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## Probing secondary coordination sphere influence on the oxygenation of zinc alkyls: formation of a unique zinc peroxide species<sup>†</sup>

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Reactions of ethylzinc derivatives of o-hydroxybiphenyl with  $O_2$ were investigated. The study revealed an essential role in the oxygenation process of intra-molecular interactions involving aromatic rings and provided a unique aryloxide (hydroxide) Zn<sub>8</sub>(OAr)<sub>8</sub>(OH)<sub>6</sub>(O<sub>2</sub>) cluster with an encapsulated peroxide species.

The role of the secondary sphere and non-covalent interactions in transformations involving O2 or O2-, apart from hydrogen bonding,<sup>1,2</sup> has not been systematically scrutinized in both chemical and biological processes.<sup>3</sup> Research in this field has been essentially focused on the role of the metal centres and their first coordination spheres. In the dioxygen activation mediated by main-group organometallic compounds, including organozinc complexes, the overall process is not complicated by redox reactions at the metal center, and these systems provide a unique opportunity to obtain insights into the details of oxygenation reactions. Our systematic investigations have convincingly demonstrated both the essential role of the coordination state of the organometallic species and the geometric requirements of the O<sub>2</sub> molecule approaching the metal center.<sup>4</sup> Another challenge in the oxygenation chemistry of metal alkyls is therefore the development of complexes with an appropriately designed secondary coordination sphere environment around the metal center that can assist autooxidative transformations.

Low-coordinated alkylzinc species have a strong propensity to form non-covalently bonded adducts based on intermolecular  $Zn \cdots \pi$  interactions.<sup>5</sup> So, we anticipated that suitably designed organozinc entities with intramolecular  $Zn \cdots \pi$ -aromatic interactions would enable us to study the role of  $\pi$  interactions in the  $O_2$  activation process. Herein we report the synthesis,

characterization, and oxygenation of ethylzinc aryloxides with a close disposition of aromatic rings toward the metal center. The study provided new results in the oxygenation chemistry of zinc alkyls, including the isolation and structural characterization of a novel octanuclear aryloxide (hydroxide) cluster with an encapsulated peroxide species.

o-Hydroxybiphenyl (ArOH) was chosen as a proligand with suitably positioned aromatic functionalities. Treatment of a toluene solution of ArOH with 1 equiv. of  $ZnEt_2$  afforded EtZn(OAr) (1) (Scheme 1). Attempts to isolate single crystals of 1 from the toluene solution were unsuccessful; however, crystallization of 1 from hexane-toluene led to the isolation of colorless crystals of a trinuclear alkylzinc aryloxide [(EtZn)<sub>2</sub>Zn(OAr)<sub>4</sub>] (2) in high yield (Scheme 1). The crystallization outcomes indicate that for the studied alkylzinc aryloxide system redistribution of the ligands takes place in solution, and the less soluble product is isolated. The resulting compounds were characterized in solution using <sup>1</sup>H NMR spectroscopy, and the identity of 2 was confirmed using singlecrystal X-ray analysis (for details, see ESI<sup>†</sup>).

The trinuclear aggregate 2 may be formally viewed as an adduct formed from two EtZnOAr and one  $Zn(OAr)_2$  moiety. It has a linear chain arrangement with one central  $Zn(OAr)_4$  unit and two outer three-coordinated EtZn units (Fig. 1).<sup>6</sup> The latter coordinatively unsaturated metal centers are unsymmetrically shielded by the terminal phenyl rings of the bridging aryloxide ligands, with the



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**Fig. 1** Molecular structure of **2** with a thermal ellipsoid set at 50% probability; H-atoms omitted for clarity. Selected bond lengths (Å): Zn1-O1 2.043(2), Zn1-O2 1.977(2), Zn2-O1 1.938(2), Zn2-O2 1.974(2), Zn2-O3 1.970(2), Zn2-O4 1.972(2), Zn3-O3 1.954(2), Zn3-O4 2.047(2), Zn1-C13 1.948(2), Zn3-C39 1.963(5), Zn3-C38 2.871(2).

shortest intramolecular Zn···C distances varying from 2.87 to 3.10 Å (the shortest being the Zn3–C38 distance). The phenyl rings of the bridging aryloxides form clefts with the outer zinc centers, and this probably has a profound effect on the reaction of 2 with dioxygen (*vide infra*).

