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From Neutral Zn_4O_4 Clusters to a Cationic ZnO Dimer in Solution

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Summary: The suitability of the tetrameric ZnO aggregates [(iPrO)ZnMe]$_4$ (**1a**) *and* [(Me_3SiO)ZnMe]$_4$ (**1b**) *as potential sources for molecular models of low-coordinated zinc centers and active sites on zinc oxide catalysts is reported. The formation and fate of the resulting cationic* Zn_4O_4 *degradation products by reaction of* **1a** *and* **1b** *with* $B(C_6F_5)_3$ *in the presence of different organic donor substrates have been studied by means of ESI mass spectrometry. While* **1a** *affords the cationic monozinc complexes* $[MeZn(L)]^+$ (**2a**: *L* = *THF*, **2b**: *15-c-5*, **2c**: *DMAP), the cluster* **1b** *furnishes in the presence of DMAP* $[MeZn(OSiMe_3)_2Zn(DMAP)_2]^+$ (**3**), *the first dimeric ZnO aggregate cation in solution, and the* $[MeB(C_6F_5)_3]$ *anion. Additionally, the neutral dinuclear ZnO aggregate* $[(Me_3SiO)Zn(C_6F_5)thf]_2$ (**4**) *results from Me/C_6F_5 exchange reactions as the final product, which has been characterized by NMR spectroscopy and a single-crystal X-ray diffraction analysis.*

Introduction

Zinc oxide is an important heterogeneous catalyst for the conversion of water gas (CO, CO_2, H_2) to methanol. Interestingly, the catalytic activity of ZnO can be significantly increased by the presence of promotors such as copper or alkali metals, which apparently change the electronic properties of the active sites at the ZnO surface.[1−3] However, the efficiency of the catalytic systems depends not only on their composition but also on the size of the particles due to several structural defects.[4] Therefore, the explanations for different activities of nondoped and doped “real” ZnO catalysts have been a matter of controversial discussions in the literature, and the complex reaction mechanism could not be understood until recently.[5,6] From results of different working groups, it is known that the reaction on the ZnO surface takes place at low-coordinate, highly electrophilic zinc centers.[7,8] Another possibility to evaluate the role of such zinc centers as active sites on ZnO surfaces is offered by using the model catalyst approach. The latter may allow changing specifically the environment of active zinc centers at the molecular level. We have reported the synthesis of a wide range of different molecular Zn_nO_m clusters[9] that are suitable single-source precursors for the synthesis of nanoscaled zinc and zinc oxide particles,[10] but they could also be promising sources for molecular models of terminal, low-coordinated zinc centers on ZnO surfaces. However, molecular compounds with such highly electrophilic zinc atoms are expected to be extremely reactive and therefore difficult to isolate. In fact, only a few reports are known on the structural chemistry of mononuclear cationic zinc complexes,[11] but no polynuclear cationic ZnO cluster could hitherto be isolated. One alternative approach to generate polynuclear ZnO cluster cations is offered by mass spectrometric (MS) methods. We have currently shown that one can easily produce polynuclear ZnO cluster cations in the gas phase under EI-MS conditions.[10f] The used ZnO cluster sources are simply accessible by Bronsted acid−base reaction of dialkylzinc compounds with silanoles or alcohols.[9,10a,g] The nuclearity and the degree of aggregation of ZnO units is easily tunable by changing the steric demand of the substituent at the oxygen center. While methyl, trimethylsilyl, or isopropyl groups lead to Zn_4O_4 clusters, the use of larger substituents such as triphenylsilyl or *tert*-butyl favors the formation of spirocyclic Zn_3O_4 or Zn_6O_{10} clusters.[9] How could one achieve the synthesis and stabilization of cationic polynuclear ZnO clusters in the condensed phase using the latter molecular Zn_nO_m clusters? This could be achieved by replacing the alkyl group at the zinc atom by a large and weakly coordinating anion such as $B(C_6F_5)_4^-$ or $Al(OR_f)_4^-$ [R_f = $CH(CF_3)_2$, $C(CH_3)(CF_3)_2$, $C(CF_3)_3$].[12] This strategy has also been successfully used for the synthesis of highly electrophilic, cationic zirconium complexes, which are valuable homogeneous catalysts.[13] The abstraction of a alkyl group at the metal center can be achieved by reaction with strong

