Inorganic Chemistry

Communication

Unveiling Complexity of the Oxygenation of Aluminum Alkyls by the Isolation of Unique Alkylperoxide and Oxoalkoxide Compounds

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ABSTRACT: While aluminum alkyls are often considered to be exemplary compounds of main-group organometallics and an in-depth understanding of their multifaceted chemistry is continually vital, the controlled oxygenation of organoaluminum complexes still remains a largely undeveloped area. In the course of our systematic studies on the relationship between the Lewis acidity of metal centers and noncovalent interactions in the secondary coordination sphere, we report the oxygenation of dialkylaluminum complexes incorporating a pyrrole−ester ligand, as purposefully selected dormant Lewis acidic octet-compliant model compounds, and the isolation and characterization of a new, dimeric aluminum *tert*-butylperoxide and an unique example of an aluminum oxoethoxide cluster. Our studies provide a more in-depth look at the diversity and complexity of the oxygenation chemistry of aluminum alkyls.

The controlled oxygenation of non-redox-active metal alkyls ([NR]MR) has been one of the key challenges since the beginning of organometallic chemistry.[1−3] Despite decades of extensive research in the field, factors controlling their outcomes are still not sufficiently understood, which has significantly prevented the more rapid design and implementation of dioxygen (O_2)-based reaction systems in various areas of chemistry, e.g., as radical initiators for organic reactions,[4−8] efficient catalysts for asymmetric epoxidation of electron-deficient olefins,[9−13] and a platform for the controlled preparation of metal oxides.[14−16] It has commonly been postulated that the oxygenation of [NR]MR proceeds via radical intermediates and thus predominantly leads to an intractable mixture of products.[17] Moreover, the widely accepted radical-chain mechanism is usually completed by the σ-bond metathesis reaction between a highly reactive metal alkylper-oxide [NR]MOOR and the parent [NR]MR moiety, which affords a metal alkoxide (Scheme 1, path 1).[17,18]

While the formation of [NR]MOOR species was already postulated at the end of 19th century, compounds of this type have been elusive for over 100 years.[2] Only the isolation and structural characterization of the first group 13 metal alkylperoxides by Barron and co-workers (for Ga and

In),[19,20] as well as our group (for Al)[21] in the 1990s seemed to be a cornerstone, demonstrating that the controlled reaction of the metal−carbon bond with O_2 is viable. Next, our systematic studies on the O_2 activation by [NR]MR compounds incorporating Al,[22,23] Zn,[24−27] and Mg[11,28] centers provided valuable insight into the mechanism of these reactions as well as the character of their outcomes. Very recently, we also shed new light on the above-mentioned autoxidation reaction of [NR]MOOR species and demonstrated that the well-defined ZnOOR compound reacts neither with a parent alkyl complex nor even with a homoleptic metal alkyl compound with formation of the respective metal alkoxides.[29] In fact, our investigations strongly indicate that formation of the metal alkoxides may be rationalized in terms of an intramolecular rearrangement of nonredox metal alkylperoxides (Scheme 1, path 2).[11,27,28] Moreover, considering the chemistry of [NR]MOOR species, particular mention should be made of the O−O bond scissions. Although regularly overlooked, homolysis of the O−O bond appears to be the critical factor responsible for the formation of a vast array of products including metal oxide,[30−33] hydroxide,[27,34,35] and even carboxylate[29,32] clusters (Scheme 1, path 3).

Another issue of key importance for the oxygenation non-redox-active metal alkyls, which remains an undeveloped area of research for decades, concerns the mode of O_2 activation by this type of organometallics. Our systematic studies on the oxygenation of [NR]MR complexes strongly indicated that the oxygenation process of metal alkyls is dramatically influenced

Scheme 1. Divergent Transformation Pathways of Nonredox Metal Alkylperoxides
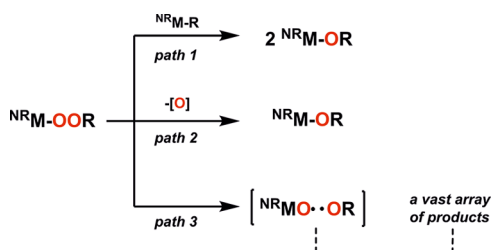
by both the coordination state of the organometallic species and the geometric requirements of an O_2 molecule approaching the metal center.[22,23,26−28] For example, the combined structural and chemical patterns provided compelling experimental evidence that the attack of O_2 on the metal center from a desired direction is the key feature in the O_2 activation by an octet-compliant four-coordinate organoaluminum complex, prior the insertion of O_2 into the Al−C bond.[22,23] Thus, for an in-depth understanding of the oxygenation of [NR]MR complexes, it is essential to rationally select an appropriate model system with tuned electronic and steric factors.