Next we used compounds **1** and **2** as suitable model systems for studying the role of  $\pi$ -aromatic interactions in the O<sub>2</sub> activation process, and tested their reactivities toward O<sub>2</sub>. In Schlenk tube experiments, a solution of the corresponding ethylzinc aryloxide compound **1** or **2** in toluene at 0 °C was treated with an excess of dry O<sub>2</sub>. The reaction mixture was stirred for 12 h<sup>7</sup> and then excess O<sub>2</sub> was removed. In the case of oxygenation of **1** an intractable mixture of products was obtained (*cf.* Fig. S2, ESI†). In contrast, the reaction of the trinuclear ethylzinc aryloxide **2** with O<sub>2</sub> provided colorless crystals of a new aryloxide(hydroxide) octanuclear cluster with an encapsulated peroxide moiety,  $Zn_8(OAr)_8(OH)_6(O_2)$  (**3**), which was deposited in high yield after several days. The identity of **3**-2ArOH was confirmed using X-ray crystallography.

The molecular structure of 3 can be formally viewed as a  $Zn_6(O_2)(\mu_2$ -OAr)<sub>6</sub> unit with zinc centers bridged by aryloxide ligands and encapsulated peroxide species with a  $\mu_6$ - $(\eta^1)_3$ -binding mode (Fig. 2).<sup>8</sup> The octahedral arrangement of zinc centers is bicapped by  $ArOZn(OH)_3$  units, giving rise to  $Zn_8(O_2)(\mu_2-OAr)_6$  moieties. All the Zn atoms have a distorted coordination geometry and the arrangement of peroxide species is analogous to that observed in simple binary  $Zn(O_2)$  peroxide,<sup>9</sup> which adopts a cubic pyrite structure. The Zn–O peroxide bond lengths fall in a very narrow range, 2.10–2.15 Å, and the O-O bond lengths in the peroxides are varied from 1.514(6) to 1.527(4) Å, which is slightly shorter than that observed in  $Zn(O_2)$ peroxide (1.465 Å).9b The average Zn-Ohvdroxide bond distances are 1.864(3)-1.971(3) Å and the Zn-Oaryloxide bond distances involving bridging aryloxides are 1.957(3)-1.983(3) Å; the terminal Zn-Oaryloxide distances are 1.898(4)-1.902(3) Å. The conformations of the terminal aryloxide ligands are largely determined by hydrogen-bonding interactions with solvating ArOH molecules that are evolved during the oxygenation process (Fig. 2). To the best of our knowledge, except for the simple binary Zn(O<sub>2</sub>) peroxide,<sup>9</sup> compound 3 is the first example of a molecular zinc peroxide complex to have been structurally characterized.<sup>10</sup> Interestingly, the unique central core of 3 resembles that observed for the octanuclear nickel cluster with



Fig. 2 Molecular structure (a) and core (b) of 3-2ArOH with a thermal ellipsoid set at 50% probability; H-atoms and minor disorder omitted. Selected bond lengths (Å): Zn1–O1 1.901(3), Zn1–O2 1.946(3), Zn1–O3 1.948(3), Zn1–O4 1.932(3), Zn2–O2 1.895(3), Zn2–O5 2.130(3), Zn2–O7 1.962(3), Zn2–O8 1.973(3), Zn3–O5 2.146(3), Zn4–O5 2.126(3), Zn5–O6 2.109(3), Zn6–O6 2.141(3), Zn6–O7 1.977(3), Zn7–O6 2.101(3), O5–O6 1.527(4).

