Structural Isomerism and Thermodynamic Properties of the Methylzinc Alkoxide Molecules (MeZnOR) n (R = Me, t Bu) and Cations [(MeZnOMe) n] + (n = 3, 4) Studied by B3LYP and PCM C…

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Structural Isomerism and Thermodynamic Properties of the Methylzinc Alkoxide Molecules $(MeZnOR)_n$ (R = Me, ^tBu) and Cations $[(MeZnOMe)_n]^+$ (*n* = 3, 4) Studied by B3LYP and PCM Calculations

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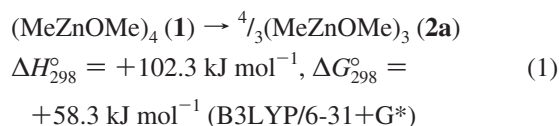
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Zinc oxide is a semiconductor as well as a catalyst in important industrial processes, and alkylzinc alkoxide species of the type $(RZnOR)_n$ are precursors for the preparation of nanoscaled zinc oxide particles. In this work, the structures, thermodynamic properties, dipole moments, and molecular vibrations of substituted zinc oxide molecules and cations have been studied by density functional calculations at the B3LYP/6-31+G(2df,p) level. The neutral tetramers $(MeZnOMe)_4$ and $(MeZnO^tBu)_4$ are cubane-like species of T_d symmetry in the gas phase, whereas the cation $[(MeZnOMe)_4]^+$ is approximately of C_{3v} symmetry due to a Jahn–Teller distortion. For the neutral trimers $(MeZnOMe)_3$ and $(MeZnO^tBu)_3$ two structural isomers of almost identical energy were located on the potential energy surfaces: A closo-cluster with eight ZnO bonds is most stable both as isolated molecule and in a polarizable continuum, but a roof-shaped structure with seven ZnO bonds differs in enthalpy by less than 8 kJ mol^{-1}. In the case of the analogous cation $[(MeZnOMe)_3]^+$, the isomer with the roof-shaped Zn_3O_3 skeleton is 31.7 kJ mol^{-1} more stable in the gas phase than the cluster isomer. A particularly long Zn–C bond in the most stable cationic tri- and tetramers explains the loss of a methyl group, observed mass spectrometrically after electron impact ionization. The dissociation of the tetramers $(MeZnOMe)_4$ and $(MeZnO^tBu)_4$ into $^4/_3$ trimers is endothermic and endergonic, but less so for the *tert*-butyl derivative compared to the all-methyl cluster. This destabilizing effect of *tert*-butyl substituents on the tri- and tetrameric clusters follows also from the larger internuclear distances between the non-hydrogen atoms in the structures of $(MeZnO^tBu)_n$ (*n* = 3 and 4) compared to the analogous all-methyl derivatives. Remarkable differences of the atomic charges of the carbon atoms of methyl or *tert*-butyl groups attached to oxygen have been found.

Introduction

Alkylzinc alkoxide molecules of the type $(RZnOR)_n$ are valuable precursors for the preparation of nanoscaled zinc oxide particles either by thermolysis under oxidizing conditions or by controlled oxidation with suitable reagents.[1] The starting compounds can easily be prepared by alcoholysis or oxygenation of dialkylzinc reagents. For example, Me_2Zn reacts with either methanol[2] or with dioxygen in the presence of water[3] to the well-known tetramer $(MeZnOMe)_4$. Because ZnO is a semiconductor and a catalyst in important industrial processes, a large number of publications addressing these topics have recently appeared.[1,4]

In 2006, we reported a comprehensive DFT study of the structures, thermodynamic properties, and reactions of substituted zinc oxide species of composition $(MeZnOMe)_n$ with *n* = 1–4, 6, and 8, calculated at the B3LYP/6-31+G* level of theory.[5] The well-studied cubane-like tetramer (**1**) was confirmed to be the most stable oligomer, and the formation of all other molecular sizes from the tetramer was predicted to be strongly endothermic and endergonic. For the trimer $(MeZnOMe)_3$ a roof-like Zn_3O_3 core of C_s symmetry (**2a**) was found and was predicted as the global minimum structure on the potential energy surface (PES) with the following thermodynamic properties:

$$(MeZnOMe)_4 \ (\mathbf{1}) \rightarrow {}^4/_3(MeZnOMe)_3 \ (\mathbf{2a})$$

$$\Delta H^\circ_{298} = +102.3 \text{ kJ mol}^{-1}, \ \Delta G^\circ_{298} = \tag{1}$$

$$+58.3 \text{ kJ mol}^{-1} \text{ (B3LYP/6-31+G*)}$$

In 1968 the preparation of the all-*tert*-butyl substituted trimer $(^tBuZnO^tBu)_3$ (**3**) has been reported by Noltes and Boersma.[6,7] It was shown that the molecular weight determined cryoscopically as well as ebullioscopically in benzene did not change on heating the solvent to the boiling point, indicating a thermodynamically stable species.[6] The ^1H NMR spectrum of **3** consists of two singlets at 1.27 and 1.32 ppm, assigned to the methyl protons of the two types of ^tBu groups linked to either zinc or oxygen. However, in a roof-like structure as proposed by us for the all-methyl trimer **2a**, the zinc and oxygen atoms are not all magnetically equivalent, and the proton spectrum of **2a** would be expected to consist of at least four singlets unless some kind of fluxionality is assumed. However, Janusz Lewiński[8] recently informed us that his group structurally characterized the trimer **3** and found a cluster-like Zn_3O_3 skeleton slightly different from the roof-structure of the above-mentioned methyl derivative **2a**. The Zn_3O_3 core of **3** contains eight Zn–O bonds whereas the roof-type structure of **2a** has only seven such bonds. Therefore, it was to be suspected that the cluster-like Zn_3O_3 unit is more stable thermodynamically than the roof geometry, which we had predicted as the global minimum structure of $(MeZnOMe)_3$ at a time when there has been no experimental structure available yet for any alkylzinc alkoxy complex of the type $(RZnOR')_3$.

