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Trapping and Reactivity of a Molecular Aluminium Oxide Ion

Jamie Hicks,^[a] Andreas Heilmann,^[a] Petra Vasko,^[a,b] Jose M. Goicoechea^{*[a]} and Simon Aldridge^{*[a]}

Abstract: Aluminium oxides constitute an important class of inorganic compound that are widely exploited in the chemical industry as catalysts and catalyst supports. Due to the tendency for such systems to aggregate via Al-O-Al bridges, the synthesis of well-defined, soluble, molecular models for these materials is challenging. Here we show that reactions of the potassium aluminyl complex $K_2[(\text{NON})\text{Al}]_2$ (**NON** = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) with CO_2 , PhNCO and N_2O all proceed via a common aluminium oxide intermediate. This highly reactive species can be trapped by coordination of a THF molecule as the anionic oxide complex $[(\text{NON})\text{AlO}(\text{THF})]$, which features discrete Al-O bonds and dimerizes in the solid state via weak $\text{O}^-\cdots\text{K}^+$ interactions. This species reacts with a range of small molecules including N_2O to give a hyponitrite $[(\text{N}_2\text{O}_2)^{2-}]$ complex and H_2 , the latter offering an unequivocal example of heterolytic E-H bond cleavage across a main group M-O bond.

Aluminium and oxygen are both among the most abundant elements in the Earth's crust, together forming over 50% of its elemental composition.^[1] As such, bonding between the two elements occurs naturally on a huge scale: many minerals, ores and gemstones contain aluminium oxygen bonds.^[2] Technologically, aluminium oxides and the related alumoxanes (e.g. methylalumoxane, MAO, $[\text{MeAlO}]_n$), have attracted significant interest due to their ability to act as catalysts and/or co-catalysts in a range of reactions, including the polymerisation of aldehydes,^[3] epoxides^[4] and olefins.^[5] Binary aluminium oxides are also active catalysts in a number of industrial transformations, including the Claus process, which converts H_2S into elemental sulphur,^[6] while alumina is widely exploited as a heterogeneous catalyst support.

Synthesising well-defined molecular, hydrocarbon soluble models of these compounds is therefore of considerable interest, as these systems may provide insight into the patterns of reactivity associated with Al-O bonds. However, the synthesis of systems of this type is challenging: aluminium-oxygen linkages are among the strongest element-element single bonds (ca. $502\text{--}585\text{ kJ mol}^{-1}$),^[7] and as such, molecular aluminium oxide units have a strong thermodynamic incentive to oligomerise to form insoluble materials.^[8] By employing sterically demanding ancillary ligands, however, a number of molecular complexes featuring bridging Al-O-Al motifs have been synthesised. Notable examples, shown in Figure 1, include $\{\text{tBu}_2\text{Al}(\text{py})\}_2(\mu\text{-O})$ (**I**, py = pyridine),^[9] $\{(\text{Nacnac})\text{Al}\}_2(\text{MeAl})(\mu\text{-O})_3$ (**II**, Nacnac =

$[(\text{DippNCMe})_2\text{CH}]$, Dipp = 2,6-diisopropylphenyl)^[10] and $[(\text{Mes}^*)\text{Al}(\mu\text{-O})]_4$, (**III**, $\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$).^[11] In addition, Roesky and co-workers have reported that the mono-alumoxine **IV** can be trapped by coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to the aluminium-bound oxygen atom.^[12]

Figure 1. Selected examples of molecular aluminium oxides.

Reports of molecular aluminium oxide ions in which the oxide bears a formal negative charge (Al-O^-) are even rarer still, presumably because of the stronger electrostatic drive to form Al-O-M bridges. Only one complex of this type has been crystallographically characterised, $[(\text{Nacnac})\text{Al}(\text{Me})\text{OLi}]_3$ (**V**, Figure 1), which exists as a tightly-bound trimer in the solid state with each oxide bonded to two lithium cations;^[13] no reactivity studies of this complex have been reported to date.

Recently we reported the potassium aluminyl complex $K_2[(\text{NON})\text{Al}]_2$ **1** (where **NON** = 4,5-bis(2,6-diisopropyl-anilido)-2,7-di-tert-butyl-9,9-dimethylxanthene)^[14] and demonstrated that it reacts as a nucleophilic source of aluminium.^[14,15] Here, we show that **1** can be used to access a highly reactive molecular aluminium oxide ion – a species that takes up N_2O via cycloaddition and heterolytically cleaves H_2 in a manner unprecedented for systems of this type.