Notably, there is still a limited understanding of the factors affecting reaction outcomes in the oxygenation of aluminum alkyls in contrast to the important breakthroughs in the oxygenation chemistry of zinc[24−27,29,36,37] and magnesium[11,28,38] alkyls, as well as a some progress in the analogous reactions involving organoindium[39,40] complexes. Up to now, there is a handful of well-defined aluminum alkoxides isolated directly from the oxygenation of metal alkyl precursors, and only one example of an aluminum *tert*-butylperoxide, $(tBuOO)(tBuO)Al(\mu\text{-}tBuO)_2Al(mesal)_2$ (mesal = deprotonated methyl salicylate; Scheme 2, upper left).[21,40−43] The

**Scheme 2. Structurally Well-Defined Aluminum Alkylperoxides**
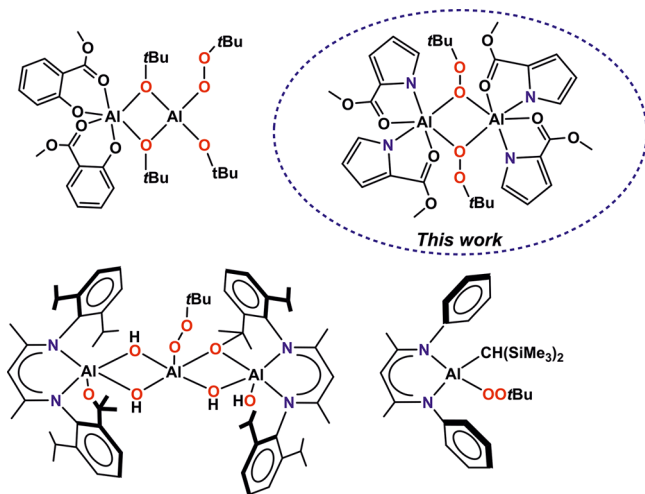
latter was derived by the controlled oxygenation of an octet-compliant di-*tert*-butylaluminum complex incorporating a O,O′-bidentate ligand. Besides, two other examples of aluminum alkyperoxides have hitherto been isolated from the protonolysis of aluminum complexes stabilized by β-

diketiminate ligands involving *tert*-butylhydroperoxide (Scheme 2, bottom).[44,45] All of the above-mentioned well-defined aluminum alkylperoxides have one common feature; namely, they possess a terminal alkylperoxo moiety. Herein, we describe the first example of a dimeric AlOOR compound with a bridging *tert*-butylperoxide ligand (Scheme 2). In the course of our systematic studies on the relationship between the Lewis acidity of metal centers in octet-compliant complexes and noncovalent interactions in the secondary coordination sphere,[22,23,46−48] we report the oxygenation of dialkylaluminum complexes with a pyrrole−ester ligand as purposefully selected dormant Lewis acidic octet-compliant model compounds (for an extended discussion on dormant Lewis acidic complexes, see refs 46 and 47); previously, the same N,O-pyrrolate ligand was successfully exploited in the controlled oxygenation of alkylzincs, leading to zinc alkoxides with unprecedented structural motifs.[49] Our studies demonstrate that the controlled reaction of four-coordinate (metpyrrol)-AlR_2 complexes with O_2 affords a novel dimeric aluminum *tert*-butylperoxide and hexanuclear aluminum oxoethoxide compounds, depending on the nature of the aluminum-bonded alkyl substituent, respectively (metpyrrol = deprotonated methyl-1H-pyrrole-2-carboxylate). While formation of the metal oxo compounds has previously been observed during the reaction of organozinc complexes with O_2, to our knowledge, this is the first example of an oxoaluminum cluster obtained directly from the oxygenation of an alkylaluminum complex.

