a**

CCDC 2074705 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.

Corresponding Authors

Michael J. Cowley - EaSTCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, United Kingdom; Email: michael.cowley@ed.ac.uk.

Stephanie J. Urwin - Current Address: Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford, OX1 3TA, United Kingdom; Email: stephanie.urwin@chem.ox.ac.uk

Author Contributions

S. J. U. conceived, designed and conducted experiments, and wrote the manuscript. G. S. N solved the X-ray crystal structure of **3a**. M. J. C. coordinated the study and edited the manuscript.

Notes

The authors declare no competing financial interest.

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