

Reversible Insertion of CO into an Aluminium–Carbon Bond

Richard Y. Kong and Mark R. Crimmin*

Department of Chemistry, Molecular Sciences Research Hub, Imperial College London, 80 Wood Lane, Shepherds Bush, London, W12 0BZ, UK.

ABSTRACT: While reversible main-group mediated processes involving H₂ and alkenes have been reported and studied for over a decade, no such reversible processes involving CO have been reported. In this paper, we show that a [2.2.1] aluminium metallobicycle is capable of reversibly inserting CO to form a [2.2.2] metallobicycle at 100 °C. Eyring analysis allowed determination of the Gibbs activation energy of the back-reaction, CO elimination reaction with $\Delta G^{\ddagger}_{298\text{K}} = 26.6 \pm 3.0 \text{ kcal mol}^{-1}$. Computational studies reveal a highly asynchronous, but concerted, transition state for CO insertion. The coordination of CO to aluminium precedes C–C bond formation. The reversible migratory insertion reaction mimics that known for transition-metal and marks an important step forward for main group systems.

Migratory insertion, and its microscopic reverse elimination, are fundamental transformations in transition metal chemistry. In a migratory insertion reaction, two ligands on the transition metal combine to form one with no changes in formal oxidation state. Perhaps the most widely studied and applied variant of this reactivity involves the 1,1-insertion of CO into metal–alkyl bonds. This reaction requires a *cis*-relation of the ligands and can be thought of in terms of an intramolecular nucleophilic attack of the alkyl group on CO to generate a new acyl ligand.¹ The coordination site vacated during the reaction may be trapped by external ligand. The reactivity underpins some of the most widely applied homogeneously catalysed industrial processes including the Cativa acetic acid synthesis² and hydroformylation. In 2008, it was estimated that hydroformylation accounted for the production of 10.4 million metric tonnes of carbonylated hydrocarbons.³ The reverse reaction elimination has been applied organic synthesis and used to decarbonylate carbonyl functional groups.⁴

Over the last decade there has been a concerted effort from both academia and industry to alleviate concerns surrounding transition metal toxicity, scarcity, and cost by replacing transition metals with more abundant main group elements.⁵ Reports on the insertion of CO into main-group–element bonds are rare. In the case of aluminium, the most abundant metal in the Earth's crust, they are limited to three examples: the insertion of CO into the Al–C bonds of a trialkylaluminium,⁶ an aluminacyclopentene,⁷ and an aluminium-bound carbon chain.⁸ In contrast to the well-established transition-metal systems, however, these insertion reactions have been reported to be

non-reversible. Thus, while the reversible activation of dihydrogen^{9–11}, carbon dioxide,¹² and alkenes^{13–17} has been documented at main-group centres,^{18,19} reports on reversible processes involving CO are hitherto unknown.

Herein we report the reversible insertion of CO into the Al–C bond of an aluminium-based metallocycle. The reversibility is demonstrated through the elimination of CO from the product under a N₂ atmosphere and isotopic exchange with ¹³CO. Through a combination of DFT calculations and kinetics, CO insertion within our system has been shown to proceed by an asynchronous but concerted mechanism. To the best of our knowledge, our findings represent the first reversible insertion chemistry of CO at a main group metal and a new variant of migratory insertion reactivity.

The reaction of the low-valent aluminium complex **1**²⁰ with 1,3-cyclohexadiene furnishes **2**, a [4+1] cycloaddition product that contains a [2.2.1] metallocycle (Scheme 1a).

Scheme 1. Synthesis of (a) [2.2.1] metallocycle **2** and (b) Reversible CO insertion.

