Communications

Oxygenation of a Me₂Zn/α-Diimine System: A Unique Zinc Methylperoxide Cluster and Evidence for Its Sequential Decomposition Pathways**

Janusz Lewiński, Karolina Suwała, Marcin Kubisiak, Zbigniew Ochal, Iwona Justyniak, and Janusz Lipkowski*

Interest in the reaction of alkylzinc complexes with O_2 has persisted for over 150 years since the pioneering studies by Frankland.[1] The nature of the products, however, has been the subject of intense controversy. The widely accepted free-radical chain-reaction mechanism for these reactions, as found in the vast majority of text books, assumes the initiation by adventitious alkyl radicals (R·) followed by a cascade of fast reactions with little opportunity for the detection of intermediates.[2] Recently, however, we provided unambiguous proof that R_2Zn compounds, or their adducts with Lewis bases, have a marked tendency to undergo oxidation of only one alkyl group under controlled conditions with subsequent formation of RZnOOR or RZnOR species, and simultaneously structurally characterized the first examples of zinc alkylperoxides.[3–5] We also proposed a plausible hypothesis for the mechanism of the reaction of alkylzinc complexes with O_2.[5,6]

In recent years there has been an increased interest in various radical additions initiated by the R_2Zn/O_2 system, especially regarding organic substrates which contain donor sites capable of forming the Lewis acid/base adducts with R_2Zn that are actually involved in the reaction with O_2.[7] This latter fact is usually ignored, and another assumption made in this field, which seems irrefutable, involves an alkyl radical R· (generated through the oxygenation reaction) acting as the chain carrier. Moreover, the most effective initiation systems involve Me_2Zn,[7f,g] which, according to recent findings,[4,8] can be selectively transformed into MeZnOMe without the generation of free Me· radicals. In light of this fact, as well as the lack of structurally characterized ZnOOMe species,[9] it seemed reasonable to wonder how the oxygenated products participate in radical reactions.

To gain a more in-depth view of both the role of the supporting ligands and the character of the radical species formed in the reactions of Me_2Zn with O_2, we have turned our attention to α-diimines, which have been widely used in fundamental coordination chemistry as noninnocent ligands.[10] In the field of zinc chemistry, van Koten et al. have extensively studied the reactions of R_2Zn compounds with 1,4-diazabutadiene (R-DAB) ligands and have demonstrated convincingly that this reaction system smoothly forms both paramagnetic and diamagnetic species.[10a,11] Herein we report the synthesis and structural characterization of a novel zinc oxo(methylperoxide) cubane along with the MeO· radical entrapped product, the formation of which involves ZnO–OMe bond homolysis.