The starting octet-compliant dialkylaluminum chelate complexes with the N,O-pyrrolate ligand, $(\text{metpyrrol})AltBu_2$ (**1**) and $(\text{metpyrrol})AlEt_2$ (**2**), were readily prepared by the equimolar reactions involving methyl-1H-pyrrole-2-carboxylate and $tBu_3Al(Et_2O)$ or Et_3Al, respectively. Both compounds were isolated in high yield as oily liquids and fully characterized spectroscopically. The resulting ^{1}H, ^{13}C, and ^{27}Al NMR spectra of **1** and **2** are fully consistent with the anticipated formula (for details, see the Supporting Information, SI). Given the pronounced susceptibility of a *tert*-butyl ligand to stabilize metal alkylperoxide species, we initially investigated oxygenation of the di-*tert*-butylaluminum chelate complex **1**. Treatment of a solution of **1** in Et_2O with dry O_2 at 0 °C, followed by concentration of the reaction mixture, and crystallization at −20 °C led to the reproducible formation of an aluminum *tert*-butylperoxide, $[(\text{metpyrrol})_2Al(\mu\text{-}OOtBu)]_2$ (**3**[2]; isolated yield ca. 75%). Remarkably, the replacement of sterically encumbered *tert*-butyl groups in **1** by ethyl groups dramatically changed the reaction outcome, and the oxygenation of a toluene solution of **2** at 0 °C for ca. 3 h, followed by the concentration of the reaction mixture, gave an oily

Scheme 3. Oxygenation of Octet-Compliant Dialkylaluminum Complexes Supported by a N,O-Chelate Ligand
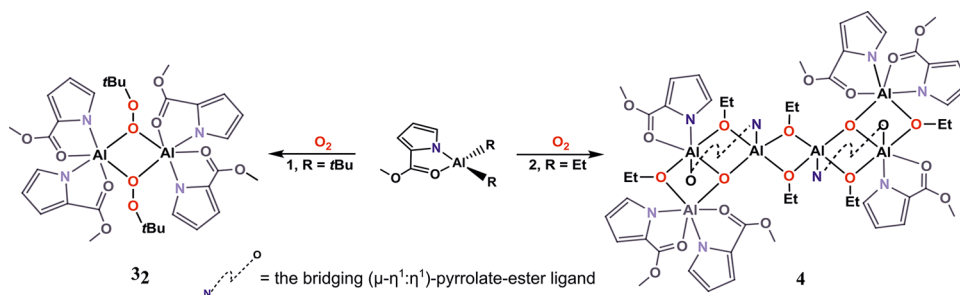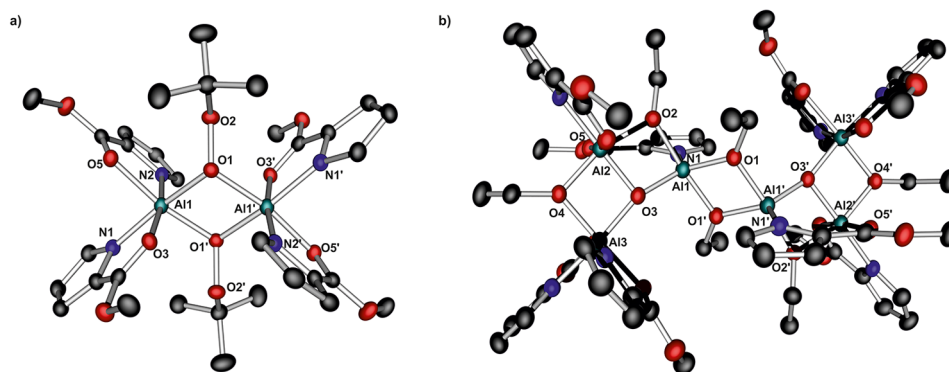
Figure 1. Molecular structures of (a) 3_2 and (b) **4** with thermal ellipsoids set at 35% probability. Hydrogen atoms are omitted for clarity.

intractable product. Interestingly, a long-time postcrystallization process (weeks) of the parent solution at 0 °C allowed one to isolate single crystals of an unprecedented hexanuclear aluminum oxoethoxide compound, $\{(metpyrrol)_4[Al(\mu\text{-}OEt)]_3(\mu_3\text{-}O)\}_2$ (**4**), in moderate yield (Scheme 3) for a putative source of the observed oxo species vide infra. Compounds 3_2 and **4** were characterized spectroscopically, and their identity in the solid state was determined by single-crystal X-ray diffraction studies. The ^{1}H NMR spectrum of the alkylperoxide 3_2 features a single set of signals characteristic of the *tert*-butylperoxide group and the pyrrole−ester ligand (for details, see the SI). Compound 3_2 is stable in the solid state as well as in a solution stored at −20 °C. However, extended storage of a toluene solution of 3_2 at room temperature leads to its decomposition with the formation of an intractable mixture of products, as judged from the ^{1}H NMR spectrum. In turn, the ^{1}H NMR spectrum of the oxoethoxide compound **4** recorded in C_6D_6 shows a complex pattern (for details, see the SI).