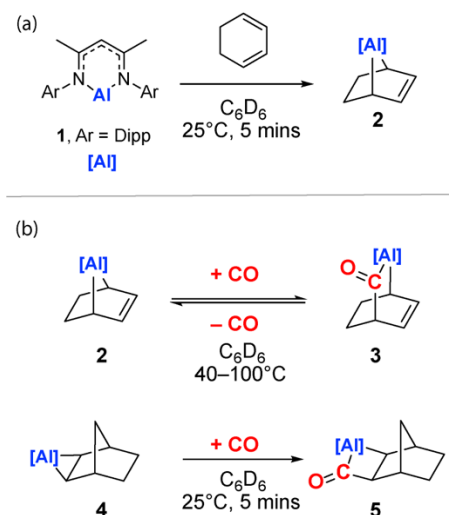
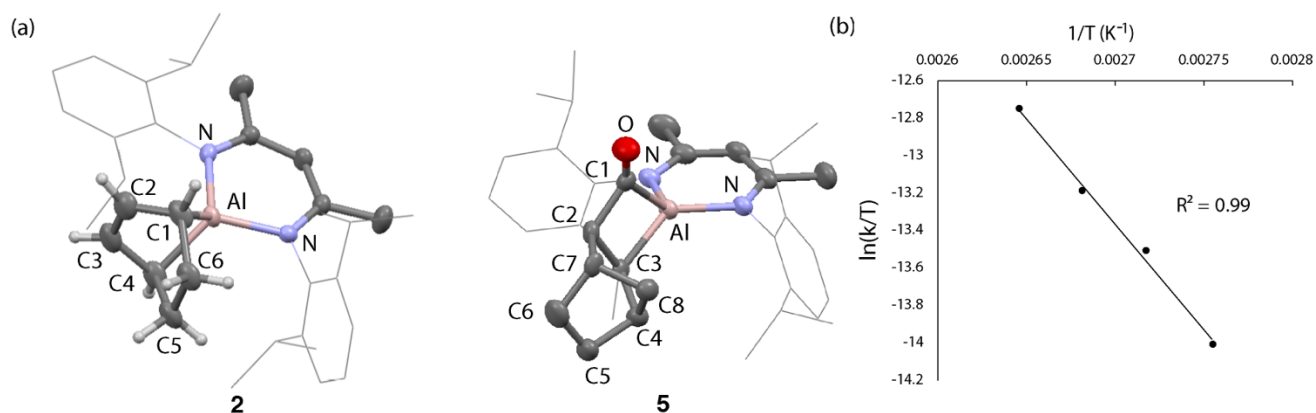


Figure 1. (a) Solid state structure of **2** and **5**. (b) Eyring analysis on the elimination of CO from **3** to form **2**.



The reaction is analogous to the recently reported reduction of 1,3,5,7-cyclooctatetraene by an aluminyl anion performed by Coles and co-workers.²¹ We have previously reported that **1** reacts reversibly with a series of terminal and strained alkenes to form metallocyclopropanes as the [2+1] cycloaddition product.¹⁷ In this case, the formation of metallocycle **2** is a non-reversible process.

Compound **2** forms single crystals that contain a unit cell which possesses a C_2 symmetry axis bisecting the N–Al–N angle of the β -diketiminate ligand. The entirety of the cyclohexene ring fragment is disordered over the mirror plane precluding unequivocal measurement of carbon–carbon bond lengths within the fragment. The shortening of the Al–N bond distance to 1.9095(15) Å and expansion of the N–Al–N angle to 95.96° in **2** compared to the metrics reported for **1** (Al–N: 1.957(2) Å, N–Al–N: 89.86(8)°)²⁰ are consistent with the formation of an Al(III) centre in **2**. The ¹H NMR spectrum of **2** in C₆D₆ shows a diagnostic alkene proton resonance at $\delta_H = 6.02$ ppm along with the bridgehead methine positions at $\delta_H = 2.04$ ppm. The latter protons are shielded due to the proximity of aluminium and so resonate further upfield relative to its hydrocarbyl homologue norbornene ($\delta_H = 2.74$). The ¹H NMR data in combination with the structural constraints imposed by Bredt's rule on the location of the alkene moiety allow the unequivocal assignment of **2**.