Previous studies have demonstrated that the treatment of Me_2Zn with tBu-DAB in diethyl ether at ambient temperature results in the formation of [Me₂Zn(tBu-DAB)] (1).[11] According to the authors, the four-coordinate adduct **1** is rather stable under these reaction conditions and only upon heating above 35°C does it undergo an inner-sphere single electron transfer to give the radical pair [MeZn(tBu-DAB·)-(Me·)], which subsequently dimerizes to the C–C coupled dinuclear compound [{MeZn(tBu-DAB·)}₂] (**2**; Scheme 1). In light of these findings, we decided to modify the reaction system slightly and, in the first instance, stirred equimolar amounts of tBu-DAB and Me_2Zn in toluene at 22°C for 7 h.[12] The solution was then cooled to −20°C and exposed to an excess of O_2 for the next 16 h, which resulted in a gradual color change from deep purple to pink. Both the novel methoxide **3** and the oxo(methylperoxide) cubane **4** were isolated from the resulting mixture, in modest yield, after workup by fractional crystallization (Scheme 1). Compound **4** was reproducibly isolated in high yield, as the sole product, when a toluene solution of tBu-DAB and Me_2Zn was prepared and subsequently exposed to O_2 at −20°C for 16 h. Furthermore, compound **4** was found to slowly rearrange to the double cubic oxo(methoxide) **5** (Scheme 1) over a few days at 0°C. The composition of the isolated products was supported by ¹H NMR and IR spectroscopy, and their molecular structures were confirmed by single-crystal X-ray diffraction studies (see below).
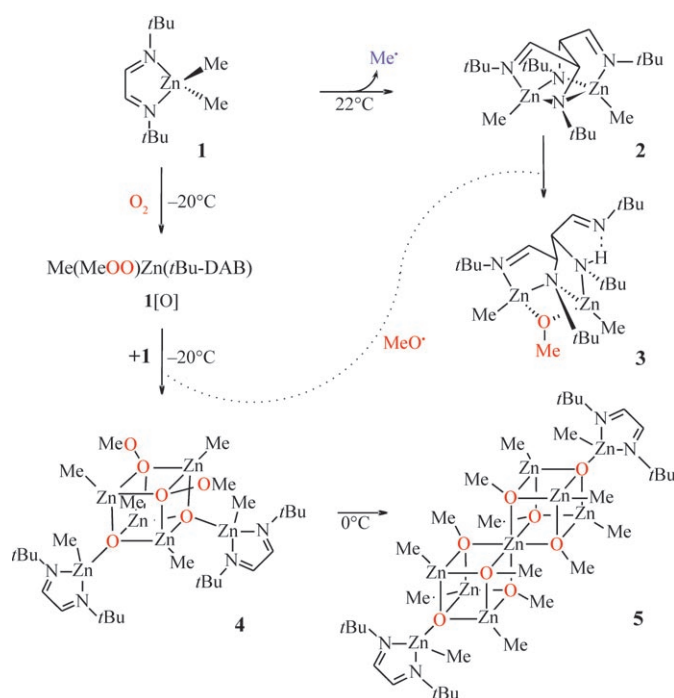
To gain further insight into the oxygenation of **1**, a solution of **1** in [D₈]toluene was saturated with dioxygen at −20°C and ¹H NMR spectra were recorded over time (Figure 1). This study confirmed that the oxygenation of **1** is relatively slow and proceeds in several distinct stages. Thus, upon addition of O_2, new sets of signals associated with

[*] Prof. Dr. J. Lewiński, K. Suwała, M. Kubisiak, Dr. Z. Ochal
Department of Chemistry, Warsaw University of Technology
Noakowskiego 3, 00-664 Warsaw (Poland)
Fax: (+48) 22-6607-279
E-mail: lewin@ch.pw.edu.pl
Homepage: http://lewin.ch.pw.edu.pl

Prof. Dr. J. Lewiński, Dr. I. Justyniak, Prof. Dr. J. Lipkowski
Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw
(Poland)

Scheme 1. Reactions of [Me₂Zn(*t*Bu-DAB)] (**1**).

Figure 1. ¹H NMR spectra for the oxygenation of **1** at −20 °C ([D₈]toluene) before introduction of O₂ (a) and during the reaction with O₂ after 5 min (b), 16 h (c), and 48 h (d); □: **1**[O], ●: **4**, ▰: other oxygenated species.

oxygenated species appear immediately in the spectrum, thereby indicating the formation of a number of oxygenated species. After 5 min, the spectrum is dominated by the signals of **1**[13] as well as those of a new intermediate species, thought to be the methylperoxide compound [Me(MeOO)Zn(*t*Bu-DAB)] (**1**[O]; Scheme 1), as a minor component of the mixture (the observed relative intensity of the corresponding OOMe and N*t*Bu signals is consistent with the proposed formula of **1**[O]). The signals associated with **1** and **1**[O] decrease in intensity with time and those corresponding to the oxo(methylperoxide) **4** increase. The reaction is completed within about two days (the observed additional sets of signals in the regions of OOMe and ZnMe protons in the final spectrum probably result from the presence of a different form of compound **4** in solution and/or additional products of an as yet unidentified structure).

