Dioxygen Activation

DOI: 10.1002/ange.200601001

Reactions of $[ZnR_2(L)]$ Complexes with Dioxygen: A New Look at an Old Problem**

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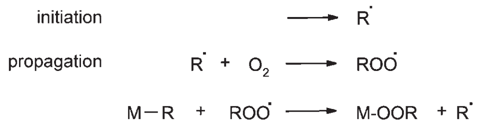
The interaction of zinc alkyls with dioxygen has received continuous interest for over 150 years, and common wisdom states that the oxygenation reactions of homoleptic zinc alkyls are uncontrollably fast. Moreover, significant uncertainties concerning both the composition of the products and mechanistic considerations have persisted. In pioneering studies, Frankland contended in 1849 that controlled oxygenation of $ZnEt_2$ affords $Zn(OEt)_2$,[1] and in 1864 Butlerov[2] and Lissenko[3] independently argued for the formation of the partly oxygenated species Zn(Et)OEt. In 1890 Demuth and Meyer postulated the formation of the alkylperoxide Zn(Et)OOEt from the insertion of an O_2 molecule into the Zn−C bond.[4] These pioneering interpretations have since been the subject of considerable debate;[5] however, most of the later studies considered the oxygenation reaction as proceeding with oxidation of both Zn−C bonds and the formation of compounds formulated as $Zn(OOR)_2$, Zn(OR)OOR, and $Zn(OR)_2$.[5c–f] Only very recently our group demonstrated convincingly that the controlled oxygenation of $ZnMe_2$ leads to the formation of partially oxygenated species in high yields,[6] and we structurally characterized the first examples of zinc alkylperoxides that were derived from the reaction of O_2 with monoalkylzinc chelate complexes.[6,7] The latter results have come in contradiction to the commonly accepted mechanism, which assumes a radical-chain process (Scheme 1).[8]

Apart from fundamental interest in the interaction of zinc alkyls with dioxygen, many practical applications have been found in both organic and materials chemistry which involve the oxygenation process. For example, the seminal studies of Chaudret and co-workers demonstrated that controlled oxygenation of the ZnR_2 precursor in THF in the presence of an amine ligand and moisture affords in one step crystalline ZnO nanoparticles of controlled size and shape.[9,10] The importance of zinc alkylperoxide complexes is also readily apparent from their continued use as reagents in organic synthesis. For decades, the reaction of organozinc complexes (particularly Zn(R)X compounds in the presence of ether solvents) with O_2 has been used to prepare hydroperoxides or alcohols, depending on the reaction conditions.[11] Furthermore, the alkylperoxide species Zn(R)OOR, prepared in situ by treating ZnR_2 with molecular oxygen, was reported as an efficient epoxidizing reagent for enones,[12] and the modified systems that were supported by auxiliary ligands enabled to conduct the epoxidation stereoselectively[13] and regioselectively.[7,14] Contemporaneously, there has also been increased interest in various radical additions initiated by the ZnR_2/O_2 system, in which an alkyl radical, as it has been commonly assumed, is generated through the reaction of dialkylzinc with dioxygen and acts as the chain carrier.[15] In spite of many contributions in this area, there is no answer to the question of how the oxygenated products participate in the radical reactions. Pertinent to the subject of our studies is also the fact that in the latter reactions, organic substrates usually bear electron-donor sites that are capable of forming Lewis acid–base adducts with ZnR_2, and essentially adducts of the type $[ZnR_2(L)_n]$ are actually involved in the reaction with dioxygen.



Scheme 1.

To obtain a deeper understanding of the factors that control reactions involving the ZnR_2/O_2 system, detailed information about the structure and properties of the organozinc intermediates is undoubtedly needed. However, it is perhaps astonishing that the reported systematic studies on the mechanistic aspects concerning the oxygenation of homoleptic zinc alkyls essentially end in the late 1960s.[5] As part of the ongoing exploration of the fundamental question as to whether well-defined zinc peroxides/alkoxides can be synthesized by the selective oxygenation of dialkylzinc complexes, we have conducted several control experiments to probe for factors that influence the reactivity and selectivity in the reaction of $Zn\mathit{t}Bu_2$ with dioxygen in the presence of donor ligands.

