New Insights into the Reaction of Zinc Alkyls with Dioxygen

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The activation of dioxygen by organometallic compounds remains a largely unexplored area, despite extensive literature on the subject.[1] This fact well expresses a history of investigations of zinc alkyls with O_2, which was recently nicely shown by Seyferth .[2] It has been over 150 years since the high reactivity of zinc alkyls toward oxygen was noted by Frankland.[3] Since that time, the interaction of zinc alkyls with O_2 has been of continuous interest from a fundamental and practical point of view. Zinc alkyls react spontaneously with O_2, and according to common beliefs these reactions are so fast that little control of the desired products is possible. Frankland had already noted that controlled oxidation of Et_2Zn affords the alkoxides $Zn(OEt)_2$.[4] Interestingly, in 1864, Lissenko argued for the formation of RZnOR compounds.[5] However, most of the later studies considered the oxygenation reaction as proceeding with oxidation of both Zn−C bonds. For example, the formation of partly oxidized species was questioned by Abraham (1960): "we cannot explain Lissenko's observation that EtZnOEt is the final product."[6] According to Abraham,[6] and also Davies,[7] both Zn−C bonds in R_2Zn molecules are easily oxidized in several minutes after the start of the reaction with the formation of compounds formulated as $Zn(OOR)_2$, ROZnOOR, and $Zn(OR)_2$. Nevertheless, despite the long-lasting history of studies, significant uncertainties in the composition of the products and mechanistic considerations have been observed, and only recently have we reported the first structurally characterized zinc alkylperoxide, the dimeric $[EtOOZn(BDI)]_2$ (BDI $= \beta$-diketiminate ligand).[8]

We note that the alkylperoxide RZnOOR or ROOZn(O,N) (O,N = deprotonated amino alcohol) species prepared in situ by treating zinc alkyls with O_2 have been used as an efficient epoxidizing reagent for enones.[9,10] Contemporaneously, there has also been an increased interest in various radical additions initiated by the R_2Zn/O_2 system.[11] On the other hand, zinc alkoxides have attracted much attention on account of their rich structural and bonding features and potential applications, and a large number of the structurally characterized zinc alkoxides have been obtained from reactions between alcohols and zinc alkyls.[12] It is thus of interest to probe the fundamental question whether well-defined zinc alkyl-peroxides/alkoxides can be synthesized by the selective oxygenation of organozinc compounds. To explore this issue, we studied the interaction of O_2 with the alkylzinc chelate complex of type EtZn-(O,N) and reexamined the oxygenation of R_2Zn compounds.

The reaction of Et_2Zn with 1 equiv of 1-aziridineethanol (*azol*-H) in toluene affords the aggregate $[EtZn(azol)]_n$ (1) in an essentially quantitative yield. Molecular weight measurements of 1 in benzene solution suggest the presence of the trimer as the predominant species in solution. When the solution of 1 was exposed to an excess of dry O_2 at 0 °C for approximately 5 min and then stored at −20 °C, a white crystalline precipitate of $[EtOOZn(azol)]_2[EtZn(azol)]_2$ (2) was deposited (yield 92%).

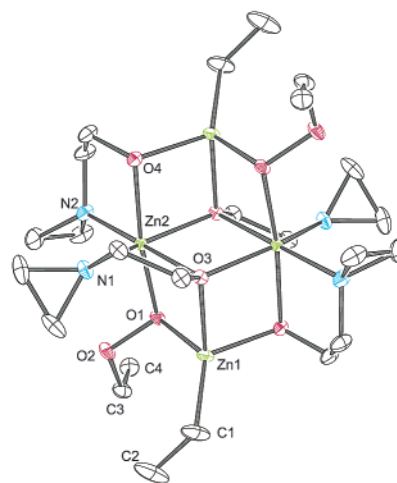† Warsaw University of Technology.
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Figure 1. Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level.