Although it is premature to discuss the precise mechanism at this stage, the oxygenation of **1** can be rationalized by assuming the following pathways. The spectroscopic data clearly indicate that the methylperoxide **1**[O] is formed in the first step. This intermediate decomposes by initial homolysis of the oxygen–oxygen bond to yield MeZnO· and MeO· radicals, and the putative oxyzinc radical then recombines with the parent complex **1** to produce a zinc–oxo species and generate the Me· radical [Eq. (1); the *t*Bu-DAB ligand is omitted for clarity]. Subsequent rearrangements of the resulting zincoxane with **1**[O] lead to oxo(methylperoxide) **4**. Such an interpretation is consistent with the observation
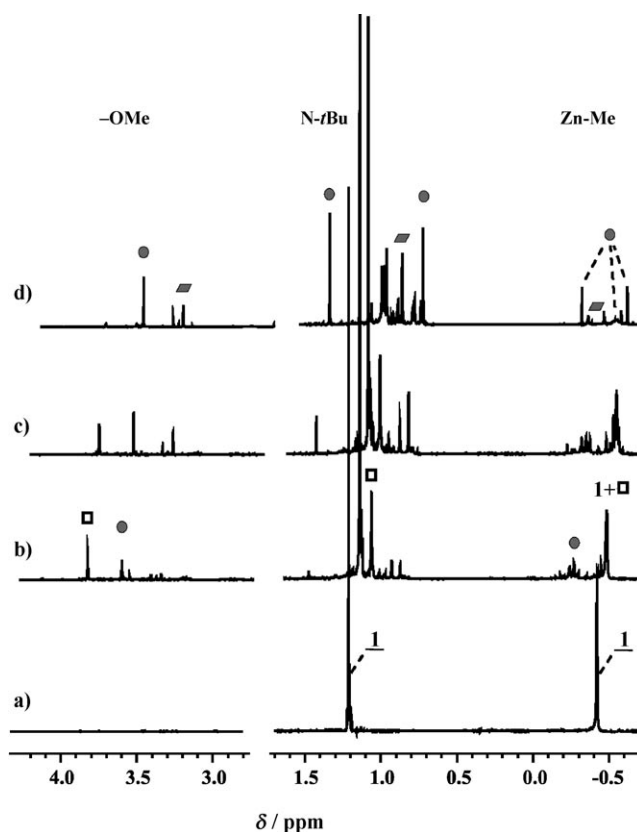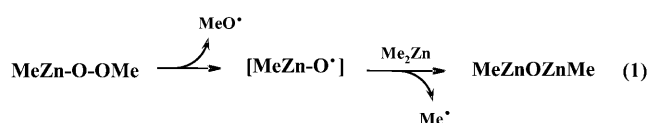

that every zinc atom in **4** retains one Me group and that the other half of the Zn−Me bonds from the starting reaction mixture are consumed during the oxygenation process. Moreover, this mechanism explains the source of the methoxide unit, which is essential for the formation of **3**.[14] In addition, we have identified N-methylated *t*Bu-DAB in the reaction mixture, which supports the formation of Me· radical as a reaction intermediate.[15]

The formation of **4** is in strong contrast to the observations made in the controlled oxygenation of *t*Bu₂Zn in the presence of 4-methylpyridine (py-Me), which affords exclusively the dimeric alkylperoxide [{*t*BuZn(μ-OO*t*Bu)(py-Me)}₂].[5] Nevertheless, the observed transformation of the ZnOOMe species to the zincoxane is fully consistent with our recent studies on the oxygenation of an alkylzinc carboxylate complex, which leads to the oxo-encapsulated aggregate.[6] It is also worth noting that oxide entrapment in the oxygenation reactions of alkylzinc compounds has also occasionally been observed,[16] although homolytic O−O bond cleavage to give metal–oxo species has not generally been considered to be an efficient mode of decomposition for main-group metal alkylperoxides.[17,18] Furthermore, this transformation of zinc alkylperoxides into oxo species could also be relevant to the recently developed methodologies for the preparation of ZnO nanoparticles from alkylzinc precursors, especially the high-temperature method based on the R₂Zn/O₂/amine

system[19] or the low-temperature procedure involving the R$_2$Zn/O$_2$/H$_2$O/amine system,[20] and thermolysis of [RZnOR']$_4$ precursors in the presence of O$_2$ (the presence of oxyzinc radicals has been demonstrated for the latter procedure in the resulting ZnO samples).[21]