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Thus, we have studied the PES of (MeZnOMe)$_3$, again searching for more-stable isomers than **2a**. Indeed, we could locate a cluster-type isomer **2b** with eight Zn−O bonds that is nearly of the same Gibbs energy as **2a**. These calculations were performed at the B3LYP/6-31+G(2df,p) level of theory, that is, with a larger basis set than applied in our previous investigation.[5] To study the influence of substitution by ^{t}Bu groups we have also calculated the structures and thermodynamics of the mixed derivatives (MeZnO^{t}Bu)$_4$ (**4**) and (MeZnO^{t}Bu)$_3$ (**5**) at the same level of theory. The fully ^{t}Bu substituted species such as **3** and (^{t}BuZnO^{t}Bu)$_4$ (**6**) which both were characterized crystallographically by Lewiński et al.[8] are beyond our computational resources at the present level of theory.

In addition, we have investigated the thermodynamic properties of **1**, **2a**, and **2b** in a polarizable continuum simulating both the solid phase of these compounds as well as solutions in polar solvents by using the PCM method developed by Tomasi et al.,[9] which takes the influence of polar neighboring molecules as in crystalline **3** into account.

The trimer cation [(MeZnOR)$_3$]$^+$ and the related species [Me$_2$Zn$_3$(OR)$_3$]$^+$ with one methyl group missing ($R = {}^i$Pr) have been observed as prominent peaks in the EI mass spectra of the corresponding tetranuclear cluster.[10] To find out the reason for the methyl group elimination on electron impact ionization, we have calculated the formerly unknown structures of the related gaseous tetramer and trimer monocations of **1**, **2a**, and **2b**, which are labeled here as species **1**$^+$, **2a**$^+$, and **2b**$^+$.

Computational Details

The structures and energies of the various molecules and cations were examined at the B3LYP/6-31+G(2df,p) level of theory using the Gaussian 03[11] program package. The B3LYP functional in connection with a not too small basis set was found to reproduce the experimental structure and the first homolytic Zn−C bond dissociation enthalpy of Me$_2$Zn very well.[5] Nevertheless, novel reference calculations with the present basis set have been performed (see below). Harmonic fundamental vibrations were calculated at the B3LYP/6-31+G(2df,p) level to characterize stationary points as equilibrium structures, with all frequencies real. The reported wavenumbers are unscaled, but for the calculation of the zero point energies and thermal corrections a scaling factor of 0.9854 was applied. For all investigated species, a charge density analysis was performed by a natural population analysis (NPA) based on the B3LYP/6-31G+(2df,p) wave function.[12] All enthalpies (ΔH_{298}°) and Gibbs energies (ΔG_{298}°) as well as the structural parameters reported in the text correspond to the B3LYP/6-31+G(2df,p) level.

Since the trimers **2a** and **2b** have nonzero dipole moments, it was to be expected that the thermodynamic properties of these species in the solid state and in polar solvents will be different from those of the free molecules. To study the influence of a polar environment, calculations according to Tomasi's polar continuum model (PCM)[9] as implemented in Gaussian03 were carried out at the B3LYP/6-31+G(2df,p) level. In this model, the solvent is represented by a continuous dielectric, characterized by a given dielectric constant (ε). The solute is assumed to be embedded in a cavity in the medium. The size of the cavity is calculated using atomic radii from the united force field (UFF) scaled by 1.1 with individual spheres for hydrogen (default version of PCM). The permanent dipole moment of the solute induces a dipole moment in the medium, which in turn interacts with the molecular dipole leading to stabilization. A dielectric constant of 80.0 was used for the PCM calculations to represent

the solid phase, but no geometry reoptimization was carried out. In the following, the polarizable continuum will simply be termed "polar phase" for convenience.

Results and Discussion

Reference Calculations. The experimental structure of dimethylzinc and its first Zn−C bond dissociation enthalpy have been used as references to check the quality of our calculations at the B3LYP/6-31+G(2df,p) level of theory. The Me$_2$Zn molecule is of D_{3h} symmetry; the calculated Zn−C internuclear distance of 195.06 pm compares well with the two experimental values of 193.0(2) pm[13a] and 192.9(4) pm.[13b] The absolute energies and enthalpies of Me$_2$Zn and its dissociation products are given in Table S1 in the Supporting Information. From these data the first Zn−C bond dissociation enthalpies follow as ΔH_{298}° = 270.2 kJ mol^{-1} and ΔG_{298}° = 228.6 kJ mol^{-1}, which are in line with the three reported experimental dissociation enthalpies (ΔH_{298}°) of 266 ± 6,[14a] 285 ± 17,[14b] and 276−298 kJ mol^{-1}.[14c]

Structures and Thermodynamics of the Neutral Complexes. The calculated structure of the isolated tetramer (MeZnOMe)$_4$ (**1**) is in accord with the crystal structure[15] as well as with our previous calculations.[5] The isolated molecule is of exact T_d symmetry, and the most interesting bond lengths are d_{ZnO} = 210.3 pm, d_{ZnC} = 196.8 pm, and d_{CO} = 142.7 pm. The corresponding crystallographic values are 207.8, 195, and 143 pm.[15] The atomic coordinates of all molecules calculated in this work are provided in the Supporting Information.

The structures and some internuclear distances of the two isomeric trimers (MeZnOMe)$_3$ (**2a** and **2b**) as well as of the monomer MeZnOMe (**7**) are shown in Figure 1.