Our study was driven by a desire to investigate the reactivity of the strongly nucleophilic (and reducing) aluminyl system **1** towards small unsaturated molecules. Accordingly, a benzene solution of **1** was exposed to one atmosphere of CO_2 at room temperature, resulting in a rapid colour change from yellow/orange to colourless and the formation of a single new product. This species was identified as the aluminium carbonate complex $K_2[(\text{NON})\text{Al}(\text{CO}_3)]_2$ **2** on the basis of spectroscopic, analytical and crystallographic measurements (Scheme 1 and ESI). A similar reaction occurs between **1** and two equivalents (or excess) of phenyl isocyanate, yielding the isoelectronic aluminium carbamate complex $K_2[(\text{NON})\text{Al}(\text{O}_2\text{CNPh})]_2$ **3**, the solid-state structure of which was also confirmed crystallographically (see ESI).

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Supporting information for this article is given via a link at the end of the document. Structural data has been deposited with the CCDC (ref: 1943804-1943808)

Scheme 1. Reactivity of the potassium alumanyl complex **1** towards CO_2 , PhNCO and N_2O .

The reactions of **1** with CO_2 and phenyl isocyanate both require two equivalents of the substrate, and by analogy with related (isoelectronic) silylene systems,^[16] are hypothesized to occur via initial reduction of the substrate, to give CO/PhNC and a common highly reactive aluminium oxide intermediate of the general formula $[\text{K}\{(\text{NON})\text{AlO}\}]_n$. Experimental evidence for this proposal comes from the ^1H NMR spectrum of the reaction mixture that yields **3**, which confirms the presence of one equivalent of phenyl isocyanide. In addition, an *in situ* $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture generating **2** also confirms the presence of CO .

From this aluminium oxide intermediate, the reaction proceeds via assimilation of a second equivalent of the substrate to give the isolated products **2** and **3**. Similar mechanisms have been reported for other low-oxidation state main group complexes with CO_2 , such as $[(\text{Nacnac})\text{Mg}]_2$ reported by Jones^[17] and the acyclic silylene $[(\text{NHI})\text{Si}-\text{Si}(\text{SiMe}_3)_3]$ (NHI = *N*-heterocyclic iminato ligand) reported by Inoue.^[16g]

In an attempt to observe this oxide intermediate, the reactions between **1** and CO_2/PhNCO were monitored by variable temperature (VT) ^1H NMR in d_8 -toluene (-80 to 25°C). However, even at -80°C , both reactions were complete in seconds, and no evidence of any intermediate species could be obtained from these measurements. Furthermore, the reaction of **1** with one equivalent of PhNCO (per aluminium centre) gives a 1:1 mixture of **3** and unreacted starting material **1**, suggesting that the oxide intermediate is even more reactive towards the substrate than potassium alumanyl complex **1**.

With this in mind, a more direct route to the oxide was sought: a benzene solution of **1** was exposed to N_2O (1 atm.) at room temperature. *In situ* ^1H NMR monitoring reveals the clean formation of a single new product, which can be identified by X-ray crystallography not as the target oxide, but remarkably as the *cis*-hyponitrite complex $\text{K}_2[(\text{NON})\text{Al}(\text{N}_2\text{O}_2)]_2$ (**4**) (Scheme 1). In a similar fashion to the reactions to give **2** and **3**, it appears that **1** reacts with *two equivalents* of N_2O to give **4**, presumably also via the same highly reactive aluminium oxide intermediate. The formation of the *cis*-hyponitrite ligand has been previously reported in *d*-block chemistry, via the radical coupling of two metal-bound NO ligands.^[18] Metal *cis*-hyponitrite complexes

have also been proposed to be transient intermediates in catalytic NO reductions,^[19] however the synthesis of the ligand directly from N_2O is to the best of our knowledge, unprecedented. Structurally, **4** is dimeric in the solid state (Figure 2), held together by electrostatic interactions between two $[(\text{NON})\text{Al}(\text{O}_2\text{N}_2)]^-$ anions and the two potassium cations. The 5-membered AlO_2N_2 heterocycle is planar, with the *cis*-hyponitrite ligand lying approximately perpendicular to the plane of the ancillary NON ligand.

Scheme 2. Trapping of the aluminium oxide ion **5** by the reaction of **1** with N_2O in THF.

