Transformation of Ethylzinc Species to Zinc Acetate Mediated by O₂ Activation: Reactive Oxygen-Centered Radicals Under Control**

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The mechanisms of O₂ activation by main-group metal alkyl compounds and the character of reactive intermediate oxygen species, along with the origins of reaction outcomes, have been a challenge to understand since the Frankland's pioneering studies.^[1] For decades, these oxygenation reactions have been commonly considered as difficult to control owing to their radical-chain character.^[2] Metal alkyl peroxide complexes have been proposed as intermediates in these reactions,^[3,4] and the formation of the most commonly observable alkoxides as final products has traditionally been explained by σ bond metathesis involving an alkyl peroxide intermediate and the starting metal alkyl complex.^[2,4a] Our recent systematic investigations have not only advanced a plausible hypothesis concerning the mechanism of O₂ activation by organometallic compounds,^[4b,c,k,l,5] but also convincingly demonstrated a high tendency of incipient zinc peroxide species to form relatively stable adducts with the parent zinc alkyl complex.^[4m,5] Moreover, we have revealed a long overlooked decomposition pathway of zinc alkyl peroxides via homolysis of the O-O bond, which is responsible for the formation of oxo complexes.^[41,m,5] To date, the formation of alkyl peroxide (path a, Scheme 1), alkoxide (path b), and oxo species (path c) in the oxygenation of Zn-R species has been



Scheme 1. Species formed by the oxygenation of alkyl zinc compounds Zn-R. See text for details.

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well-documented. To our knowledge, homolytic MO–OR bond cleavage to give the corresponding metal carboxylate species (path d, scheme 1) has not been considered as a mode of decomposition of both zinc and other metal alkyl peroxides.^[6]



Our previous studies demonstrated that N,N-donor pyrroloimines, HL¹, are versatile supporting ligands that can have diverse bonding modes to metal centers.^[4m,7] Moreover, the controlled oxygenation of $[RZn(L^1)]$ complexes provides a novel zinc alkyl peroxide or a zinc oxo-encapsulated cluster, the formation of which was mediated by the nature of the zinc-bonded alkyl substituents.^[4m] Herein we present a novel extension of the latter investigations, which involves 2,5bis[(2,6-diisopropylphenyl)aldimino]pyrrole (HL²) as a *N*,*N*,*N*-donor supporting ligand, and the oxygenation of the corresponding ethylzinc derivative $[EtZn(L^2)]$ leading to the zinc acetate species.

The reaction of Et_2Zn with one equivalent of HL^2 in toluene affords the alkyl zinc complex $[{EtZn(L^2)}_n]$ (1) in quantitative yield. Although we were not able to obtain single crystals of 1, the ¹H NMR data (see below) are fully consistent with the anticipated formula. Molecular weight measurements revealed that 1 occurs predominantly as a dimeric species in a benzene solution. In the next step, a solution of 1 in toluene at -20°C was treated with an excess of dry dioxygen, the reaction mixture was stirred for 10 minutes, and then the excess O₂ was removed. From this oxygenation reaction, we expected new zinc alkyl peroxide or oxo aggregates. To our surprise, colorless crystals of the zinc carboxylate $[{(L^2)Zn_2(\mu-O_2CMe)_3}_2]$ (2) deposited in high yield after several days. Upon decantation of the liquid residue and following the addition of Et₂O, a mixture of products deposited at 0 °C as a yellow precipitate, from which some light yellow crystals of complex $[Zn(L^2)_2]$ (3) could be isolated by manual separation.

Single-crystal X-ray diffraction measurements revealed that **2** consists of two dinuclear zinc carboxylate units $\{Zn_2(O_2CMe)_3\}$ supported by two monodeprotonated L^2 ligands (Figure 1 a).^[8a] The dinuclear carboxylate units are related by symmetry through an inversion center, and feature a novel paddle-wheel-type coordination of zinc(II) pairs. Owing to the monoanionic character of the L^2 ligand, the



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Figure 1. Molecular structures of **2** (a) and **3** (b). Ellipsoids set at 30% probability; hydrogen atoms omitted for clarity.

dinuclear units in 2 each require three carboxylate ligands for charge compensation, which contrasts with the typical paddle-wheel structure of neutral dimeric zinc species $[Zn_2(O_2CR)_4]$ that involve four bridging carboxylate ligands.^[9] Two L^2 ligands in 2 cooperatively bind the carboxylate units, generating a neutral tetranuclear cluster. The two zinc atoms in the dinuclear unit have different coordination environments. The essentially bipyramidal zinc site is bonded to three acetate oxygen atoms and two nitrogen atoms in a chelate fashion, and the tetrahedral zinc site is surrounded by an O4/N ligating environment. The structure of 2 shows zincligand bond distances that are typical for zinc carboxylate complexes supported by nitrogen ligands.^[9]

The molecular structure of **3** is shown in Figure 1 b.^[8b] The pyrroloimine L^2 ligands are

bound in a N,N' chelate fashion to the tetrahedral zinc center, and the remaining imine groups have neither intra- or intermolecular association with zinc atoms. The metal coordination environment is comparable to that previously observed for the related bis(pyrrolylaldiminato)zinc complex.^[10]