The structure of monomeric MeZnOMe obtained with the present basis set (Figure 1) is slightly different from the previously published C_s symmetric structure obtained with the 6-31+G* basis set.[5] The new symmetry is C_1 with a very small deviation from C_s symmetry (bond angle at zinc: 174.6°, and at oxygen: 131.5°; torsion angle CZnOC: 179.7°) and the methyl groups have now a different, almost eclipsed conformation to each other while previously a staggered conformation was obtained.[5] Enforcing a C_s symmetric or a staggered structure resulted in imaginary frequencies. The present structure was also obtained using the larger 6-31+G(3df,2p) basis set. No experimental structure is known for this molecule.

The roof-like trimer structure **2a** is approximately of C_s symmetry if the hydrogen atoms are neglected. Two zinc and two oxygen atoms are three-coordinate whereas the remaining Zn and O atoms are four-coordinate. As a result of the differing coordination numbers and the low symmetry, the ZnO bond lengths are in the range 189.9−223.6 pm (arithmetic mean 203.8 pm). In contrast, the cluster-like isomer **2b** is of C_1 symmetry with two zinc and two oxygen atoms four-coordinate and the remaining ones three-coordinate. The 8 ZnO bonds of **2b** are also quite different with d_{ZnO} ranging from 195.7 to 223.3 pm with an arithmetic mean of d_{ZnO}(average) = 209.6 pm. From these bond lengths one could conclude that **2a** is more stable than **2b** since its ZnO bonds are on average shorter and therefore probably stronger. However, species **2b** contains one additional ZnO bond, and this may be the reason that the two isomers are almost of identical enthalpy. The conversion of **2a** into **2b** releases only ΔH_{298}° = −2.2 kJ mol^{-1} whereas the Gibbs energy difference for this reaction is positive: ΔG_{298}° = +3.2 kJ mol^{-1}. In the polar phase the conversion **2a** → **2b** is predicted to be slightly endothermic, by ΔE_e(PCM) = +7.1 kJ mol^{-1}, which may be compared to ΔE_e = −1.5 kJ mol^{-1} calculated for the isolated molecules. The absolute values of E_e, E_e(PCM), H_{298}°
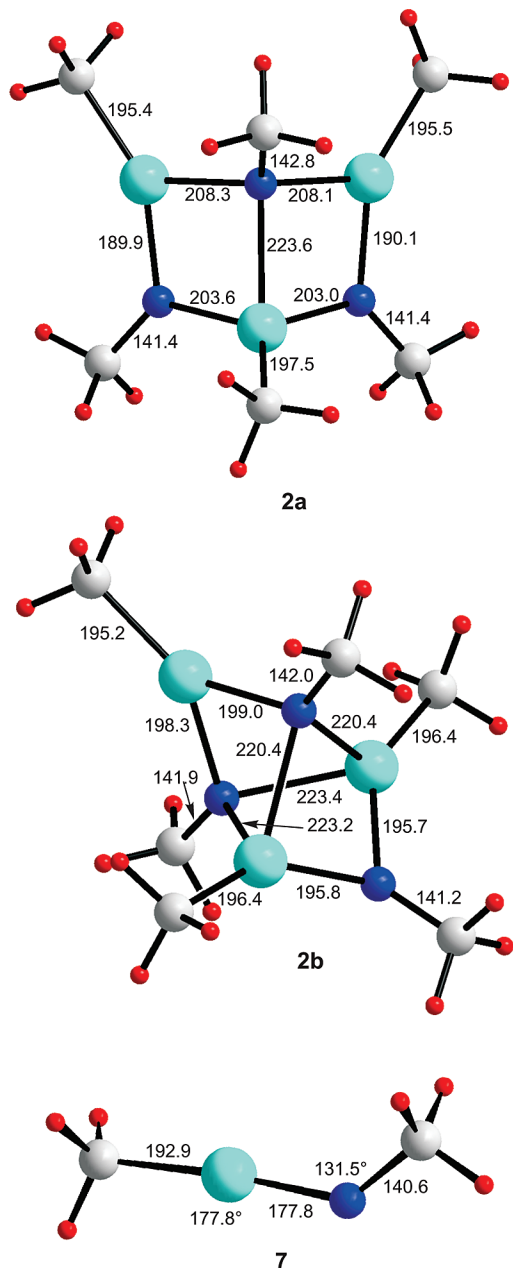
2a

2b

7

Figure 1. Structures of the isomeric trimers (MeZnOMe)$_3$ (**2a** and **2b**) and of the monomer MeZnOMe (**7**), calculated at the B3LYP/6-31+G(2df,p) level (isolated molecules; bond lengths in pm). Color code: Zn, turquoise; C, gray; O, blue; H, red.

and G°_{298} as well as the dipole moments of all species calculated in this work are listed in Table 1.

At the B3LYP/6-31+G(2df,p) level of theory the reaction enthalpy and Gibbs energy of the dissociation of the tetramer **1** into $^4/_3$ trimer **2a** as shown in eq 1 are $\Delta H^{\circ}_{298} = +96.0$ kJ mol^{-1} and $\Delta G^{\circ}_{298} = +59.6$ kJ mol^{-1}, respectively. However, in the presence of bulky substituents as in (^{t}BuZnO^{t}Bu)$_3$ (**3**), the tetramer seems to be destabilized thermodynamically to such an extent that the trimer becomes the preferred molecular size.[6,8] In our previous investigation[5] we have shown that the dissociation of tetramer **1** into two dimers (MeZnOMe)$_2$ is endothermic by $\Delta H^{\circ}_{298} = +122.2$ kJ mol^{-1}, but for the analogous dissociation of (MeZnO^{t}Bu)$_4$ (**4**) to give two molecules of (MeZnO^{t}Bu)$_2$ a reaction enthalpy of only $+90.6$ kJ mol^{-1} was predicted, clearly showing a destabilizing effect of ^{t}Bu substitution on the tetramer. Therefore, we have now calculated the structure of the mixed