Exposure of a C₆D₆ solution of **2** to 1 atm. of CO results in its slow conversion to **3** at 25°C (Scheme 1). **3** is the result of insertion of CO into the Al–C bond of **2**. The reaction converts an alkyl ligand into an acyl ligand and results in a ring-expansion to form a [2.2.2] metallocycle. Despite multiple attempts at crystallisation, single crystals of **3** suitable for X-ray diffraction were not obtained due to the instability of this compound. Nevertheless,

the structure of **3** can be determined through multinuclear NMR spectrometry. The desymmetrisation of the metallacycle is clear in the now two unique alkene environments which resonate at $\delta_{\text{H}} = 5.56$ and 6.61 ppm $\delta_{\text{C}} = 121.7$ and 139.4 ppm in the respective spectra. The newly incorporated acyl group is identifiable in the ^{13}C NMR spectrum as a broad singlet at $\delta_{\text{C}} = 255.3$ ppm consistent with our previous reports of aluminium acyls.⁸ A correlation between the acyl carbon and the bridgehead methine ($\delta_{\text{H}} = 2.77$) is identifiable in the ^1H - ^{13}C HMBC spectrum. While prolonged heating at 40°C (>48 h) allows for the formation **3** as the major product, at higher temperatures (100°C) equilibration to an approximate 1:1 mixture of **2**:**3** is observed. The data suggest that insertion of CO into the Al-C bond of **2** is reversible.

Reversible CO insertion was confirmed in two separate experiments. Heating samples of **3** in C_6D_6 at 100°C under an atmosphere of N_2 results in quantitative reformation of **2**. Furthermore, heating a solution of **3** in C_6D_6 at 100°C for 3 h under 1 atm. of ^{13}CO results in the exchange of the ^{13}C isotopic label into the ^{12}C position of the acyl group. This degenerate exchange reaction is evident by the change in multiplicity of the bridgehead methine resonance in the ^1H NMR spectrum due to a $^2J_{^{13}\text{C}-^1\text{H}}$ coupling of 5.5 Hz as well as the signal intensity enhancement quaternary carbonyl resonance in the ^{13}C NMR spectrum (see the Supporting Information).

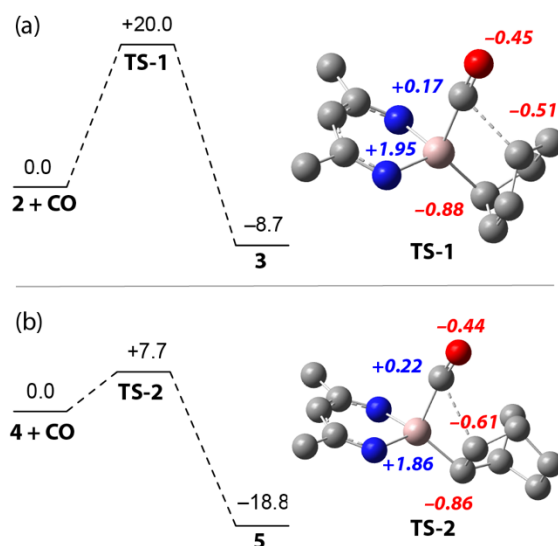
Reports of the insertion of CO into Al-C bonds remain rare. In the absence of crystallographic characterization of **3**, the insertion of CO into a related heterocycle, **4**, was studied to improve the confidence of our structural assignment. Reaction of **4** with CO generates the insertion product **5** within five minutes at 25°C (Scheme 1c). Like **2**, **5** demonstrates a diagnostic ^{13}C NMR resonance for the carbonyl moiety $\delta = 292.3$ ppm. In the solid state, **5** possesses a C_s symmetry plane bisecting the N-Al-N angle and passing through the atoms Al1 and C11 (Figure 1b). Despite disorder of the norbornyl fragment over this plane of symmetry, the insertion of CO to the Al-C bond of **4** to form a metallocyclobutanone is clear. The sum of internal angles ($\Sigma \angle = 358.66^\circ$) of the metallocycle imply a near planar geometry of the four-membered ring. While the formation of **5** is supported by solid-state and solution-state characterisation (see the Supporting Information), **5** decomposes at 25°C over 12 h to an intractable mixture of products.