In the first step of our studies, a solution of $Zn\mathit{t}Bu_2$ in THF at −78 °C was treated with an excess of molecular oxygen, and the reaction mixture was stirred for approximately one minute. Then, the excess O_2 was removed in vacuum, and a white crystalline solid deposited from the solution after several hours at −25 °C. The spectroscopic data indicated that the interaction of the putative Lewis acid–base adduct $[Zn\mathit{t}Bu_2(thf)]$ with O_2 led to the selective oxygenation of one Zn−C bond and the formation of the alkoxide compound $[\{Zn\mathit{t}Bu(\mu\text{-}O\mathit{t}Bu)(thf)\}_2]$ (**1**, Scheme 2). The IR spectrum of the resulting product did not show the characteristic O−O peroxidic stretching vibration for alkylperoxide moieties, and the ^1H NMR spectrum consisted of single resonances for each group of protons. Thus, the oxidation of the first Zn−C bond in the presence of THF does not lead to an isolable alkylperoxide species. Nevertheless, this process offers a

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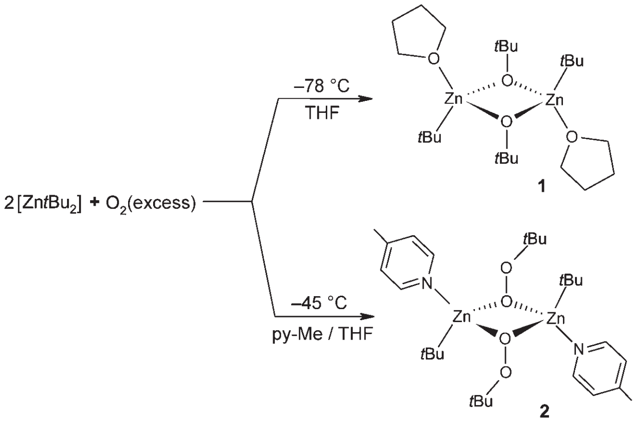
[**] This work was supported by the State Committee for Scientific Research (Grant No. 3 T09B 037 28).



Scheme 2. Synthesis of **1** and **2**.

route for the selective formation of alkylzinc alkoxides. Repetition of the reaction at room temperature resulted in the formation of a complex mixture of inseparable products. The crystals of **1** that were obtained directly by the procedure outlined above were found to be suitable for single-crystal X-ray diffraction analysis. The structure consists of a centrosymmetric dimer in which the two four-coordinate zinc centers are bridged by the *tert*-butoxide groups with the formation of a planar Zn_2O_2 core (Zn1–O1 1.982(1) Å, Zn1–O1′ 1.986 (1) Å, Figure 1). The coordination environment of the zinc atoms is completed by one *tert*-butyl group (Zn1–C5 2.016(2) Å) and one thf molecule (Zn1–O2 2.239(1) Å).[16]

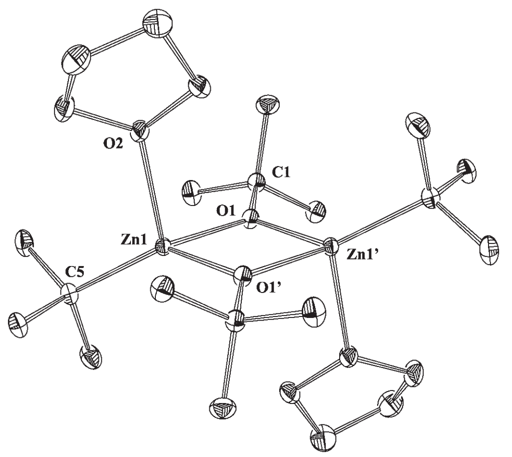


Figure 1. Molecular structure of **1** with thermal ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity.

To determine the effect of the strength of donor ligands on the oxygenation reaction, we conducted the analogous studies in the presence of 4-methylpyridine (py-Me). We expected that the application of py-Me as a strong N-donor ligand should decrease the reactivity of the Lewis acid–base adduct $[ZntBu_2(py\text{-}Me)_n]$ as well as enhance the stability of the resulting oxygenated products. Indeed, when a solution of $ZntBu_2$ in THF with one or two equivalents of py-Me was exposed to an excess of molecular oxygen (1 atm) at −78 °C, only traces of the oxygenation products were detected in the ^{1}H NMR spectrum after two hours. However, when the reaction involving the 1:1 or 1:2 $ZntBu_2$/py-Me system was conducted at about −45 °C for approximately 15 minutes, the *tert*-butylperoxide compound $[\{ZntBu(\mu\text{-}OOtBu)(py\text{-}Me)\}_2]$ (**2**) was isolated in good yield as a colorless solid after work up. Apparently, the pyridine ligand stabilizes the *tert*-butylperoxide species that results from the insertion of O_2 into one Zn–C bond. In the case of this $ZntBu_2$/py-Me system, the oxygenation reaction is easy to monitor as the reaction mixture is initially yellow and becomes colorless upon the formation of the *tert*-butylperoxide compound. Strikingly, we did not observe any induction period or inhibition of the oxygenation reaction in the presence of 0.1 mol% TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide).

