Trapping and Reactivity of a Molecular Aluminium Oxide Ion

Hicks, Jamie; Heilmann, Andreas; Vasko, Petra; Goicoechea, Jose; Aldridge, Simon (2019). Trapping and Reactivity of a Molecular Aluminium Oxide Ion. Angewandte Chemie, 131 (48), 17425-17428. DOI: 10.1002/ange.201910509
Titel: Trapping and Reactivity of a Molecular Aluminium Oxide Ion

Autoren: Jamie Hicks, Andreas Heilmann, Petra Vasko, Jose Goicoechea, and Simon Aldridge

Dieser Beitrag wurde nach Begutachtung und Überarbeitung sofort als "akzeptierter Artikel" (Accepted Article; AA) publiziert und kann unter Angabe der unten stehenden Digitalobjekt-Identifizierungsnummer (DOI) zitiert werden. Die deutsche Übersetzung wird gemeinsam mit der endgültigen englischen Fassung erscheinen. Die endgültige englische Fassung (Version of Record) wird ehestmöglich nach dem Redigieren und einem Korrekturgang als Early-View-Beitrag erscheinen und kann sich naturgemäß von der AA-Fassung unterscheiden. Leser sollten daher die endgültige Fassung, sobald sie veröffentlicht ist, verwenden. Für die AA-Fassung trägt der Autor die alleinige Verantwortung.

Zitierweise: Angew. Chem. Int. Ed. 10.1002/anie.201910509
Angew. Chem. 10.1002/ange.201910509

Link zur VoR: http://dx.doi.org/10.1002/anie.201910509
http://dx.doi.org/10.1002/ange.201910509
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$_2$[(NON)Al]$_2$ (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) with CO$_2$, PhNCO and N$_2$O 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 [(NON)Al(THF)], which features discrete Al-O bonds and dimerizes in the solid state via weak O···K interactions. This species reacts with a range of small molecules including N$_2$O to give a hyponitrite ([N$_2$O$_2$]$^+$) 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 aluminoxanes (e.g. methylaluminium, MAO, [MeAlO$_2$]), 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$_2$S 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. 502-585 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 ([Bu$_3$Al(py)]$_2$)(µ-O) (I, py = pyridine),[9] ([Nacnac]Al$_2$)(µ-O)$_2$ (II, Nacnac = [DippNCMe$_2$]$_2$CH), Dipp = 2,6-diisopropylphenyl$^{[10]}$ and [(Mes$^*$)Al(µ-O)]$_3$ (III, Mes$^*$ = 2,4,6-But$_2$C$_6$H$_2$).[11] In addition, Roessler and co-workers have reported that the mono-aluminoxane IV can be trapped by coordination of B(C$_6$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, [(Nacnac)Al(Me)OLi]$_2$ (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$_2$[(NON)Al]$_2$ (I where NON = 4,5-bis(2,6-diisopropylanilido)-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 I can be used to access a highly reactive molecular aluminium oxide ion – a species that takes up N$_2$O via cycloadition 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 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$_2$[(NON)Al(CO$_2$)$_3$] (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$_2$[(NON)Al(O$_2$CNPh)$_3$] (3, the solid-state structure of which was also confirmed crystallographically (see ESI).
The formation of the oxide intermediate is even more reactive towards the substrate than potassium aluminyl complex 1, as shown by the reaction of 1 with CO/PPhNCO and N2O to give 2, which is dimeric in the solid state (Figure 2), held together by electrostatic interactions between two [(NON)Al(O2N)2−] anions and the two potassium cations. The 5-membered AlO2N2 heterocycle is planar, with the cis-hyponitrite ligand lying approximately perpendicular to the plane of the ancillary NON ligand.

For internal use, please do not delete. Submitted_Manuscript
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, being considerably shorter than those found in the lithium aluminium oxide trimer \([\text{Nacnac}]\text{Al(OMe)OLi}\) (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 \([\text{NON}]\text{AIo(THF)}^–\) and the related THF-free species \([\text{NON}]\text{AIo}^+\) (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 px-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 \([\text{NON}]\text{AIo(THF)}^–\) 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 d₅-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 \([\text{AI-O}]^–\) fragment.

To investigate the lability of the coordinated THF in 5, exchange with d₅-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 d₅-THF (as signalled by the unchanging intensity of the signals associated with coordinated proto-THF). However, at 0 °C and above, scrambling of coordinated THF with d₅-THF is observed; distinct ¹H resonances are observed at 0 °C for coordinated (νₗ = 3.84 ppm for the OCH₃ protons) and ‘free’ proto-THF (νₗ = 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).

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 hydrixide complex \(\text{K}_2(\text{NON})\text{Al(H)OH}_2\) 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 • aluminyl • reduction • small molecule activation

COMMUNICATION


As determined from a survey of the Cambridge Crystallographic Database, March 2019.


For C-H activation by early transition metal imides, see: P. T. Wolczanski, Organometallics, 2018, 37, 505–516 (review).

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.