In order to quantify the reversible behaviour of $\mathbf{2} + \text{CO} \leftrightarrow \mathbf{3}$, kinetics measurements were made by ^1H NMR spectroscopy. Rates were measured using a low concentration of **3** (2 mM) in toluene- d_8 a J Youngs NMR tube under a N_2 atmosphere with a modest headspace, as such the liberated CO is at high-dilution and not expected to participate in the forward reaction (see the Supporting Information). Under these conditions, the elimination of CO was found to fit first order kinetics with respect to the concentration of **3**. Eyring analysis using this approach

over a 90-105°C temperature range gave activation parameters for the back reaction of $\Delta H^\ddagger = 23.5 \pm 1.7$ kcal mol⁻¹ and $\Delta S^\ddagger = -10.3 \pm 4.5$ cal K⁻¹ mol⁻¹ (Figure 1c). The negative entropy of activation is consistent with a highly ordered transition state. The associated Gibbs activation energy is $\Delta G^\ddagger_{298K} = 26.6 \pm 3.0$ kcal mol⁻¹.

To provide further insight into the reactivity, density functional theory (DFT) calculations were performed (Figure 3). The formation of **3** by insertion of CO into the Al–C bond of **2** was found to proceed *via* **TS-1** corresponding to a calculated activation barrier of $\Delta G^\ddagger_{298K} = 20.0$ kcal mol⁻¹ for the forward-reaction, $\Delta G^\ddagger_{298K} = 28.7$ kcal mol⁻¹ for the back-reaction, within error of the experimentally determined activation parameters. The conversion of **4** to **5** proceeds through **TS-2**, calculated to have an activation barrier of $\Delta G^\ddagger_{298K} = 7.8$ kcal mol⁻¹. The transformation of **4** to **5** is calculated to be more exergonic than **2** to **3**, $\Delta G^\circ_{298K} = -18.7$ kcal mol⁻¹ but the low activation barrier means that the back reaction should also be feasible, $\Delta G^\ddagger_{298K} = 26.5$ kcal mol⁻¹. Experimentally the decomposition of **5** occurs before the elimination of CO can be observed.

Figure 2. Calculated pathway and associated transition states for the formation of (a) **3** and (b) **5**. Gibbs energies in kcal mol⁻¹. Representations of **TS-1** and **TS-2** have been truncated for clarity and annotated with calculated NPA charges.



Both **TS-1** and **TS-2** directly connect reactants and products and involve an asynchronous concerted Al–C and C–C bond forming process. In contrast to more established migratory insertion reactions of transition metal complexes and a previously calculated pathway for CO insertion into a trialkylaluminium complex,²² there is no intermediate in these pathways. Despite this, there is a clear parallel between the asynchronicity of these transition

states and the stepwise coordination/insertion processes documented for transition metal mediated carbonylation. NBO analysis (Wiberg bond indices) allows the characterisation a strong Al–CO interaction in the transition states relative the products (**TS-1**, 0.45; **3**, 0.48; **TS-2**, 0.50; **5**, 0.53). Incipient C–C bond formation is also clear from these data (**TS-1**, 0.46; **3**, 0.92; **TS-2**, 0.41; **5**, 0.95). The notable disparity in values between the transition-state and product suggest that C–C bond formation occurs *after* Al–C bond formation and that CO binding to Al is an important consideration. Analysis of the NPA charges (Figure 3) indicates that C–C bond formation occurs *via* a nucleophilic attack on the bound CO by the electronegative aluminium alkyl. The role of electrophilic aluminium centres as Lewis acids in migratory insertion reactions of transition metal carbonyls has been established before.^{23,24} It has been shown that, through coordination of the CO moiety, aluminium additives such as AlBr₃ can not only lower the activation barrier of migratory insertion in transition metal carbonyls but also stabilise the resulting acyl product.