Figure 2. Molecular structures of **4** (top) and **5** (bottom) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Hydrogen atoms omitted and selected groups shown in wire frame for clarity. Selected bond lengths (Å) and angles ($^\circ$) for **4**: Al(1)-O(1) 2.0128(15), Al(1)-O(2) 1.8273(16), Al(1)-O(3) 1.8176(17), Al(1)-N(1) 1.8919(18), Al(1)-N(2) 1.8911(19), O(2)-N(3) 1.400(3), O(3)-N(4) 1.356(3), N(3)-N(4) 1.251(3), O(2)-Al(1)-O(3) 84.85(8); for **5**: Al(1)-O(1) 1.6772(12), Al(2)-O(4) 1.6754(12), Al(1)-O(2) 1.9888(13), Al(1)-O(3) 2.2336(11), Al(1)-N(1) 1.9389(13), Al(1)-N(2) 1.9343(14), O(1)-Al(1)-O(2) 178.29(6), O(1)-Al(1)-O(3) 99.88(6).

Monitoring the reaction between **1** and N_2O by VT ^1H NMR in d_8 -toluene (-80 to 25°C) provides no spectroscopic evidence for the proposed oxide intermediate. However, repeating the experiment in d_8 -THF, allows an intermediate species to be detected, which is stable up to 0°C . Above 0°C it reacts with a further equivalent of N_2O to give **4**. Repeating the reaction on a preparative scale below 0°C allows the THF-ligated aluminium oxide $\text{K}_2[(\text{NON})\text{AlO}(\text{THF})]_2$ **5** to be isolated in good yield (Scheme 2). **5** is stable in the solid state under a nitrogen

atmosphere for several weeks, however in solution (THF or benzene) it decomposes over the course of 12 h at room temperature. Over a shorter time period, X-ray quality crystals of **5** could be grown from a concentrated benzene solution. As with compounds **2-4**, **5** exists as a dimer in the solid state (Figure 2), held together by potassium counter-ions which engage in a combination of interactions with the flanking aryl rings and with the aluminium-bound oxide ligands. The two (non symmetry-related) Al–O bond lengths are identical within error (1.6772(12) and 1.6754(12) Å) and are among the shortest Al–O bond distances reported to date,^[20] being considerably shorter than those found in the lithium aluminium oxide trimer [(Nacnac)Al(Me)OLi]₃ (**V**; 1.698(1) Å).^[13] This presumably reflects weaker interactions with the counter-cations in **5**, in comparison with the relatively strong O–Li bonds found in **V** (**5**: all O...K interactions >2.5 Å; **V**: d(O–Li) = 1.791(3), 1.808(3) Å).

To investigate what effect(s) the potassium cations, and the coordination of THF have on the electronic structure of **5**, the anionic fragment [(NON)AlO(THF)][−] and the related THF-free species [(NON)AlO][−] (**5'**) were probed via calculations using Density Functional Theory (DFT). The two anions possess very similar electronic structures, with the HOMO (−1.83 and −2.09 eV for **5** and **5'**, respectively) and HOMO−1 of each (−1.88 and −2.37 eV, respectively) being primarily located on the oxide, and comprising two filled p π -orbitals perpendicular to the Al–O vector (see ESI). The LUMO of each anion is delocalized over the backbone of the NON ligand, and the HOMO–LUMO gap is similar for the two species (**5**: 4.31 eV; **5'**: 4.34 eV). The Wiberg bond index (WBI) for the Al–O bond in **5** is calculated to be 0.64, with NPA charges at Al and O of +2.07 and −1.52, respectively.

Structurally, the Al–O bond length in [(NON)AlO(THF)][−] is calculated to be 1.66 Å, i.e. almost identical to that determined crystallographically (mean: 1.676 Å). These observations suggest that interactions with the K⁺ cations perturb the Al–O unit to a minimal degree, and therefore support a description close to a 'terminal' (and highly polarised) Al–O bond. The calculated parameters for the Al–O unit in the THF-free species **5'** are similar (d(Al–O) = 1.640 Å; WBI: 0.89; NPA charges: +1.96 (Al), −1.44 (O)). That said, this compound (the likely intermediate in the reactions to give compounds **2-4**), cannot be observed (let alone isolated) in reactions carried out in d₈-toluene, even at −80 °C. We propose that the vacant coordination site at aluminium (in the absence of THF) is accessible for coordination/activation of a second molecule of the substrate. Carrying out the reaction of **1** with N₂O in the stronger donor THF, blocks this site by coordination of a solvent molecule, preventing (at least at low temperatures) coordination of a second molecule of N₂O. It therefore appears that the presence of a vacant coordination site in the aluminium oxide intermediate is key to its extremely reactive nature. On this basis, we hypothesized that if the coordinated THF in **5** could be rendered labile, then **5** might act as a 'bottle-able' molecular source of the [Al–O][−] fragment.