The ^{1}H NMR spectrum of **2** indicated two chemically inequivalent *tert*-butyl groups and one py-Me molecule. The presence of the Zn–OO*t*Bu linkage was confirmed by the IR spectrum, which exhibited a band of weak intensity at 868 cm^{-1} that is attributable to the O–O peroxidic stretching vibration. The alkylperoxide compound **2** is surprisingly stable in solution in a nitrogen atmosphere under ambient conditions. Prolonged exposure of the reaction mixture to dioxygen resulted in further oxygenation, albeit at a significantly slower rate than the first step. Presumably, the formation of relatively stable four-coordinate alkylzinc species inhibits the oxidation of the remaining Zn–C bonds.[6] Single crystals of **2** suitable for an X-ray crystal structure determination were grown from THF at −25 °C. As seen in Figure 2, the molecule adopts a dimeric aggregation in the solid state by bridging through the *tert*-butylperoxide groups and the two four-coordinate zinc centers. The coordination environment of the zinc atoms is completed by one *tert*-butyl group and one py-Me ligand. The *tert*-butylperoxide ligands are oriented in an eclipsed–staggered conformation. A similar *tert*-butylperoxide geometry was found in the related indium and gallium complexes $[\{MtBu_2(\mu\text{-}OOtBu)\}_2]$,[17] and such a geometry presumably minimizes repulsion between the lone

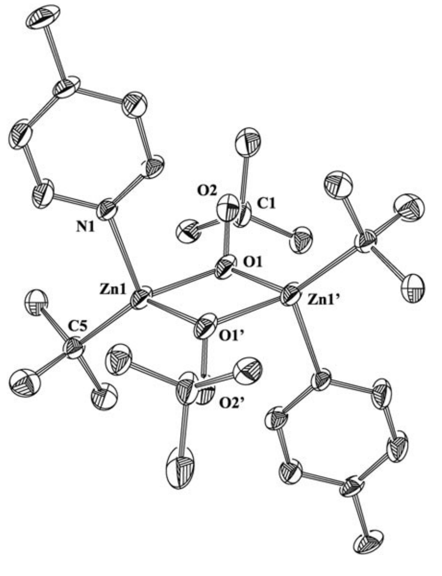
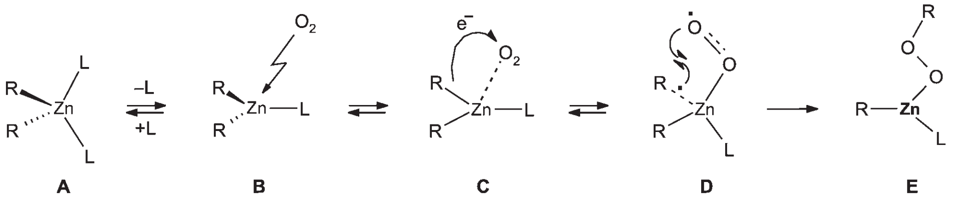


Figure 2. Molecular structure of **2** with thermal ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity.

pairs of electrons on the oxygen atoms. The aromatic rings of the py-Me ligands are perpendicular with respect to the central Zn_2O_2 ring. The corresponding bond lengths Zn1−C5 (2.008(11) Å), Zn1−O1 (1.990(8) Å), and Zn1−O1′ (1.987(8) Å) and the Zn1-O1-Zn1′ angle (101.88(27)°) are similar to those found for **1**. The O1−O2 bond length of 1.4289(11) Å is close to that found in other zinc alkylperoxides.[6,7]