TABLE 1: Negative Absolute Energies (*E*), Enthalpies (*H*), and Gibbs Energies (*G*) (all in Hartree) of the Isolated Zinc Complexes (MeZnOR)$_n$ and [(MeZnOMe)$_3$]$^+$ (*R* = Me, ^{t}Bu; *n* = 1, 3, 4) As Well As Their Dipole Moments (*μ*) (Debye)^a

species	E_e	H°_{298}	G°_{298}	μ (D)
(MeZnOMe)$_4$ **1** T_d	7737.14953	7737.11480	7737.21516	0.00
[(MeZnOMe)$_4$]$^+$ **1**$^+$	7736.85427	7736.82038	7736.92246	5.38
(MeZnOMe)$_3$ **2a**	5802.83517	5802.80869	5802.89453	0.79
	5802.84088PCM			1.00PCM
(MeZnOMe)$_3$ **2b**	5802.83575	5802.80954	5802.89330	0.43
	5802.83817PCM			0.53PCM
[(MeZnOMe)$_3$]$^+$ **2a**$^+$	5802.55367	5802.52672	5802.61352	5.13
[(MeZnOMe)$_3$]$^+$ **2b**$^+$	5802.54142	5802.51466	5802.60090	1.90
(MeZnO^{t}Bu)$_4$ **4** T_d	8209.00326	8208.95665	8209.07511	0.00
(MeZnO^{t}Bu)$_3$ **5a** C_1	6156.72912	6156.69281	6156.79828	0.22
(MeZnO^{t}Bu)$_3$ **5b** C_1	6156.72976	6156.69290	6156.80033	0.79
MeZnOMe **7** C_1	1934.25039	1934.24220	1934.28388	1.57

^{a} Calculated at the B3LYP/6-31+G(2df,p) level of theory. The data marked by PCM apply to the molecules in a polarizable continuum with $\varepsilon = 80.0$ and without geometry reoptimization.
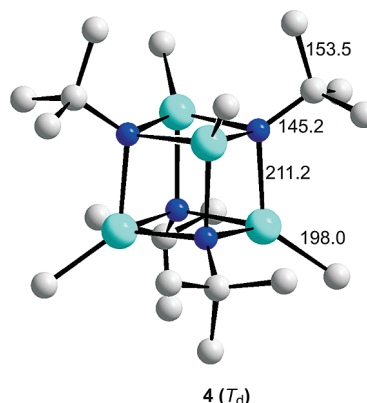

4 (T_d)

Figure 2. Structure of the isolated tetramer (MeZnO^{t}Bu)$_4$ (**4**), calculated at the B3LYP/6-31+G(2df,p) level (H atoms omitted, symmetry T_d; bond lengths in pm).

methyl butyl tetramer **4** and of the corresponding isomeric trimers **5a** and **5b** to study the dissociation of **4** into $^4/_3$ trimers in analogy to eq 1 but at a higher level of theory.

To the best of our knowledge, the tetramer **4** has not been prepared yet. Our present calculations predict a tetrahedral geometry with the bond lengths $d_{ZnO} = 211.2$ pm, $d_{ZnC} = 198.0$ pm, and $d_{CO} = 145.2$ pm. These bond lengths are all slightly larger than in the all-methyl tetramer **1** ($d_{ZnO} = 210.3$ pm, $d_{ZnC} = 196.8$ pm, and $d_{CO} = 142.7$ pm); see Figure 2. The most important bond angles of **4** are: Zn–O–Zn, 95.3°; O–Zn–O, 84.4°; O–Zn–C, 129.2°; and Zn–O–C, 121.4°. The space-filling model of **4** shown in Figure S1 in the Supporting Information demonstrates that the Zn$_4$O$_4$ core is well protected by the four methyl and four *tert*-butyl groups and that eight ^{t}Bu groups would hardly find enough space on the surface of a Zn$_4$O$_4$ core of T_d symmetry unless all ZnC and CO bonds become considerably longer than in **1** and **4** to make room for the additional bulky substituents. Thus, the all-*tert*-butyl tetramer (^{t}BuZnO^{t}Bu)$_4$ (**6**) may be thermodynamically unstable in dilute solution with respect to conversion to smaller oligomers such as the trimer and the dimer, in agreement with the available experimental reports on the preparation of (^{t}BuZnO^{t}Bu)$_3$ when the formation of the tetramer **6** was to be expected.[6,8]

The charge distribution in **4** is slightly different from that in **1**, as can be seen from the data in Table 2, which contains the calculated NPA atomic charges. Although the zinc and oxygen atoms bear similar charges (*q*) in both tetramers, the carbon atoms attached to oxygen are positively charged in **4** (+0.23;

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TABLE 2: NPA Atomic Charges of the Isolated Zinc Complexes (MeZnOMe)$_n$ and (MeZnO^{t}Bu)$_n$ (n = 3, 4)^a

atom	(MeZnOMe)$_4$ **1** (T_d)	(MeZnOMe)$_3$ **2a** (C_s)	(MeZnOMe)$_3$ **2b** (C_1)	(MeZnO^{t}Bu)$_4$ **4** (T_d)	(MeZnO^{t}Bu)$_3$ **5a** (C_1)	(MeZnO^{t}Bu)$_3$ **5b** (C_1)
Zn:	+1.26	+1.45 to +1.48	+1.44 to +1.46	+1.30	+1.29 to +1.31	+1.29 to +1.31
C at Zn:	−1.31	−1.34 to −1.38	−1.35 to −1.36	−1.33	−1.31 to −1.33	−1.31
C at O:	−0.32	−0.32 to −0.34	−0.33	+0.23	+0.23	+0.23
C at ^{t}C:				−0.69	−0.69 to −0.70	−0.69
O:	−1.10	−1.10 to −1.12	−1.10 to −1.12	−1.05	−1.03 to −1.04	−1.04