To investigate the lability of the coordinated THF in **5**, exchange with d₈-THF was monitored in solution by VT ¹H NMR. At temperatures below −10 °C, the coordinated THF in **5** does not appear to exchange with d₈-THF (as signalled by the unchanging intensity of the signals associated with coordinated

protio-THF). However, at 0 °C and above, scrambling of coordinated THF with d₈-THF is observed; distinct ¹H resonances are observed at 0 °C for coordinated (δ_{H} = 3.84 ppm for the OCH₂ protons) and 'free' protio-THF (δ_{H} = 3.62 ppm), while at 10 °C only the signal at 3.62 ppm is seen. This suggests that at temperatures above 0 °C, the coordinated THF molecule is chemically labile. Accordingly, while **5** does not react with N₂O below −10 °C (in THF), it is rapidly converted to the *cis*-hyponitrite complex **4** above this temperature. In addition, **5** also reacts rapidly with CO₂ and PhNCO at room temperature to give **2** and **3**, respectively (Scheme 3).

Scheme 3. Reactivity of **5** with CO₂, PhNCO, N₂O and H₂.

A defining feature of transition metal complexes bearing highly polarised bonds is their ability to heterolytically cleave kinetically inert E–H bonds under mild conditions; *d*-block metal imide systems, for example, have been shown to cleave H–H and C–H bonds.^[21,22] As the extent of the polarisation of the Al–O bond in **5** appears to be comparable to that of M=N bonds in early transition metal imides, we were interested to investigate the reactivity of **5** towards H₂. Accordingly, a solution of **5** in benzene reacts with H₂ at room temperature and pressure over the course of 16 h to give the aluminium hydride hydroxide complex K₂[(NON)Al(H)OH]₂ **6** in high (87%) isolated yield (Scheme 3). This chemistry represents the first structurally authenticated example of H₂ activation across an aluminium oxygen bond.

The inability of **5** (or its more reactive THF-free form) to form Al–O–Al bridges presumably leads to significant unquenched Lewis basic character (at O), which in conjunction with the Lewis acidic aluminium centre offers some parallels with frustrated Lewis pair (FLP) chemistry in the activation of H₂.^[23] Investigation of the broader scope of E–H activation by **5** and related systems will be reported in due course.

Keywords: aluminium • oxide • alumanyl • reduction • small molecule activation

- [1] F. K. Lutgens, E. J. Tarbuck in *Essentials of geology*, 7th ed.; Prentice Hall 2000.
- [2] A. S. Marfunin in *Advanced Mineralogy*; Springer, Berlin, Heidelberg, 1994.
- [3] Selected examples include: a) T., Saegusa, Y. Fujii, H. Fujii, J. Furukawa, *Makromol. Chem.* **1962**, 55, 232–235; b) S.–I. Ishida, *J. Polym. Sci.* **1962**, 62, 1–14.