In summary, we report the reversible insertion of CO into an Al–C bond that results in equilibration between aluminium alkyl and acyl complexes. To the best of our knowledge, this is the first example of such reversible behaviour in main group systems and a long overdue parallel of the migratory insertion reaction established for transition metal chemistry.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data for **2** and **5** are available from the Cambridge Crystallographic Data Centre (CCDC 1905522-1905523) and as a .cif file, full details of the experiments and calculations are available as a .pdf. This material is available free of charge via the internet at <http://pubs.acs.org>.

Acknowledgements

We are grateful to the Royal Society for provision of a University Research Fellowship (MRC) and the ERC (FluoroFix: 677367) for generous funding. We thank Imperial College London for the award of a President's Scholarship (RYK). Dr. Clare Bakewell is thanked for running preliminary experiments with compound **4**.

AUTHOR INFORMATION

The authors declare no financial conflicts.

Correspondence should be addressed to m.crimmin@imperial.ac.uk.

REFERENCES

- (1) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books, 2010, pp 349–365.
- (2) Jones, J. H. The Cativa™ Process for the Manufacture of Acetic Acid. *Platin. Met. Rev.* **2000**, *44* (3), 94–105.
- (3) Franke, R.; Selent, D.; Börner, A. Applied Hydroformylation. *Chem. Rev.* **2012**, *112* (11), 5675–5732. <https://doi.org/10.1021/cr3001803>.
- (4) Ohno, K.; Tsuji, J. Organic Synthesis by Means of Noble Metal Compounds. XXXV. Novel Decarbonylation Reactions of Aldehydes and Acyl Halides Using Rhodium Complexes. *J. Am. Chem. Soc.* **1968**, *90* (1), 99–107. <https://doi.org/10.1021/ja01003a018>.
- (5) Power, P. P. Main-Group Elements as Transition Metals. *Nature* **2010**, *463* (7278), 171–177. <https://doi.org/10.1038/nature08634>.
- (6) Mason, M. R.; Song, B.; Kirschbaum, K. Remarkable Room-Temperature Insertion of Carbon Monoxide into an Aluminum–Carbon Bond of Tri-Tert-Butylaluminum. *J. Am. Chem. Soc.* **2004**, *126* (38), 11812–11813. <https://doi.org/10.1021/ja046411n>.
- (7) Li, X.; Ni, C.; Song, H.; Cui, C. Formation of Aluminacyclobutenes via Carbon Monoxide and Isocyanide Insertion. *Chem. Commun.* **2006**, *0* (16), 1763–1765. <https://doi.org/10.1039/B601056C>.
- (8) Kong, R. Y.; Crimmin, M. R. Carbon Chain Growth by Sequential Reactions of CO and CO₂ with [W(CO)₆] and an Aluminum(I) Reductant. *J. Am. Chem. Soc.* **2018**, *140* (42), 13614–13617. <https://doi.org/10.1021/jacs.8b09761>.
- (9) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. Reversible, Metal-Free Hydrogen Activation. *Science* **2006**, *314* (5802), 1124–1126. <https://doi.org/10.1126/science.1134230>.
- (10) Ullrich, M.; Lough, A. J.; Stephan, D. W. Reversible, Metal-Free, Heterolytic Activation of H₂ at Room Temperature. *J. Am. Chem. Soc.* **2009**, *131* (1), 52–53. <https://doi.org/10.1021/ja808506t>.
- (11) Wang, S.; Sherbow, T. J.; Berben, L. A.; Power, P. P. Reversible Coordination of H₂ by a Distannyne. *J. Am. Chem. Soc.* **2018**, *140* (2), 590–593. <https://doi.org/10.1021/jacs.7b11798>.
- (12) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. Reversible Metal-Free Carbon Dioxide Binding by Frustrated Lewis Pairs. *Angew. Chem., Int. Ed.* **2009**, *48* (36), 6643–6646. <https://doi.org/10.1002/anie.200901636>.
- (13) Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P. Reversible Reactions of Ethylene with Distannynes Under Ambient Conditions. *Science* **2009**, *325* (5948), 1668–1670. <https://doi.org/10.1126/science.1176443>.
- (14) Lips, F.; Fettinger, J. C.; Mansikkamäki, A.; Tuononen, H. M.; Power, P. P. Reversible Complexation of Ethylene by a Silylene under Ambient Conditions. *J. Am. Chem. Soc.* **2014**, *136* (2), 634–637. <https://doi.org/10.1021/ja411951y>.
- (15) Wu, D.; Ganguly, R.; Li, Y.; Hoo, S. N.; Hirao, H.; Kinjo, R. Reversible [4 + 2] Cycloaddition Reaction of 1,3,2,5-Diazadiborinine with Ethylene. *Chem. Sci.* **2015**, *6* (12), 7150–7155. <https://doi.org/10.1039/C5SC03174E>.
- (16) Boutland, A. J.; Carroll, A.; Alvarez Lamsfus, C.; Stasch, A.; Maron, L.; Jones, C. Reversible Insertion of a C=C Bond into Magnesium(I) Dimers: Generation of Highly Active 1,2-Dimagnesioethane Compounds. *J. Am. Chem. Soc.* **2017**, *139* (50), 18190–18193. <https://doi.org/10.1021/jacs.7b11368>.
- (17) Bakewell, C.; White, A. J. P.; Crimmin, M. R. Reversible Alkene Binding and Allylic C–H Activation with an Aluminium(I) Complex. *Chem. Sci.* **2019**, *10* (8), 2452–2458. <https://doi.org/10.1039/C8SC04865G>.
- (18) Chu, T.; Nikonov, G. I. Oxidative Addition and Reductive Elimination at Main-Group Element Centers. *Chem. Rev.* **2018**, *118* (7), 3608–3680. <https://doi.org/10.1021/acs.chemrev.7b00572>.
- (19) Weetman, C.; Inoue, S. The Road Travelled: After Main-Group Elements as Transition Metals. *ChemCatChem* **2018**, *10* (19), 4213–4228. <https://doi.org/10.1002/cctc.201800963>.
- (20) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. Synthesis and Structure of a Monomeric Aluminum(I) Compound [$\{HC(CMeNAr)_2\}Al$] (Ar=2,6-IPr₂C₆H₃): A Stable Aluminum Analogue of a