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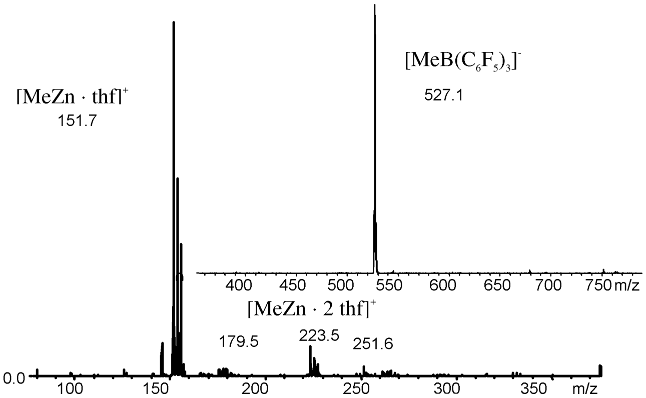


Figure 1. ESI(+)- and ESI(−)-MS of the samples taken from the reaction mixture of **1a** and B(C_6F_5)$_3$ in THF.

Lewis acids such as B(C_6F_5)$_3$. Here we report our results on the formation of the first cationic polynuclear ZnO clusters in solution. In order to synthesize polynuclear ZnO aggregate cations, we studied the reaction of the neutral Zn_4O_4 cluster precursors **1a** and **1b** with B(C_6F_5)$_3$ in the presence of different organic donor substrates. A suitable method for monitoring the reaction progress in the reaction mixtures is provided by the ESI-MS technique (ESI = electrospray ionization), because it gently transfers preformed ions directly from solution to the gas phase.[14] It is an effective method to investigate reaction pathways and to characterize reactive ionic intermediates.[15,16] Thus, we studied the behavior of the starting materials [(*i*PrO)ZnMe]$_4$ (**1a**) and [(Me$_3$SiO)ZnMe]$_4$ (**1b**) under ESI-MS conditions.

Solutions of **1a** and **1b**, respectively (0.09 mol in 10 mL of THF), were stirred at room temperature in an argon atmosphere. After 30 min, 100 μL of the solution was transferred into the ESI source by a syringe pump at a flow rate of 3 μL min^{-1} for the MS detection. In the beginning, a CapExit voltage of 98.5 V was applied. In both cases no signals of fragments of the Zn_4O_4 aggregates in the cation or in the anion mode were detected. When CapExit voltages ranging from 60 to 120 V were applied, no obvious differences were observed. Thus we fixed the standard procedure for MS detection. Subsequently, we investigated the reaction of [(*i*PrO)ZnMe]$_4$ (**1a**) with B(C_6F_5)$_3$ in THF without any additional stabilizing agent. A solution of **1** (0.09 mol) in 10 mL of THF was treated with B(C_6F_5)$_3$ (0.09 mol) at room temperature in an argon atmosphere. After the standard treatment, the signals of ions [MeB(C_6F_5)$_3$]$^-$ (principal ion *m*/*z* 527.1) and [MeZnthf]$^+$ (principal ion *m*/*z* 151.7) and a weak signal with low intensity of the ion [MeZn(thf)$_2$]$^+$ (principal ion *m*/*z* 223.5) were detected (Figure 1). We interpret the presence of the [MeB(C_6F_5)$_3$]$^-$ ion as the result of the transfer of one methyl group at the zinc center to the boron atom, and concomitantly, formation of the tetranuclear ZnO cluster cation [(ZnOiPr)(iPrOZnMe)$_3$]$^+$ occurs. Apparently, the initial tetranuclear aggregate cation is not stable in solution and affords, under liberation of [Zn(O*i*Pr)$_2$] and recombination of **1a**, the monozinc complex [MeZn(thf)]$^+$ (**2a**) with a low-coordinated zinc center (Scheme 1).

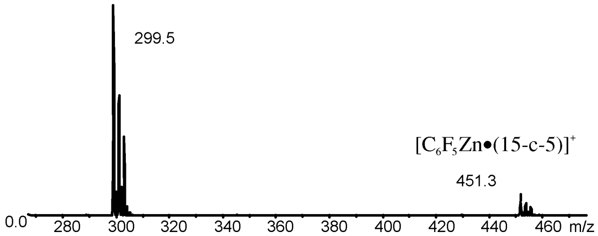
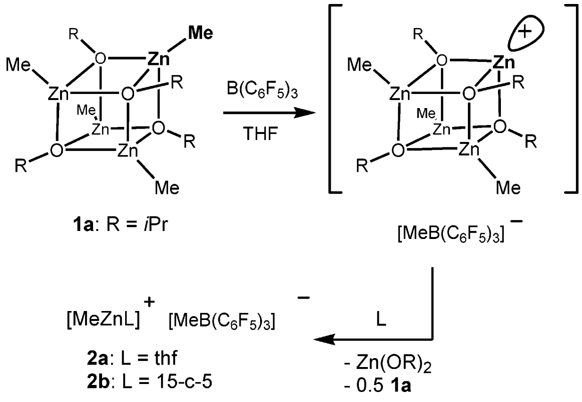


Figure 2. ESI(+)-MS of the samples taken from the reaction mixture of **1a** and B(C_6F_5)$_3$ in the presence of 15-c-5 in THF.