- [4] Selected examples include: (a) E. J. Vandenberg, *J. Polym. Sci. A1* **1969**, *7*, 525–567; b) E. J. Vandenberg, *J. Pure Appl. Chem.* **1976**, *48*, 295–306; c) Z. Florjańczyk, A. Plichta, M. Sobczak, *Polymer* **2006**, *47*, 1081–1090.
- [5] See: H. S. Zijlstra, S. Harder, *Eur. J. Inorg. Chem.* **2015**, *1*, 19–43; and references therein.
- [6] J. H. Gary, J. H. Handwerk, M. J. Kaiser, D. Geddes in *Petroleum Refining, Technology and Economics*; 5th ed., CRC Press, Boca Raton, **2007**.
- [7] A. J. Downs, H.-J. Himmel in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium; Chemical Patterns and Peculiarities* (Eds.: S. Aldridge, A. J. Downs), Wiley, Chichester, **2011**.
- [8] The lattice energies of α - and γ - Al_2O_3 are of the order of 18,200 kJmol⁻¹: W. J. Borer, H. H. Günthard, *Helv. Chim.* **1970**, *53*, 1043–1050.
- [9] M. R. Mason, J. M. Smith, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.* **1993**, *115*, 4971–4984.
- [10] G. Bai, H. W. Roesky, J. Li, M. Noltemeyer, H.-G. Schmidt, *Angew. Chem. Int. Ed.* **2003**, *42*, 5502–5506.
- [11] R. J. Wehmschulte, P. P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 8387–8388.
- [12] D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, B. Walford, D. Stalke, *Angew. Chem. Int. Ed.* **2002**, *41*, 4294–4296.
- [13] S. Singh, J. Chai, A. Pal, V. Jancik, H. W. Roesky, R. Herbst-Irmer, *Chem. Commun.* **2007**, 4934–4936.
- [14] a) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature*, **2018**, 557, 92–95. See also: b) R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles, *Angew. Chem. Int. Ed.*, **2019**, *58*, 1489–1493; c) M. D. Anker, M. P. Coles, *Angew. Chem. Int. Ed.*, **2019**, *58*, 13452–13455.
- [15] a) J. Hicks, A. Mansikkamäki, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nat. Chem.* **2019**, *11*, 237–241; b) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *J. Am. Chem. Soc.* **2019**, *141*, 11000–11003.
- [16] Recent examples of carbonate formation from a silylene and CO_2 include: a) P. Jutzi, D. Eikenberg, A. Möhrke, B. Neumann, H.-G. Stammer, *Organometallics* **1996**, *15*, 753–759; b) X. Liu, X.-Q. Xiao, Z. Xu, X. Yang, Z. Li, Z. Dong, C. Yan, G. Lai, M. Kira, *Organometallics* **2014**, *33*, 5434–5439; c) Y. Wang, M. Chen, Y. Xie, P. Wei, H. F. Schaefer, G. H. Robinson, *J. Am. Chem. Soc.* **2015**, *137*, 8396–8399; d) F. M. Mück, J. A. Baus, M. Nutz, C. Burschka, J. Poater, F. M. Bickelhaupt, R. Tacke, *Chem. Eur. J.* **2015**, *21*, 16665–16672; e) A. Burchert, S. Yao, R. Müller, C. Schattenberg, Y. Xiong, M. Kaupp, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 1894–1897; f) R. Rodriguez, I. Alvarado-Beltran, J. Saouli, N. Safferon-Merceron, A. Baceiredo, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2018**, *57*, 2635–2638; g) D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 8134–8137; h) D. Wendel, T. Szilvási, D. Henschel, P. J. Altmann, C. Jandl, S. Inoue, B. Rieger, *Angew. Chem. Int. Ed.* **2018**, *57*, 14575–14579.
- [17] R. Lalrempuia, A. Stasch, C. Jones, *Chem. Sci.* **2013**, *4*, 4383–4388.
- [18] a) S. Bhaduri, B. F. G. Johnson, A. Pickard, P. R. Raithby, G. M. Sheldrick, C. I. Zuccaro, *Chem. Commun.* **1977**, 354–355; b) A. M. Wright, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2012**, *134*, 9930–9933.
- [19] See, for example a) T. W. Hayton, W. B. Sharp, P. Legzdins, *Chem. Rev.* **2002**, *102*, 935–992; b) P. Legzdins, G. B. Richter-Addo in *Metal Nitrosyls*; Oxford University Press: New York, **1992** and references therein.
- [20] As determined from a survey of the Cambridge Crystallographic Database, March 2019.
- [21] Recent examples of H_2 activation by early transition metal imides include: a) X. Han, L. Xiang, C. A. Lamsfus, W. Mao, E. Lu, L. Maron, X. Leng, Y. Chen, *Chem. Eur. J.* **2017**, *23*, 14728; b) H. S. la Pierre, J. Arnold, F. D. Toste, *Angew. Chem. Int. Ed.* **2011**, *50*, 3900–3903; c) A. M. Geer, C. Tejel, J. A. López, M. A. Ciriano, *Angew. Chem. Int. Ed.* **2014**, *53*, 5614–5618.
- [22] For C-H activation by early transition metal imides, see: P. T. Wolczanski, *Organometallics*, **2018**, *37*, 505–516 (review).
- [23] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441.

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COMMUNICATION

Jamie Hicks, Andreas Heilmann, Petra Vasko, Jose M. Goicoechea*, Simon Aldridge*

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Trapping and Reactivity of a Molecular Aluminium Oxide Ion

Polar opposites: An isolable molecular aluminium oxide anion bearing a highly polarised Al-O bond has been found to heterolytically cleave H₂ at room temperature and pressure.