The ^{1}H NMR spectrum of **2** reveals two chemically inequivalent ethyl groups, that is, the Zn-bonded and O-bonded ethyl groups. The observed equal intensity of the corresponding ethyl resonances implies that only 50% of the Zn−C(Et) bonds were oxygenated (eq 1). The remaining Zn−C bonds undergo oxidation very slowly

$$4EtZn(azol) \xrightarrow{O_2} [EtOOZn(azol)]_2[EtZn(azol)]_2 \quad (1)$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$
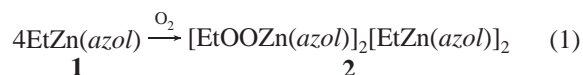
(in hours) as judged from the ^{1}H NMR spectra. The crystals of **2** obtained directly by the procedure outlined above were found to be suitable for an X-ray structure determination. The molecular structure of **2** (Figure 1) consists of a centrosymmetric cluster with two pairs of zinc atoms of a different coordination mode, and it may be viewed as being formed by association of the putative monomeric EtZn(*azol*) and EtOOZn(*azol*) moieties. The basic skeletal arrangement of **2** can be best described as an inversion-related, corner-removed face-shared cube (the four zinc atoms are located at four corners of a defective double cubane). There are two four-coordinate zinc atoms with the terminally Zn-bound ethyl group and the $ZnCO_3$ core, and two six-coordinate zinc atoms with peripheral ligation provided by the four chelating amine groups. The four zinc atoms of **2** are within the central core, two μ- and μ_3-alkoxide bridges provided by bidentate *azol* ligands, and two μ-peroxide bridges. The most striking point of the structure of **2** is the presence of the Zn−OOEt moiety. The ethyl peroxide group acts as bridging ligands between the tetrahedral and octahedral zinc atoms with the Zn2−O1 distance of 2.082(1) Å and Zn1−O1 distance of 2.025(1) Å.[13] The peroxo O1−O2 bond distance of 1.483(2) Å is close to that found for $[(BDI)ZnOOEt]_2$ (1.451(2) Å).[8]

The selective formation of **2** is striking, and its resistance toward further oxygenation may seem unexpected in view of the commonly assumed highly reactive nature of zinc alkyls toward O_2. Moreover, we revealed that, in solution, **1** and **2** are unaffected by O_2 as long as the sample is handled at -78 °C. We observed also significant inhibition of the reaction when a tetrahydrofurane solution of **1** was exposed to an excess of dry dioxygen at 0 °C.

Encouraged by the above results, we came back to the old problem of whether zinc alkoxides may be prepared in a desired manner by oxygenation of R_2Zn compounds. Therefore, we carried out the controlled reaction between Me_2Zn and O_2, which resulted in the isolation of the $Me_6Zn_7(OMe)_8$ (**3**), in high yield. X-ray crystallography reveals **3** as consisting of two distorted cubes which share a corner (Figure 1S). The resulting compound is isostructural with the previously reported $Me_6Zn_7(OMe)_8$[12c] and $Et_6Zn_7(OMe)_8$[12d] alkoxides (which were synthesized from the corresponding R_2Zn and methanol). Thus, formally, the reaction between Me_2Zn and O_2 may be depicted by eq 2, and **3** may be considered as an aggregate formed from the six partly oxygenated MeZnOMe species and one $Zn(OMe)_2$ unit. On the basis of earlier reports on the

$$7\ Me_2Zn \xrightarrow{\ O_2\ } \text{(structure 3)} \qquad (2)$$

3
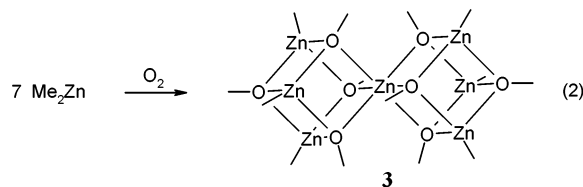
methanolysis of R_2Zn compounds,[12b,c,d,14] it is reasonable to assume that, in the controlled oxygenation of Me_2Zn, tetramer $[MeZnOMe]_4$ is formed initially, which then rearranges to the less soluble higher aggregated compound **3**. Nevertheless, irrespective of how **3** is formed, its isolation in high yield demonstrates that the selective oxygenation of R_2Zn is viable.