An X-ray crystal structure analysis demonstrated that **3** contains a monoanionic unsymmetrical amido–imino *t*Bu-DAB-DAB(H)-*t*Bu ligand, two MeZn moieties, and one methoxide anion (Figure 2a). Thus, the molecular structure of **3** can be considered as arising from the trapping of a MeO˙ radical by the C–C coupled dinuclear [{MeZn(*t*Bu-DAB)}$_2$] moiety followed by an intriguing reorganization of the

a)

b)

c)

Figure 2. Molecular structure of a) **3**, b) **4**, and c) **5**, with thermal ellipsoids set at 30% probability; hydrogen atoms have been omitted for clarity.

diamido-diimino ligand. The amido-imino core acts as a tridentate ligand, with one imine group remaining uncoordinated and becoming involved in the formation of an intra-molecular N−H⋯N hydrogen bond (dotted line in Figure 2a). The metal–ligand bond lengths are typical for zinc complexes with R-DAB ligands.[22]

The molecular structure of **4** consists of a discrete asymmetric hexanuclear unit which may be formally viewed as being formed by the association of two dimethylzincoxanes (MeZnOZnMe) and two MeZnOOMe moieties (Figure 2b). The basic skeletal arrangement of **4** consists of a central Zn$_4$O$_4$ heterocubane motif with the two terminally bonded MeZn units supported by *t*Bu-DAB ligands. The peroxide O−O distances (1.460(7) and 1.459(6) Å) are similar to the corresponding bond lengths found in zinc μ$_2$-ethylperoxide complexes.[3,4] The distances between the bridged oxo centers and the terminal zinc atoms (mean: 1.926 Å) are slightly shorter than the corresponding Zn−O distances within the central cube (mean: 1.999 Å), whereas the peroxide Zn−O distances are the longest (mean: 2.132 Å).

The molecular structure of **5** consists of two corner-sharing distorted oxo-methoxide cubanes flanked by two MeZn units chelated by *t*Bu-DAB (Figure 2c). Thus, **5** may formally be considered as a bis(heterocubane) formed from cubane **4** with concomitant decomposition of the methylperoxide groups. The rearrangement of cubane **4** to bis(cubane) **5** resembles that observed for alkylzinc alkoxide heterocubanes, which for the latter group is likely determined by steric factors.[8,23] The Zn−O(oxo) (1.933–2.000 Å) and the Zn−N distances (mean: 2.186 Å) in **5** are similar to those observed for **4**.

In summary, *t*Bu-DAB appears to be a very efficient supporting ligand for both the selective oxygenation of Me$_2$Zn and the transformation of ZnOOMe species, and the alternative view provided herein of the source of radical species in the oxygenation reaction may be of importance in comprehending the mechanism operating in radical organic reactions promoted by the R$_2$Zn/O$_2$ system.[7] This synthesis of oxo(methylperoxide) and oxo(methoxide) cubanes with preformed Zn−O bonds could also provide access to potentially efficient precursors of ZnO nanoparticles, and work along these lines is currently underway.

Experimental Section

3: *t*Bu-DAB (0.314 g, 1.85 mmol), Me$_2$Zn (0.176 g, 1.85 mmol), and an excess of dry dioxygen (1 atm) were used, and **3** was isolated as reddish crystals (0.028 g, 23%). See text for further details. C,H,N analysis (%) calcd for C$_{23}$H$_{50}$N$_4$OZn$_2$: C 52.17, H 9.52, N 10.58; found: C 52.20, H 9.58, N 10.55; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = −0.31 (s, 3H; CH$_3$Zn), −0.35 (s, 3H; CH$_3$Zn), 1.04 (s, 9H; (CH$_3$)$_3$C), 1.05 (s, 18H; (CH$_3$)$_3$C), 1.07 (s, 9H; (CH$_3$)$_3$C), 2.71 (d, 2H, *J* = 5.9 Hz; C*H*-CH=), 2.81 (s, 1H; NH), 3.52 (s, 3H; CH$_3$OZn), 7.74 ppm (d, 2H, *J* = 5.9 Hz; CH=N).