^{a} Calculated at the B3LYP/6-31+G(2df,p) level of theory.
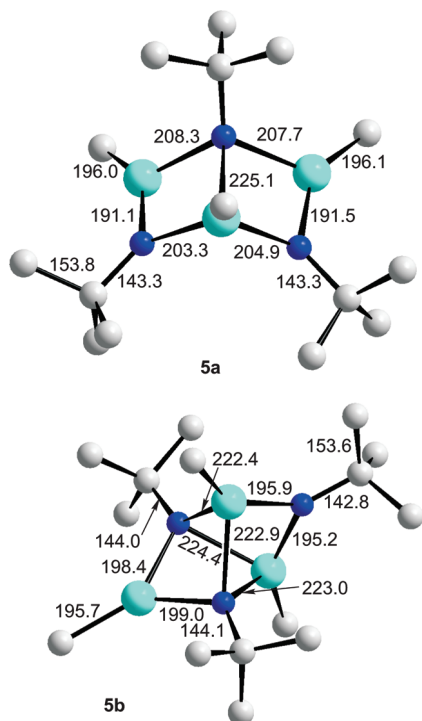
Figure 3. Structures of the isolated isomeric trimers (MeZnO^{t}Bu)$_3$ (**5a** and **5b**), calculated at the B3LYP/6-31+G(2df,p) level (H atoms omitted, bond lengths in pm). For Figures including H atoms, see Supporting Information.

tertiary carbon atoms) but negatively in **1** (−0.32; primary carbon atoms). Thus, the C−O bonds in **4** (Δq = 1.28) are considerably more polar than in **1** (Δq = 0.78) and even the C−C bonds within the ^{t}Bu group are highly polar (Δq = 0.92). The same holds for the analogous trimers (Table 2).
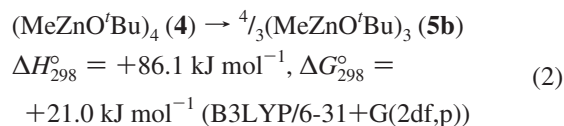
The two possible trimers (MeZnO^{t}Bu)$_3$ (**5a,b**) originating from the tetramer **4** have been designed in analogy to the methyl trimers **2a** and **2b**. Geometry optimization resulted in the structures shown in Figure 3 (without H atoms) as well as in Figures S2 and S3 (with H atoms). Both trimers (**5a** and **5b**) are of C_1 symmetry since in each case one of the *tert*-butyl groups does not obey the mirror symmetry of the rest of the molecule. Evidently, the repulsion between the bulky groups is minimized in this way. Optimization of a structure of C_s symmetry resulted in imaginary frequencies. The dipole moment of **5a** (0.22 D) is smaller than that calculated for **2a** (0.79 D), whereas in the case of **5b** this moment is predicted as 0.79 D, which is larger than that calculated for the all-methyl derivative **2b** (0.43 D), which is also of C_1 symmetry.

The proposed repulsion between the substituents within the isomeric trimer molecules (MeZnO^{t}Bu)$_3$ can also be derived from the internuclear distances within the Zn$_3$O$_3$C$_6$ skeleton, which are generally larger than in the analogous (MeZnOMe)$_3$ isomers **2a** and **2b**. For example, the ZnO distances of **5a** range from 191.1−225.1 pm with an arithmetic mean of 204.6 pm,

compared to 203.8 pm in **2a**. Similarly, the ZnC and CO bonds are on average by 0.7 pm (ZnC) and 2.0 pm (CO) pm, respectively, longer in **5a** than in **2a**. The interplanar angle between the two rectangles in the Zn$_3$O$_3$ skeleton of **5a** is 73.5° compared to the 72.0° of the all-methyl species **2a**.

For the 8 ZnO bonds of **5b**, internuclear distances in the range 195.2−224.5 pm have been calculated with an arithmetic mean of 210.2 pm, which is 0.6 pm larger than those obtained for the all-methyl trimer **2b**. Interestingly, the ZnC (196.5 pm) and CO bonds (143.6 pm) of **5b** are on average shorter than in the tetramer **4** (198.0 and 145.2 pm, respectively). Thus, the destabilizing effect of ^{t}Bu groups seems to decrease on dissociation of the tetramer **4** to smaller oligomers.

As an isolated molecule, the cluster-like isomer **5b** is slightly more stable than the roof-type species **5a**, by $\Delta H_{298}^\circ = -0.2$ kJ mol^{-1} and $\Delta G_{298}^\circ = -5.4$ kJ mol^{-1}; see Table 1. From the data in this Table it can be seen that the dissociation of the tetramer **4** into $^4/_3$ trimer **5b** is still highly endothermic; eq 2.

$$(\text{MeZnO}^t\text{Bu})_4\ (\mathbf{4}) \rightarrow {}^4/_3(\text{MeZnO}^t\text{Bu})_3\ (\mathbf{5b})$$
$$\Delta H_{298}^\circ = +86.1 \text{ kJ mol}^{-1}, \Delta G_{298}^\circ =$$
$$+21.0 \text{ kJ mol}^{-1} \text{ (B3LYP/6-31+G(2df,p))} \quad (2)$$

However, the calculated reaction enthalpy is by 6.9 kJ mol^{-1} smaller than predicted for the analogous dissociation of the all-methyl tetramer **1** at this level of theory, and the Gibbs reaction energy of this dissociation is much smaller than for the methyl tetramer (+59.6 kJ mol^{-1}). In other words, the substitution of Me by ^{t}Bu at the oxygen atoms of the tetramer reduces the Gibbs energy change for the dissociation reaction by 38.6 kJ mol^{-1}. Extrapolation to the all-*tert*-butyl tetramer **6** may therefore give a negative Gibbs energy change for the analogous dissociation reaction. Thus, the corresponding trimer (^{t}BuZnO^{t}Bu)$_3$ may be equally stable or even more stable than the tetramer **6**, in agreement with various reports on the preparation of the former.[6,8]

