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

Citation for published version:

Digital Object Identifier (DOI):
10.1021/acs.organomet.1c00278

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Organometallics

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
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 dicyclohexylcarbodiimide 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

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 δ = 1.55. Now inequivalent in 3a, they give three singlet signals at δ = 1.55, 1.51 and 1.47 with a relative ratio of 2:1:2.

Looking to the aromatic region confirms that only one compound is present. The phenyl groups give three multiplet signals at δ = 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 δ = 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
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 AlO₆C 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 carboximidates 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 resulted 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 favoured 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-d₅ 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 (J_H-H = 7.5 Hz) and a multiplet signal 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 carboximide 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: 769.33992 au), which is consistent with the incorporation of two equivalents of CO₂ into dialuminalimicyclohexadiene 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 and 1627 cm⁻¹ indicates a symmetrical carboxylate unit with a low C-O bond order. This data fits well with the bidentate bonding mode proposed in 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. Several stretches are seen in the alkyl region, at 2699 cm⁻¹, 2911 cm⁻¹ and 2856 cm⁻¹, are most likely at higher wavenumber. Several stretches are seen in the aromatic region, at 3039 cm⁻¹, 3086 cm⁻¹ and 3095 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-dialuminimicyclohexadiene 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. 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.

ACKNOWLEDGMENTS
The authors would like to thank the European Commission, the EPSRC and the University of Edinburgh for financial support. This work was supported by a career integration grant, funded by the FP7 Marie Curie Actions of the European Commission (PCIG14-GA-2013-631483).

REFERENCES
(13) Bethley, C. E.; Aitken, C. L.; Harlan, J.; Koide, Y.; Bott, S. G.;