The results not only highlight the marked tendency of zinc dialkyls to undergo oxidation of only one alkyl group under controlled conditions but also demonstrate that the identity of the donor ligand has a significant influence on the oxygenation process. The relatively strong Lewis base py-Me essentially inhibited the oxygenation of Zn*t*Bu$_2$ at −78 °C, whereas the reaction at slightly elevated temperature (ca. −45 °C) resulted in the highly selective formation of the alkylzinc peroxide compound **2**. In contrast, the thf-solvated species [Zn*t*Bu$_2$(thf)] reacted rapidly with dioxygen even at −78 °C to selectively form the alkylzinc alkoxide **1**. Our recent studies demonstrated that the attack of O_2 on the three-coordinate metal center is the initial step in the oxygenation of the alkylzinc chelate complexes [{RZn-(L,L′)}$_n$] (L,L′ = deprotonated amino alcohol).[6] Thus, the lower reactivity of the methylpyridine adduct(s) [Zn*t*Bu$_2$(py-Me)$_n$] toward O_2 at −78 °C compared to that of the tetrahydrofuran adduct(s) [Zn*t*Bu$_2$(thf)$_n$] may be understood in terms of the more hindered access of the oxygen molecule to the low-coordinate metal centers of the former species. Presumably, the dissociation of a ligand from the putative four-coordinate [ZnR$_2$(L)$_2$] complex is required prior to the effective attack of dioxygen (see **A** and **B**, Scheme 3).[18]



Scheme 3. Proposed reaction pathways for dioxygen insertion into the Zn−C bond.

Furthermore, the selective formation of the partially oxygenated four-coordinate compounds **1** and **2** are perhaps unexpected in view of the high reactivity of previously reported zinc dialkyls toward dioxygen, though this result is fully consistent with our recent findings that four-coordinate alkylzinc species are inert toward further oxygenation.[6] Another key observation is the stabilization of the resulting alkylperoxide Zn(*t*Bu)OO*t*Bu species by the nitrogen ligand.

The observed high selectivity is not consistent with the widely accepted mechanism involving a free-radical chain reaction that is initiated by an advantageous radical R$^\bullet$ (Scheme 1). Moreover, our earlier studies demonstrated that the initial step in the oxygenation of the main-group-metal alkyls involves the attack of O_2 on the metal center and that the approaching O_2 molecule has strong geometric requirements.[19] These findings indicate that O_2 must enter the first coordination sphere to oxidize alkylzinc complexes (**B**, Scheme 3), and one may view the primary step as involving the noncovalent activation of O_2 by the metal center (**C**). This weak interaction changes the electronic structure of the dioxygen molecule and induces low-energy pathways. Accordingly, the coordination of dioxygen to the metal center is followed by electron transfer from the Zn−C bond to O_2 to afford a solvent-caged radical pair **D**. At low temperature the postulated caged radical pair rearranges to generate selectively the alkylperoxide **E** (triplet-to-singlet surface crossing is required in order to transform **D** into **E**). However, at higher temperature the alkyl radical may diffuse away from the cage, which potentially constitutes the source of alkyl radical. This view finds support in the mentioned observation that the thf solvate of Zn*t*Bu$_2$ reacted with O_2 with the formation of a complex mixture of products at ambient temperature.

In conclusion, the reported studies open the way for the preparative exploitation of reactions involving zinc dialkyls and dioxygen. Moreover, a plausible hypothesis concerning the mechanism of O_2 activation by organometallic compounds has certainly been advanced. With more experimental results, it should then be possible to test and quantitatively improve the accuracy of the description of the proposed stepwise mechanism for the insertion of dioxygen into M−C bonds.

Experimental Section

1: A stirred solution of Zn*t*Bu$_2$ (0.403 g, 2.25 mmol) in THF (5 mL) was cooled to −78 °C. Under slightly reduced pressure an excess of dry dioxygen (1 atm) was introduced. After a minute the excess O_2 was removed, and the system was purged with nitrogen by using a vacuum–nitrogen line. The reaction mixture was stored at −25 °C, and white crystalline product deposited. Yield: 76 %; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C, TMS): $\delta = 1.00$ (s, 9H, C(CH$_3$)$_3$), 1.15 (s, 9H, OC(CH$_3$)$_3$), 1.67 (m, 4H, CH$_2$), 3.5 ppm (m, 4H, OCH$_2$); IR (nujol): $\tilde{\nu} =$ 1465(s), 1389(s), 1377(s), 1368(s), 1360(s), 1241(s), 1175(s), 1075(m), 1023(m), 1009(m), 940(m), 932(m), 895(s), 808(m), 756(m), 535 cm^{-1} (s). Elemental analysis (%) calcd for $C_{24}H_{52}O_4Zn_2$: C 53.93, H 9.74; found: C 53.82, H 9.78.