Scheme 1. Proposed Mechanism for the Degradation of [(*i*PrO)ZnMe]$_4$ in the Presence of B(C_6F_5)$_3$ in THF[a]



[a] 15-c-5 is 15-crown-5.

The recombined [(*i*PrO)ZnMe]$_4$ crystallized from the reaction solution and was characterized by X-ray determination. Additionally, the simultaneous formation of [Zn(O*i*Pr)$_2$] (**2**) and the re-formation of [(*i*PrO)ZnMe]$_4$ (**1a**) were proven by ^{1}H NMR spectroscopy.

In order to probe whether the initial tetranuclear ZnO cluster cation can be stabilized in the presence of other donor molecules than THF, we used the crown ether 15-c-5 because this ligand is able to stabilize RMg$^+$ and RZn$^+$ cations (R = Et, neopentyl) appropriately.[17] Treatment of a solution of **1a** (0.09 mol) in 10 mL of THF with B(C_6F_5)$_3$ (0.09 mol) in the presence of 15-c-5 (0.09 mol) at room temperature in an argon atmosphere leads to a clear solution. Using the aforementioned standard measurements for ESI-MS, the signals of the [Me(B(C_6F_5)$_3$]$^-$ anion and [MeZn(15-c-5)]$^+$ cation **2b** (principal ion *m*/*z* 299.5), respectively, and a weak signal with low intensity that can be assigned to the [C_6F_5Zn(15-c-5)]$^+$ cation (principal ion *m*/*z* 431.5) were detected (see Figure 2). The formation of the [C_6F_5Zn(15-c-5)]$^+$ cation indicates a methyl/C_6F_5 ligand exchange as side reaction. Hence, the presence of 15-c-5 does not stabilize the tetrameric ZnO aggregate cation but instead leads to similar cationic degradation products as outlined in Scheme 1. Attempts to use other strong donor molecules such as *p*-(dimethylamino)pyridine (DMAP) for the stabilization of the desired Zn_4O_4 cluster cation failed.

Since the steric and electronic nature of the substituent at the oxygen atom should have a noticeable influence on the stability of the primary polynuclear ZnO cluster cations, the siloxy-substituted cluster **1b** was probed. In analogy, solutions of [(Me$_3$SiO)ZnMe]$_4$ (**1b**) (0.09 mol) in 10 mL of THF were treated with B(C_6F_5)$_3$ (0.09 mol) in the presence of several organic donor substrates. However, only in the case of the use of DMAP (0.09 mol) were we able to detect the novel dinuclear ZnO cluster cation [MeZn(OSiMe$_3$)$_2$Zn(DMAP)$_2$]$^+$ (**3**) (principal ion *m*/*z* 569.4), besides the counterion MeB(C_6F_5)$_3$$^-$, as preferred

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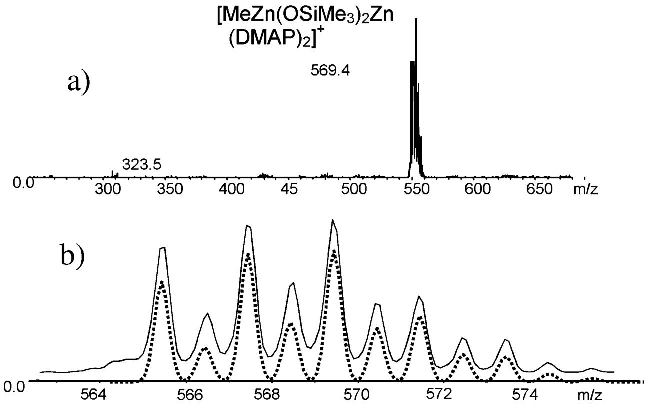
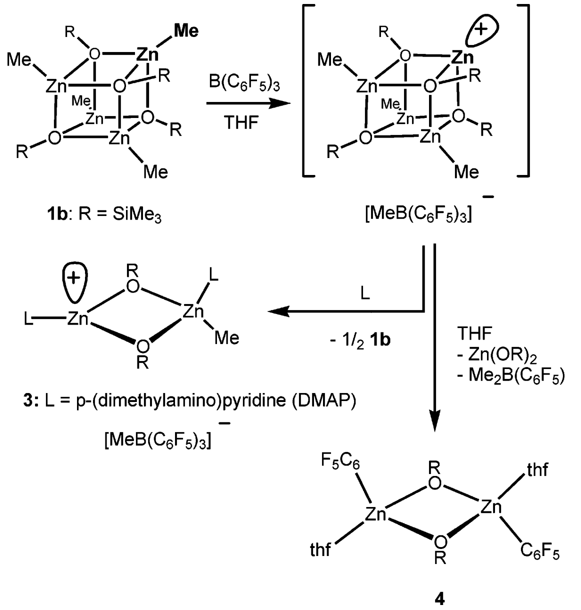