If the molecules **5a** and **5b** were rigid structures in solution, their ^{1}H NMR spectra should consist of more than two lines since the low molecular symmetry (C_1) means that there are two types of methyl groups on zinc as well as two types of *tert*-butyl groups on oxygen. However, the proton spectrum of the all-*tert*-butyl trimer **5** has been reported to consist of just two signals (see above).[6] This finding can only be understood on the basis of a fluxional molecule, regardless whether it adopts a structure similar to **5a** or **5b** in solution. In our previous study we had already shown that the roof-structure **2a** is likely to interconvert to an equivalent structure via a monocyclic transition state of C_{3h} symmetry in which all non-hydrogen atoms are located in one plane and in this way become magnetically equivalent. The activation energy calculated for this transition is just 13.5 kJ mol^{-1}.[5]

For the formation of trimers from tetramers we previously proposed a "ladder mechanism"[5] which involves the opening

of the Zn_4O_4 heterocubane to a stair-shaped ladder structure by cleavage of two parallel edges (ZnO bonds). This first step may be followed by the transfer of a monomer unit to a neighboring molecule, for example to a dimeric species that probably exists in equilibrium with the tetramer in solution.[5] Alternatively, the ladder-type intermediate may oligomerize to a longer ladder from which smaller units of any size including trimers and dimers may be split off.

Structures and Thermodynamics of the Trimer and Tetramer Cations. Above it was mentioned that EI mass spectra of $(MeZnO^iPr)_4$ did not show a signal for the molecular ion (M^+), but the fragment $[M-Me]^+$ was the ion with the largest mass recorded. The relative intensity of this ion was only 1%. The most prominent fragments observed (100% intensity each) were $[(MeZnO^iPr)_3]^+$ and $[Me_2Zn_3(O^iPr)_3]^+$.[10] In other words, besides the loss of a monomeric unit, the homolytic cleavage of one Zn–C bond is a dominating fragmentation pattern on electron impact. To find the reasons for this type of fragmentation, we have calculated the formerly unknown structures of the isolated cations $[(MeZnOMe)_4]^+$ (1^+) and $[(MeZnOMe)_3]^+$ ($2a^+$ and $2b^+$). In Figure 4 the structures and some of the bond lengths of these ions are shown.

The tetrameric ion 1^+ is considerably less symmetric than the tetrahedral neutral species **1**. The overall symmetry of 1^+ is close to C_{3v} but with a small distortion toward C_1 since the Zn–O bond lengths differ slightly. The lower symmetry of 1^+ compared to **1** is probably the result of the well-known Jahn–Teller effect operating in systems with partly occupied degenerate molecular orbitals. This distortion results in a formidable dipole moment of 5.38 D for the cation 1^+. Therefore, the ZnO bond lengths of 1^+ range from 197.4 to 219.7 pm with an arithmetic mean of 210.6 pm (**1**: 210.3 pm) but three types of such bonds can be recognized. Three of the 12 ZnO bond lengths are in the range 197.4–198.6 pm; these bonds originate from the Zn atom located on the 3-fold axis. The 3 ZnO bonds originating from the oxygen atom located on the C_3 axis are of length 207.5–208.1 pm, whereas the remaining 6 bonds are between 216.7 and 219.7 pm long. Similarly, 3 of the CO bonds are of length 143.8 pm, whereas the fourth one is 144.7 pm long, and all are somewhat longer than in **1** (142.7 pm). Three of the ZnC bonds are of equal length (196.0 pm), but the fourth bond originating from the unique Zn atom is much longer (216.0 pm). As a consequence, the HCH bond angles of this methyl group are much larger (116.8°) than those of the other three Me groups (109.0 ± 0.4°). This result is in agreement with the fact that the free methyl radical is planar. The latter results are also in line with the observation of the fragment ion $[M-Me]^+$ in the mass spectrum of the related tetramer $(MeZnO^iPr)_4$ as discussed above.

The lower than tetrahedral symmetry of 1^+ can also be seen from the OZnO and ZnOZn bond angles that vary from 81.3 to 92.5° at zinc and from 92.8 to 100.4° at oxygen.