2: 4-Methylpyridine (0.209 g, 2.25 mmol) was added to a solution of Zn*t*Bu$_2$ (0.403 g, 2.25 mmol) in THF (4 mL) at ambient temperature. The resulting yellow solution was then cooled to −45 °C, and an excess of dry dioxygen (1 atm) was introduced. The oxygenation was continued until the solution became colorless (ca. 15 min). The reaction mixture was cooled to −78 °C, and the system was purged with nitrogen by using a vacuum–nitrogen line. The mixture was stored at −25 °C, and white crystalline product deposited. Yield: 67 %; ^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C, TMS): $\delta = 0.95$ (s, 9H, C(CH$_3$)$_3$), 1.00 (s, major, 9H, C(CH$_3$)$_3$), 1.02 (s, major, 9H, OOC(CH$_3$)$_3$), 1.10 (m, 9H, OOC(CH$_3$)$_3$), 2.31 (s, 3H, py-CH$_3$), 7.20 (d, ^3J(H,H) = 5.6 Hz, 2H, py), 8.52 ppm (d, ^3J(H,H) = 5.6 Hz, 2H, py); the two observed inequivalent signals for the *t*Bu group and the OO*t*Bu group in the relative ratio 1:8 for each group indicates the presence of geometrical isomers of **2**; IR (nujol): $\tilde{\nu} = 1670$(m), 1622(s), 1607(m), 1584(m), 1562(m), 1504(m), 1463(s), 1377(s), 1355(s), 1251(m), 1238(m), 11228(m), 1218(m), 1195(s), 1162(w), 1117(w), 1099(w), 1070(m), 1024(s), 1010(m), 979(w), 958(w), 938(w), 919(w), 895(w), 868(w), 840(m), 811(s), 804(s), 748(m), 722(m), 540 cm^{-1} (s). Elemental analysis (%) calcd for $C_{28}H_{50}N_2O_4Zn_2$: C 55.26, H 8.22, N 4.61; found: C 55.35, H 8.31, N 4.59.

Crystal data for **1**, $C_{24}H_{52}Zn_2O_4$: $M_r = 535.40$, crystal dimensions $0.45 \times 0.38 \times 0.22$ mm^3, monoclinic, space group $P21/c$ (no. 14), $a = 8.8503(2)$, $b = 9.6881(2)$, $c = 18.0968(3)$ Å, $\beta = 117.2500(10)°$, $V = 1379.79(4)$ Å^3, $Z = 2$, $F(000) = 576$, $\rho_{calcd} = 1.289$ g cm^{-3}, $\theta_{max} = 27.49°$, $R_1 = 0.0335$, $wR_2 = 0.0845$ for 2841 reflections with $I_o > 2\sigma(I_o)$. The structure was solved by direct methods with the SHELXS-97[20] program and was refined by full matrix least squares on F^2 by using the program SHELXL-97.[21] H-atoms were included in idealized positions and refined isotropically. Crystal data for **2**, $C_{28}H_{50}Zn_2N_2O_4$: $M_r = 609.44$, crystal dimensions $0.50 \times 0.45 \times 0.25$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.9759(9)$, $b = 9.2799(8)$, $c = 10.8850(12)$ Å, $\alpha = 113.108(4)$, $\beta = 98.931(6)$, $\gamma = 101.346(6)°$, $V = 790.18(15)$ Å^3, $Z = 1$, $F(000) = 324$, $\rho_{calcd} = 1.281$ g cm^{-3}, $\theta_{max} = 20.98°$. The structure was solved by direct methods with the SHELXS-97[20] program and was refined by full matrix least-squares on F^2 by using the program SHELXL-97.[21] H-atoms were included in idealized positions and refined isotropically. Final R indices: $R_1 = 0.0694$, $wR_2 = 0.1824$ for 1359 reflections with $I_o > 2\sigma(I_o)$. CCDC-297287 (**1**) and CCDC-297288 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: March 14, 2006
Published online: June 23, 2006

Keywords: alkylperoxo ligands · dioxygen activation · reaction mechanisms · structure elucidation · zinc

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