Figure 3. (a) ESI(+)-MS (CapEx 98.5 V) of the samples taken from the reaction mixture of **3** and $B(C_6F_5)_3$ in the presence of DMAP in THF. (b) Calculated (···) and experimental pattern for $[MeZn(OSiMe_3)_2Zn(DMAP)_2]^+$, **3**.

Scheme 2. Proposed Mechanism for the Conversion of 1b with $B(C_6F_5)_3$ in THF in the Presence of DMAP



ionic species (Scheme 2). Its composition is proven by pattern calculation (Figure 3).

Additionally, the ESI-MS measurements were carried out again, using different parameters with CapEx 113.5 V and Skimmer 40 V. These led to the observation of additional signals of the stabilized cationic MeZn species $[MeZnDMAP]^+$ (**2c**) (principal ion *m*/*z* 201.7) and $[MeZn(DMAP)_2]^+$ (**2d**) (principal ion *m*/*z* 323.6). Clearly, the latter result implies a degradation process similar to that observed for **1a**. However, after 6 h the formation of the neutral dimeric ZnO cluster **4** is complete, which precipitates off in the reaction solution. Compound **4** can be isolated in the form of colorless cubes in 22% yield. Its constitution and composition are confirmed by NMR spectroscopy and a single-crystal X-ray structure analysis (Figure 5). The dimeric ZnO cluster **4** crystallizes in the monoclinic space group $P2_1/n$ and shows a nearly planar central four-membered ring (Figure 5). The Zn atoms are tetrahedral, while the O atoms are trigonal-planar coordinated. The values of the Zn−O distances (1.97 Å) and the Zn···Zn distances (2.88 Å) are in the same region as observed for other dimeric ZnO clusters.[4,10] Although the mechanism for the formation of **4** is hitherto unknown, its formation can be rationalized by a complete methyl/C_6F_5 exchange between the zinc and boron atoms and additional exchange of the DMAP ligand at zinc through THF (Scheme 2).

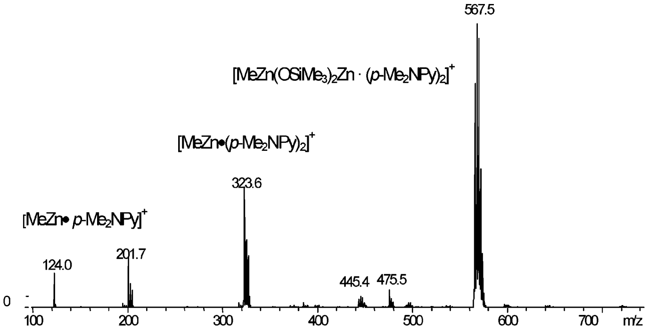


Figure 4. a. ESI(+)-MS (CapEx 113.5 V) of the samples taken from the reaction mixture of **1b** and $B(C_6F_5)_3$ in the presence of DMAP in THF.