Moreover, our studies permit principal inferences concerning the reaction mechanism of zinc alkyls with O_2. The observed clean nature of the oxygenation reaction, the temperature control of this reaction, and the selective formation of the zinc alkylperoxide or alkoxide species are strong indications that the reaction may not be classified as the free radical chain process, that is, the commonly assumed mechanism.[7,15] Considering that $[RZn(O,N)]_n$ complexes are essentially aggregated species, which are at best only slightly dissociated into the three-coordinate monomers $RZn(O,N)$ in non-coordinating solvents, the fast oxygenation of alkylzinc chelate complexes proceeds to a large extent along a pathway requiring the low-coordinate species (Scheme 1). The observed inhibition of the alkoxides formation when the oxygenation of **1** was carried out in THF, the lack of the reaction for **1** at -78 °C, and the relatively slow oxygenation of the Zn—C bonds for **2** are all consistent with this contention. The substantial influence of THF on the reaction rate undoubtedly results from the formation of the four-coordinate $RZn(O,N)(THF)$ adduct, while decreasing of the reaction temperature would be expected to suppress the dissociation of $[RZn(O,N)]_n$ aggregates to the monomeric $RZn(O,N)$ species. In addition, **2** and **3** comprise tetrahedral alkylzinc centers, and they are also not prone to further reaction with O_2. Thus, the oxygenation reaction is inhibited or even completely suppressed if the availability of the low-coordinate species is under control. In line with these considerations also are our recent studies on the reaction of the well-defined three-coordinate EtZn(BDI) complex with O_2, which revealed fast and complete oxygenation of the Zn—C

bond (the reaction was completed in several minutes at 0 °C, to give the ethylperoxide $[EtOOZn(BDI)]_2$ in very good yield).[8]

Scheme 1

$$[RZn(O,N)]_n \rightleftharpoons R—Zn(\text{structure}) \rightleftharpoons [ROOZn(O,N)]_2[RZn(O,N)]_2$$

1   **2**
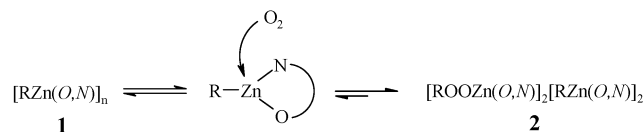
Finally, it is reasonable to propose that the initial step of the alkylzinc chelate complexes oxygenation involves a direct O_2 attack at the low-coordinate metal center followed by the insertion of dioxygen into the Zn—C bond (further studies are required to achieve an intimate understanding of this process). Moreover, the isolation of **2** clearly indicates that the resulting alkylperoxide is not reduced by a second equivalent of the organozinc reagent, as commonly postulated, but it forms with the latter a relatively stable adduct with tetrahedral alkylzinc centers. The lower reactivity of the $[ROOZn(O,N)][RZn(O,N)]$ type adduct toward O_2 than that of the $[RZn(O,N)]_n$ aggregates may be understood in terms of the stronger association of the $ROOZn(O,N)$ and $RZn(O,N)$ species in comparison to self-associated $[RZn(O,N)]_n$ complexes.

In conclusion, aside from any fundamental curiosity concerning the structure characterization of zinc alkylperoxide **2**, a plausible hypothesis concerning the reaction mechanism of zinc alkyls with O_2 has certainly been advanced. Further studies on the oxygenation of zinc alkyls are in progress.

Supporting Information Available: Crystallographic data of **2** and **3** (CIF) and experimental preparation details of **1**, **2**, and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) A significant drawback in the mechanistic studies is the fact that radical scavengers can act as donor ligands and they may simply affect the oxygenation reaction by complex formation with alkylzinc compounds.

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