The NPA atomic charges of 1^+ exhibit an interesting pattern. Three of the Zn atoms bear a charge of +1.26 electrostatic units, but for the Zn atom from which the long ZnC bond originates a value of +1.36 is calculated. The charges calculated for the oxygen atoms differ only slightly: −0.99 (three times) and −1.02, resulting in a total charge of the Zn_4O_4 skeleton of +1.15. This value may be compared to the +0.64 total charge of the Zn_4O_4 core of the neutral tetramer **1** (charge difference between the Zn_4O_4 units of 1^+ and **1**: 0.51). The highest spin density of 1^+ is found at the carbon atom located on the 3-fold axis, and this fact is probably responsible for the corresponding ZnC bond being unusually long (216.0 pm). Evidently, to a first
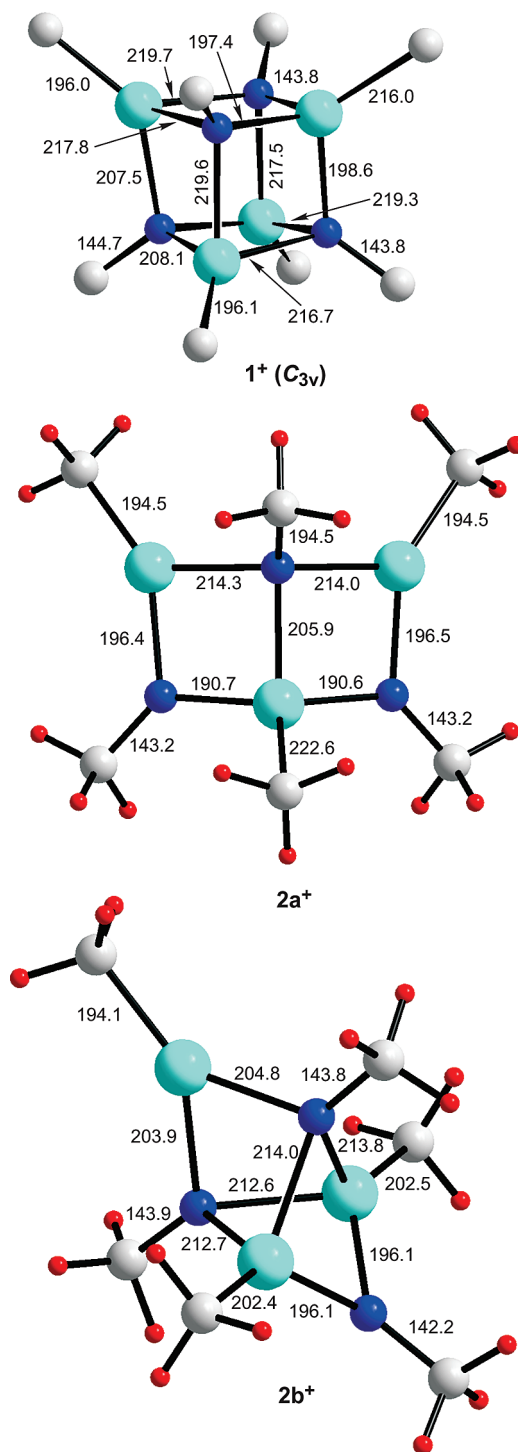

Figure 4. Structures of the tetrameric cation $[(MeZnOMe)_4]^+$ (1^+; H atoms omitted) and of the two isomeric trimer cations $[(MeZnOMe)_3]^+$ ($2a^+$ and $2b^+$), calculated at the B3LYP/6-31+G(2df,p) level (bond lengths in pm; for the structure of 1^+ with H atoms included, see Figure S5).

approximation the missing electron has been removed from a bonding molecular orbital that is mainly localized at the corresponding ZnC bond. The discussed carbon atom bears a much smaller charge (−0.76) than the other three carbons attached to Zn (−1.28). In contrast, the four carbon atoms linked to oxygen atoms bear equal charges (−0.34) that are practically identical to those of the neutral tetramer **1**.
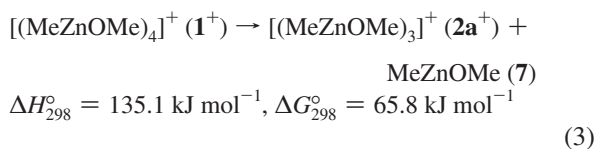
The elimination of a monomeric unit as observed in the discussed mass spectrum of $(MeZnO^iPr)_4$ can be understood on

Properties of the Methylzinc Alkoxide Molecules

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TABLE 3: Wavenumbers (Unscaled; cm^{-1}) of Characteristic Stretching Vibrations (ν) of the Isolated Methylzinc Alkoxide Species 1, 2a, 2b, 2a$^+$, 2b$^+$, and 4^a

species	(MeZnOMe)$_4$ **1** (T_d)	(MeZnOMe)$_3$ **2a** (C_s)	(MeZnOMe)$_3$ **2b** (C_1)	[(MeZnOMe)$_3$]$^+$ **2a$^+$** (C_s)	[(MeZnOMe)$_3$]$^+$ **2b$^+$** (C_1)	(MeZnO^{t}Bu)$_4$ **4** (T_d)
ν(ZnO)	324 (A$_1$)	338 (A)	362 (A)	367 (A)	366 (A)	207 (A$_1$)
ν(ZnC)	530 (F)	523	539	268	417	518 (F)
	536 (A$_1$)	555	541	556	454	527 (A$_1$)
		562	555	558	563	
ν(CO)	1044 (F)	1038	1059	1000	1008	1195 (F)
	1076 (A$_1$)	1088	1088	1047	1038	1196 (A$_1$)
		1102	1109	1060	1063	

^{a} Calculated at the B3LYP/6-31+G(2df,p) level of theory. For the ZnO skeletons only the totally symmetrical breathing vibration is given because of coupling between the less symmetric modes ν_{ZnO} with other fundamentals.

the basis of the structure of the cation [(MeZnOMe)$_4$]$^+$ shown in Figure 4. If the MeZnOMe unit on the left edge of the cubane-like cluster is to be removed, for instance, two ZnO bonds of length 208.0 and 208.1 pm as well as two of length 217.8 and 219.7 pm, respectively, have to be broken while all of the shortest and probably strongest ZnO bonds of **1$^+$** remain intact. This elimination reaction is of course endothermic and ender-gonic; see eq 3.

$$[(MeZnOMe)_4]^+ \ (\mathbf{1^+}) \rightarrow [(MeZnOMe)_3]^+ \ (\mathbf{2a^+}) +$$
$$MeZnOMe \ (\mathbf{7})$$
$$\Delta H^\circ_{298} = 135.1 \text{ kJ mol}^{-1}, \Delta G^\circ_{298} = 65.8 \text{ kJ mol}^{-1}$$

(3)

These calculated enthalpies are much smaller than those obtained for the analogous dissociation of the neutral tetramer **1** to afford the trimer **2a** and the monomer **6**: $\Delta H^\circ_{298} = 167.8$ kJ mol^{-1} and $\Delta G^\circ_{298} = 96.5$ kJ mol^{-1} (see Table 1).