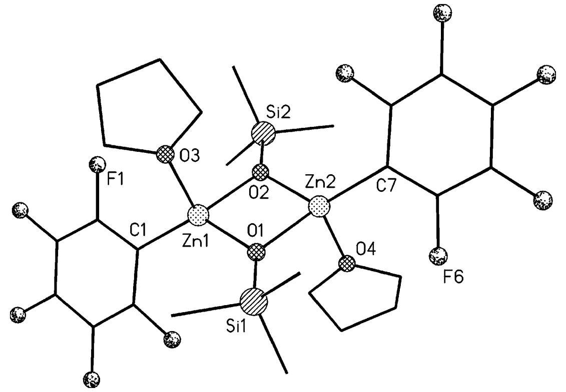


Figure 5. Molecular structure of $[(Me_3SiO)ZnC_6F_5(thf)]_2$, **4**. The hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Zn(1)−O(1) 1.967(2), Zn(1)−O(2) 1.966(3), Zn(2)−O(1) 1.963(3) Zn(2)−O(2) 1.966(2), Zn(1)−Zn(2) 2.8768(9) O(1)−Zn(1)−O(2) 85.87(10) O(1)−Zn(2)−O(2) 85.9(1), Zn(1)−O(1)−Zn(2) 94.1(1), Zn(1)−O(2)−Zn(2) 94.0(1).

The present investigation shows that the neutral tetrameric ZnO aggregates **1a** and **1b** undergo a $B(C_6F_5)_3$-assisted degradation, affording two types of highly electrophilic zinc complexes as ionic products, which could be unequivocally identified only by ESI-MS: (i) $[MeZnL]^+$ (**2a**−**2c**) or $[MeZnL_2]^+$ (**2d**) $[MeB(C_6F_5)_3]^-$ and (ii) $[MeZn(OSiMe_3)_2Zn(DMAP)_2]^+$ (**3**) $[MeB(C_6F_5)_3]^-$. However, due to Me/C_6F_5 exchange reactions, the latter ion pair converts slowly into the neutral dimeric ZnO compound **4**, which can be isolated in crystalline form. The simple access and the reasonable stability of the first dimeric ZnO cluster cation **3** in THF solutions offers a promising and versatile basis for model reactions of bonding activation and chemisorption processes of small molecules such as H_2, CO_2, and CO relevant in ZnO catalysis. Such studies are currently underway.

Experimental Details

All ESI-MS experimenets were performed on a Bruker Daltonics Esquire 3000+. The vacuum was maintained by a turbomolecular pump (ion source: 2×10^{-6} Torr). The ions were generated from an external electrosray ionization source. Typically the electrospray flow rate was 3 μL/min, which was maintained by a syringe pump. The spray was directed into a heated glass capillary drying tube with Pt coating in both ends, remaining at a temperature of about 500 K. Typically a high voltage of about 4000 V is applied between the endplate and the spray needle.

Preparation of 4. A solution of 50 mg (0.9 mmol) of **1b** and 10 mg (0.9 mmol) of DMAP in 5 mL of THF was slowly treated with a solution of 50 mg (0.9 mmol) of $B(C_6F_5)_3$ in 5 mL of THF at room temperature. Cooling of the clear solution at −20 °C affords colorless crystals of **4**. Yield: 30 mg (0.4 mmol; 22%); mp 134−137 °C (dec). ^{1}H NMR (C_6D_6): δ 3.7 (m, 4H, OCH_2CH$_2$), 1.8 (m, 4H, OCH$_2$CH_2), 0.2 ppm (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 0.8 (s, Si(CH$_3$)$_3$), 37.7 (s, O-CH$_2$), 17.6 (s, O-CH$_2$-CH$_3$), 137.4 (d, $^1J_{C-F}$ = 246.5 Hz, C_6F_5), 141.5 (d, $^1J_{C-F}$ = 208.1 Hz, C_6F_5), 149.0 (d, $^1J_{C-F}$ = 240.0 Hz, C_6F_5). Anal. Calcd for **4** ($C_{26}H_{34}F_{10}O_4Si_2Zn_2$): C 39.66, H 4.35. Found: C 39.45, H 4.30.

Crystal Structure Analysis of 4. A crystal of **4** was placed on a glass capillary in perflourinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker axs area detector (Mo Kα radiation), $\lambda = 0.71073$ Å (ω scan) at −60 °C; monoclinic, $P2_1/n$, $a = 12.272(4)$ Å, $b = 14.036(5)$ Å, $c = 19.540(6)$ Å, $\beta = 97.91(1)°$, $V = 3333(2)$ Å^3, $Z = 4$, $\mu = 1.596$ mm^{-1}. A total of 18 311 reflections were collected ($2\theta_{max} = 50°$), 3907 independent, 5863 observed ($F_o > 4\sigma(F_o)$), 397 parameters; R1 = 0.0439, wR2 (all data) = 0.1085. Structure solution was by direct methods (SHELXS 97); refinement against F^2 with all measured reflections (SHELXTL 97). The positions of the H atoms were calculated and considered isotropic according to a riding model.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 286904. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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