entrapped peroxide species,  $[Ni_8(L)_{12}(O_2)]^{2+}$  (L = *N*-substituted 3-hydroxy-2-pyridinonate; the latter cluster was synthesized from an inorganic nickel salt and an aqueous solution of H<sub>2</sub>O<sub>2</sub>).<sup>11</sup>

Thus, the course of the metal-π-assisted oxygenation of zinc alkyls differs significantly from those of other organozinc systems systematically studied previously, in which formation of ZnOOR or ZnOR species was commonly observed.<sup>12</sup> The following question therefore arises: *where have all the ethyl and/or ethoxy radicals gone?* To clarify the fates of the Et<sup>•</sup> and EtO<sup>•</sup> radicals, a standard workup procedure for the post-reaction mixtures derived from the oxygenation of 1 and 2 was performed. After hydrolysis, a range of organic products were identified by GCMS and ESI-MS: ethanol, the parent ArOH, ethyl-, benzyl- and hydroxy-substituted ArOH, and a number of dihydroxybiphenyl derivatives variously substituted by one or more ethyl and hydroxy and/or ethoxy groups (for details, see ESI<sup>†</sup>). Overall, the character of identified organic products confirms the anticipated formation of various radical species, including Et<sup>•</sup> and EtO<sup>•</sup> radicals, in the course of the studied reactions.

The mechanism by which aggregate 3 is formed is not known. The composition of 3 corresponds to a formal transformation of eight molecules of 2 mediated by reactive oxygen species. The Zn(OAr)<sub>2</sub> moiety in the trinuclear aggregate 2 acts as a scaffold for the complex transformations, building up aromatic cavities around reactive centers. We speculate that the initial step involves the attack of an O2 molecule on one of the outer three-coordinated zinc centers in 2; this is consistent with the newly proposed mechanism for the oxygenation of zinc alkyls.<sup>4d</sup> This attack is followed by an electron transfer from the Zn-C bond to O2, affording a caged radical pair A with a coordinated superoxide anion. The Et radical may diffuse away from the putative radical pair A (path 1) or, alternatively, may collapse to generate the alkyl peroxide C after spin conversion (path 2). These initial events set off a cascade of reactions ultimately producing a zinc aryloxide (hydroxide) and peroxide species (Scheme 2).

Further transformation according to path 1 leads to the formation of superoxide intermediate **B**, with a possible entrapment of the superoxide anion within the cleft formed by the outer zinc center



and the phenyl ring of the bridging aryloxide ligand. This type of stabilisation of the superoxide anion<sup>13</sup> favors the mentioned Et<sup>•</sup> radical diffusion and suppresses the formation of ethylperoxide species according to path 2. The zinc hydroxide species may arise from homolytic cleavage of peroxide species followed by hydrogen entrapment from the reaction bulk.

In conclusion, the observed reaction outcomes resulting from the oxygenation of ethylzinc derivatives with suitably positioned aromatic functionalities close to the metal center are completely different from those previously observed in reactions of various alkylzinc complexes with O<sub>2</sub>. To date, the formation of alkyl peroxide,  ${}^{4d-f,12b,14}$  alkoxide,  ${}^{4c-e,12,16}$  oxo,  ${}^{4f,15}$  and even carboxylate species<sup>16</sup> in the oxygenation of Zn-R units has been well documented (Scheme 3). The oxygenation of 2 to 3 for the first time not only demonstrates the formation of hydroxide species but also substantiates the transformation of dioxygen into a peroxo anion in the O2 activation processes mediated by zinc alkyls (Scheme 3e and f). Finally, these new reaction outcomes clearly indicate that the outlined approach involving suitable positioning of aromatic functionalities near the metal center may be useful as a model system for examining transformations involving either O2 or reactive oxygen species and mediated by organometallic compounds and various bioinorganic oxygenation systems.

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