- Carbene. *Angew. Chem., Int. Ed.* **2000**, *39* (23), 4274–4276. [https://doi.org/10.1002/1521-3773\(20001201\)39:23<4274::AID-ANIE4274>3.0.CO;2-K](https://doi.org/10.1002/1521-3773(20001201)39:23<4274::AID-ANIE4274>3.0.CO;2-K).
- (21) Schwamm, R. J.; Anker, M. D.; Lein, M.; Coles, M. P. Reduction vs. Addition: The Reaction of an Aluminyl Anion with 1,3,5,7-Cyclooctatetraene. *Angew. Chem., Int. Ed.* **2019**, *58* (5), 1489–1493. <https://doi.org/10.1002/anie.201811675>.
- (22) Mason, M. R.; Song, B.; Han, Y.; Hu, X. Reaction of Carbon Monoxide with Tri-Tert-Butylgallium: The First Example of CO Insertion into a Gallium–Carbon Bond. *Inorg. Chim. Act.* **2008**, *361* (11), 3332–3337. <https://doi.org/10.1016/j.ica.2007.11.021>.
- (23) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. Activation of Coordinated Carbon Monoxide toward Alkyl and Aryl Migration (Carbon Monoxide Insertion) by Molecular Lewis Acids and x-Ray Structure of the Reactive Intermediate. *J. Am. Chem. Soc.* **1980**, *102* (15), 5093–5100. <https://doi.org/10.1021/ja00535a048>.
- (24) Richmond, T. G.; Basolo, F.; Shriver, D. F. Bifunctional Activation of Coordinated Carbon Monoxide: A Kinetic Study of Lewis Acid Induced Alkyl Migration. *Inorg. Chem.* **1982**, *21* (3), 1272–1273. <https://doi.org/10.1021/ic00133a082>.
-