4: This compound was synthesized following a similar procedure, except that the reaction mixture was not stirred at room temperature initially. Compound **4** was isolated as yellow crystals that are stable at room temperature under an inert atmosphere (yield: 0.185 g, 72%). C,H,N analysis (%) calcd for C$_{28}$H$_{64}$N$_4$O$_6$Zn$_6$: C 35.59, H 6.83, N 5.93; found: C 35.50, H 6.80, N 5.91; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = −0.39 (s, 6H; CH$_3$Zn), −0.37 (br s, 6H; CH$_3$Zn), −0.30 (s, 6H; CH$_3$Zn), 1.10
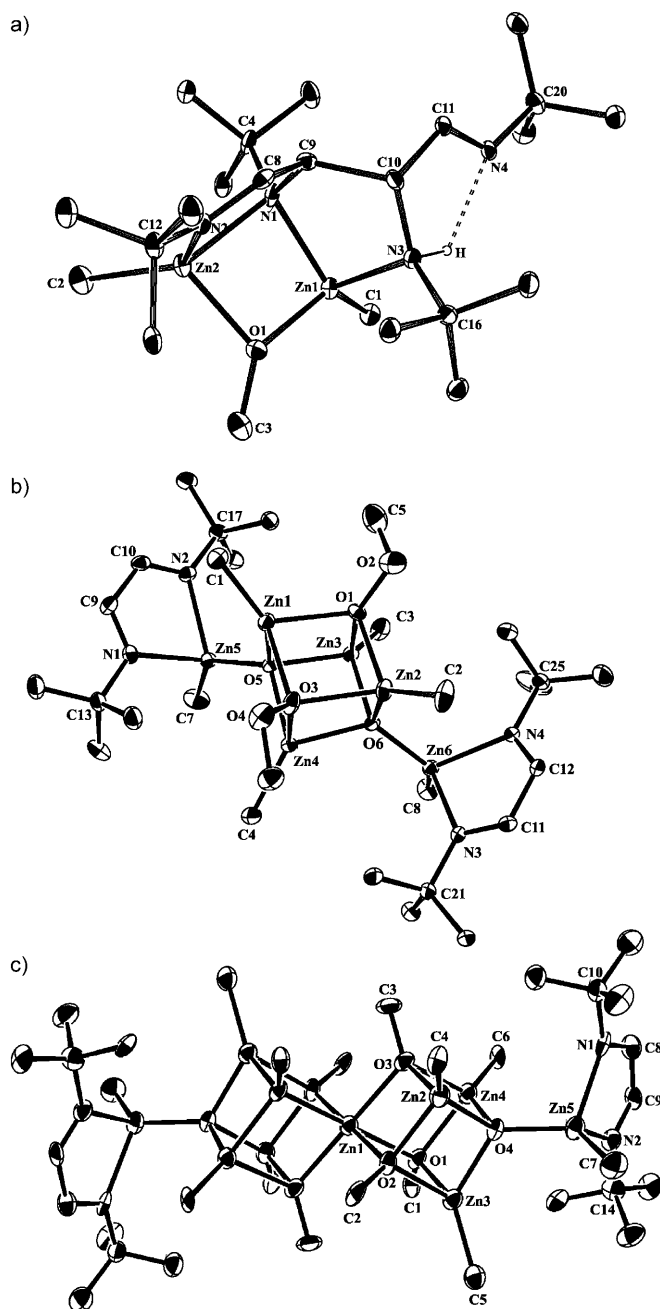
(s, 18 H; (CH$_3$)$_3$C), 1.35 (s, 18 H; (CH$_3$)$_3$C), 3.83 (s, 6 H; CH$_3$OO), 8.05 ppm (s, 4 H; CH=N). IR (nujol): $\tilde{\nu}$ = 813 cm^{-1} (w, ZnOOMe).