Compound 3_2 crystallizes in the space group $P\,21/c$ as a centrosymmetric dimer, with the aluminum centers bridged by the *tert*-butylperoxide groups (Figure 1a). The six-coordinate metal centers adopt a distorted octahedral geometry, and their coordination sphere is completed by two pyrrolate−ester ligands. The O1−O2 bond length [1.480(3) Å] in 3_2 is slightly longer than that observed in the terminally aluminum-bound *tert*-butylperoxide group [1.38(2) Å].[21] Compound **4** crystallizes in the $P\bar{1}$ space group as a centrosymmetric hexanuclear cluster (Figure 1b). This cluster may be formally viewed as two trinuclear units $\{(metpyrrol)_4[Al(\mu\text{-}OEt)]_3(\mu_3\text{-}O)\}$ bridged by the μ-ethoxide ligands with formation of a central four-membered $Al_2(\mu\text{-}O)_2$ ring. These units incorporate three inequivalent aluminum centers joined by the μ_3-oxo and μ-ethoxide bridges, and their coordination spheres are supported by pyrrolate−ester ligands. The two five-coordinate aluminum atoms of the central $Al_2(\mu\text{-}O)_2$ ring adopt a square-pyramidal geometry, and their coordination sphere is completed by the nitrogen atom from the bridging $(\mu\text{-}\eta^1\text{:}\eta^1)$-pyrrolate−ester ligand. The remaining aluminum atoms exhibit a distorted octahedral geometry. Besides the ethoxide and oxo groups, the coordination sphere of the Al2 atom is completed by an oxygen atom from the bridging $(\mu\text{-}\eta^1\text{:}\eta^1)$-pyrrolate−ester ligand as well as the second pyrrolate−ester ligand. The coordination sphere of the distal Al3 atom is terminated by the two N,O-chelating ligands.

Although the exact mechanism of the formation of 3_2 and **4** remains obscure, there are a number of possible scenarios that may be responsible for the observed divergent reaction outcomes. It seems reasonable to suggest that, under given conditions, both Al−R bonds in the octet-compliant complexes **1** and **2** react with O_2, leading presumably to a putative dialkylperoxide, $(metpyrrol)Al(OOR)_2$. In the case of oxygenation of **1**, the anticipated alkylperoxide likely undergoes a ligand-exchange reaction to give 3_2 and an elusive $[(tBuOO)_3Al]_n$ species. This suggestion is in line with our previous observations concerning the oxygenation of (mesal)-$AltBu_2$, in which a putative $(mesal)Al(OOtBu)_2$ likely disproportionates to $(tBuOO)(tBuO)Al(\mu\text{-}tBuO)_2Al(mesal)_2$ with a concomitant partial rearrangement of the alkylperoxide Al-OOtBu to the alkoxide Al−OtBu species.[21] Conversely, the isolation of **4** demonstrates the pronounced difference in the stability and reactivity between *tert*-butylperoxide and an ethylperoxide group. While the former is relatively stable under given conditions (vide supra), the latter easily transforms with the formation of aluminum ethoxide or oxo species. Moreover, the presence of oxo species in **4** seems to be the most striking feature, being commonly formed during the reaction of alkylaluminum compounds with H_2O.[50] Owing to the fact that the oxygenation of **2** was conducted in a highly controlled manner, minimizing the possibility of serendipitous hydrolysis, it appears reasonable to suggest that O_2 is the source of the oxo ligand. Remarkably, the formation of metal oxo species in the course of oxygenation of nonredox metal alkyl complexes has very rarely been encountered,[37,51] and our previous studies indicate that homolytic cleavage of the MO−OR bond, affording oxo MO• and alkoxide RO• radicals, is likely the long-time-overlooked pathway leading to a vast array of oxygenated products (cf. Scheme 1, path 3).[27,29−35]

In summary, the synthesis of novel dimeric aluminum *tert*-butylperoxide and hexanuclear aluminum oxoethoxide compounds supported by the pyrrole−ester ligand was achieved using the controlled oxygenation of dormant Lewis acidic octet-compliant dialkylaluminum chelate complexes. The results have demonstrated, for the first time, that not only aluminum alkylperoxides and alkoxides but also metal oxo species can be formed during the oxygenation of aluminum alkyls. Further in-depth studies on the oxygenation chemistry of organoaluminum compounds and an investigation of the reactivity of aluminum alkylperoxides are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01962.

Experimental supplements, including NMR and IR spectra and X-ray structure determination (PDF)

Accession Codes

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■ DEDICATION

Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 90th birthday.

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