To gain further insights into the observed non-trivial oxygenation of 2, the reaction progress was monitored by ¹H NMR and EPR spectroscopy. The ¹H NMR investigations at 0 °C demonstrated that the oxygenation of 1 in $[D_8]$ toluene proceeds in several distinct stages (Figure 2). The ¹H NMR spectrum of 1 has no complexity, and consists of two broad resonances (0.72 and 1.28 ppm) of the ethyl protons and one set of resonances which results from the L² ligand. Upon addition of dry O_2 to 1, the spectrum of the reaction mixture changes dramatically, and after the first five minutes it exhibits two independent patterns (Figure 2b). Well-resolved multiplets of comparable intensity of the Et-Zn and EtOOZn groups and two sets of signals that are characteristic of the protons of L^2 ligand indicate that approximately half of the Zn-C bonds were consumed and a new cluster of tentative composition $[EtZn(L^2)][EtOOZn(L^2)]$ (1-A) is formed; this observation is consistent with our previous studies.^[4j,m,5] The second group of signals, that is, additional resonances of a coordinated L² ligand along with the characteristic doublet (1.34 ppm) and quartet (3.87 ppm), were assigned to a putative intermediate 1-D (see Scheme 2). Strikingly, the latter pattern is accompanied by the appearance of a singlet attributable to the evolving ethane. During the next 20 minutes, the 1-D intermediate was generated concomitantly with the decay of the cluster 1-A (Figure 2c). After one hour, the spectrum is rather featureless, and is dominated by a pattern characteristic of ligand L² (Figure 2d). Interestingly, over a period of a few days at 0°C, a much slower accumulation of the carboxylate species 1-E and 2 was observed, as indicated by the appearance of two singlets characteristic for the acetate methyl protons (at 1.30 and 1.36 ppm), along with the disappearance of signals assigned to **1-D** and significant changes in the regions of L^2 protons



Scheme 2. Proposed mechanism of the transformation of ethylzinc species to zinc acetate mediated by the O-O bond activation.



Figure 2. Representative ¹H NMR spectra for the oxygenation of **1** in $[D_8]$ toluene at 0°C: a) before introduction of O_2 ; b–e): during the reaction with O_2 : b) 5 min, c) 20 min, d) 1 h, and e) 72 h. For a putative assignment of the signal at $\delta = 3.42$ ppm (*), see Ref. [13].

(Figure 2e). It is also notable that EPR spectra for the $1/O_2$ system do not reveal the formation of persistent radical species in the course of reaction.

Although it is premature to discuss the precise mechanism at the present stage, based upon the reaction outcome (namely 2 and 3), the spectroscopic data, and the earlier results for the controlled oxygenation of various alkyl zinc complexes supported by bifunctional ligand,^[4i-m,5,7] the title reaction can be rationalized by assuming the following pathways (Scheme 2). Initially, 1 reacts with O_2 to give the alkyl peroxide species $[EtOOZn(L^2)]$ followed by generation of an intermediate that corresponds to the observed cluster $[{EtOOZn(L^2)}_n][{EtZn(L^2)}_n]$ (1-A) of as yet unidentified structure. The resulting zinc alkyl peroxide is unstable, and to our knowledge, its further multiple transformations leading to the zinc acetate species has no precedence in metal alkyl peroxide chemistry. The selectivity of these transformations involving highly reactive oxygen species can be interpreted in terms of the pronounced "cage effect" and multiple in-cage recombination events in small-molecule systems.^[11] We therefore suggest that the putative cage 1-A supported by multidentate L² ligands has inherent propensity to form a capsule, thus allowing the greater tunability of reactive oxygen species, which is undoubtedly crucial for the proposed pathway to zinc carboxylates. Thus, further in-cage transformations occur by initial homolysis of the O-O bond, generating a caged radical pair ZnO[•] and EtO[•]. The generation of zinc oxyl and alkoxy radicals from homolysis of the ZnO-OR bond have been well-documented in our previous studies; however the nascent RO radicals have always diffused out of the cage. $\ensuremath{^{[4l,m,5]}}$ We suggest that in the present case, the putative capsule suppresses the escape of EtO[•] radical from the cage. During subsequent recombination of the intercalated oxygen-centered radicals, the zinc oxyl radical induces a 1,2-H shift in the 'OCH₂CH₃ radical, leading to the zinc 2hydroxy-2-ethoxide 1-C.^[12] The in-cage protonolysis reaction between 1-C and the remaining $\{EtZn(L^2)\}$ moiety releases the observed ethane and produces the zinc gemdiolate intermediate 1-D, the identity of which was confirmed by the ¹H NMR signature resonances of the CH and CH₃ protons. Metastable 1-D produces the carboxylate 1-E, most likely by slow Lewis acid-assisted hydride elimina-

tion.^[13] Finally, 1-E rearranges to 2 with the concomitant formation of the bischelate complex 3.

In conclusion, this study has revealed new reaction pathways previously unseen for zinc $alkyl/O_2$ systems, namely the transformation of ZnOOR species into the corresponding zinc carboxylate unit. The reaction system described herein that is based on a pyrrolic scaffold may be helpful in achieving more sophisticated design of model compounds for numerous biochemical reactions and small molecule catalysts. The results also promise greater tuning of transformations involving reactive oxygen-centered radicals.

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