5: Compound **4** (0.15 g, 0.159 mmol) was dissolved in toluene and left at 0°C and colorless crystals of **5** deposited after three days (0.123 g, 82%). C,H,N analysis (%) calcd for C$_{34}$H$_{82}$N$_4$O$_8$Zn$_9$: C 32.32, H 6.54, N 4.43; found (after drying in vacuo for 10 h): C 32.35, H 6.50, N 4.38; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = −0.42 (s, 18 H; CH$_3$Zn), −0.37 (s, 6 H; CH$_3$Zn), 1.14 (s, 36 H; (CH$_3$)$_3$C), 3.46 (s, 18 H; CH$_3$OZn), 8.01 ppm (s, 4 H; CH=N).

Crystal data for **3**: C$_{23}$H$_{50}$N$_4$OZn$_2$, M_r = 529.41, triclinic, space group P$\bar{1}$ (no. 2), a = 8.6014(5), b = 11.0696(6), c = 15.1818(10) Å, α = 75.827(3), β = 82.690(3), γ = 79.250(4)°, V = 1371.87(14) Å^3, Z = 2, F(000) = 568, ρ_{cald} = 1.282 g cm^{-3}, T = 100(2) K, $R1$ = 0.0476, $wR2$ = 0.0909 for 2712 reflections with $I_0 > 2\sigma(I_0)$; crystal data for **4**: C$_{28}$H$_{64}$N$_4$O$_6$Zn$_6$, M_r = 945.05, monoclinic, space group P2$_1$/c (no. 14), a = 17.1410(5), b = 12.9560(4), c = 20.1740(4) Å, β = 109.849(2)°, V = 4214.0(2) Å^3, Z = 4, ρ_{cald} = 1.490 g cm^{-3}, T = 100(2) K, $R1$ = 0.0420, $wR2$ = 0.0967 for 4034 reflections with $I_0 > 2\sigma(I_0)$; crystal data for **5**: C$_{34}$H$_{82}$N$_4$O$_8$Zn$_9$·toluene, M_r = 1355.50, triclinic, space group P$\bar{1}$ (no. 2), a = 9.4810(7), b = 10.6910(9), c = 15.1790(14) Å, α = 87.115(4), β = 77.923(5), γ = 75.790(5)°, V = 1458.5(2) Å^3, Z = 1, ρ_{cald} = 1.543 g cm^{-3}, T = 100(2) K, $R1$ = 0.0677, $wR2$ = 0.1324 for 2626 reflections with $I_0 > 2\sigma(I_0)$. The structures were solved by direct methods using the program SHELXS-97[24] and refined by full-matrix least-squares calculations on F^2 using the program SHELXL-97.[25] All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically. All hydrogen atoms were included at geometrically calculated positions and refined using a riding model. CCDC 687805 (**3**), 687806 (**4**), and 687807 (**5**) 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.

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[12] The ^{1}H NMR spectrum of this reaction mixture displayed signals characteristic for the C−C coupled product, which suggests that the choice of solvent has a significant effect on the stability of the R$_2$Zn(R′-DAB) type adducts.

[13] The relatively slow oxygenation of **1** observed at −20°C is likely to be a consequence of an inhibition of the "on-off" process, which involves η$_1$-monodentate and η$_2$-bidentate coordination of *t*Bu-DAB as activation of O$_2$ proceeds via the three-coordinate η$_1$-DAB-ZnMe$_2$ adduct: the system is much less fluxional at low temperature and low-coordinate domains capable of activating O$_2$ are not available.

[14] The resulting readily diffusible MeO$^\bullet$ radical can be trapped directly by compound **2** to form **3** or, alternatively, this radical can abstract hydrogen from the solution bulk to produce MeOH and subsequently recombine with **2**.

[15] (*Z*)-N^1,N^2-di-*tert*-butyl-N^1-methylethene-1,2-diamine was extracted with hexane from the solid residue of the post-reaction mixture; GC-MS (EI) data found for C$_{11}$H$_{24}$N$_2$: *m/z* 184; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.93 (s, 9 H), 1.02 (s, 9 H), 3.09 (br s, 1 H), 3.37 (s, 3 H), 4,43 (d, J = 7.2 Hz, 2 H), 7.28 ppm (d, J = 7.2 Hz, 2 H).

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