The conformations of the trimeric cations **2a$^+$** and **2b$^+$** agree with those of the neutral molecules (**2a** and **2b**), but some of the bond lengths are different. The more stable roof-type cation **2a$^+$** is of C_s symmetry with d_{ZnO} in the range 190.6–214.3 pm and d_{ZnO}(average) = 201.2 pm. Thus, the spread of the ZnO bond lengths is much smaller than in **2a**, and the arithmetic mean is 2.6 pm smaller than predicted for **2a**. The same is found for the cluster-type cation **2b$^+$**, which is of symmetry C_1 with d_{ZnO} = 196.1–214.0 pm and d_{ZnO}(average) = 206.8 pm. However, some of the ZnC bonds show remarkable differences between the neutral and the cationic molecules. The average ZnC distance in **2a** is 196.1 pm. In **2a$^+$** there are two ZnC bonds of similar distance (194.5 pm), but the remaining ZnC bond is much longer (222.6 pm). This finding is in accord with the observation of the cation [(Me$_2$Zn$_3$(O^{i}Pr)$_3$]$^+$ in the EI mass spectrum of (MeZnO^{i}Pr)$_4$.

The interplanar angle between the two nearly rectangular halfs of the "roof" **2a** is 72.0°, which decreases to 53.3° in **2a$^+$**. The torsion angles OZnOZn at the shortest bonds within the two rectangles of **2a$^+$** are ±5.4°.

In the case of the two cluster-like isomers **2b** and **2b$^+$**, one of the ZnC bonds of the cation is much shorter (194.1 pm) than the other two bonds (202.3 pm) that are symmetry related. In the neutral trimer **2b** these bonds are all between 195.2 and 196.4 pm long; see Figure 1.

In contrast to the almost isoenergetic neutral isomers **2a** and **2b** (see above), there is a substantial energy difference between **2a$^+$** and **2b$^+$**, and the isomerization **2a$^+$** → **2b$^+$** requires a reaction enthalpy of $\Delta H^\circ_{298} = +31.7$ kJ mol^{-1} and a Gibbs energy of $\Delta G^\circ_{298} = +33.1$ kJ mol^{-1} (see Table 1).

Molecular Vibrations of the Methylzinc Alkoxide Clusters 1, 2a, 2b, 2a$^+$, 2b$^+$, and 4. The most important stretching modes of the skeletons of the complexes **1**, **2a**, **2b**, **2a$^+$**, **2b$^+$**, and **4** are listed in Table 3. For the ZnO bonds only the breathing vibration is considered in order to eliminate the influence of coupling effects to other modes. This totally symmetric mode is predicted in the range 324–367 cm^{-1} for the all-methyl derivatives but at 207 cm^{-1} for the methyl-*tert*-butyl tetramer **4**, demonstrating once more the destabilizing effect of the ^{t}Bu groups on the core bonds of the complex.

The differing strength of the bonds between the nonhydrogen atoms of the trimeric methylzinc methoxide clusters and their monocations can also be concluded from the Zn–C stretching frequencies (ν_{ZnC}) listed in Table 3. For **2a** and **2b** these modes are predicted in the range 523–562 cm^{-1}. However, in the case of the cations **2a$^+$** and **2b$^+$** several considerably lower frequencies are calculated for ν_{ZnC} (range 268–558 cm^{-1} for **2a$^+$** and 417–563 cm^{-1} for **2b$^+$**). The same holds for the C–O stretching modes that are calculated at lower wavenumbers for the trimer cations than for the related neutral trimers.

These results are in line with the unusual fragmentation pattern of the tetramer (MeZnO^{i}Pr)$_4$ (**8**) on electron impact ionization observed by tandem mass spectrometry[10] as mentioned above. The heaviest ion observed was [**8**-Me]$^+$ (with 1% relative intensity) from which a neutral monomeric unit MeZnO^{i}Pr was then eliminated resulting in [Me$_2$Zn(O^{i}Pr)$_3$]$^+$ as a major cation in the spectrum. The bond distance patterns calculated for the related tetrameric ion **1$^+$** and the derived trinuclear cation **2a$^+$** (Figure 4) demonstrate that the missing electron has been removed from a bonding molecular orbital consisting of major contributions from one of the Zn–C bonds located on the 3-fold axis of **1$^+$** or on the mirror plane of the ion **2a$^+$**, respectively. The resulting much lower bond orders of these Zn–C bonds make the corresponding methyl groups subject to elimination. A similar fragmentation pattern can therefore be expected for the cation of (MeZnO^{i}Pr)$_4$ and its daughter ions. In cation **2b$^+$** the bond weakening effect is less pronounced but can still be seen from the two equivalent ZnC bonds of length 202.4 pm, which are considerably longer than the ZnC bonds in **2b** (196.4 pm).

Summary

In extension of our previous DFT calculations of methylzinc alkoxy complexes we have shown that the isolated tetramers (MeZnOMe)$_4$ (**1**) and (MeZnO^{t}Bu)$_4$ (**4**) adopt exact tetrahedral structures at the B3LYP/6-31+G(2df,p) level of theory. Most of the skeleton bonds in **4** are longer than in **1**, showing a destabilizing effect of the bulky ^{t}Bu substituents. This effect can also be derived from the ZnO and ZnC stretching vibrations. The trimers (MeZnOMe)$_3$ (**2a,b**) and (MeZnO^{t}Bu)$_3$ (**5a,b**) as

well as their monocations exist as two isomeric structures. A roof-shaped and a cluster-like Zn_3O_3 core are practically of equal energy for the $(MeZnOMe)_3$ species, whereas in the case of $(MeZnO^tBu)_3$ the cluster with eight Zn−O bonds is slightly more stable than the roof with its seven Zn−O bonds; this holds both for the isolated molecules as well as in a polarizable continuum. In contrast, the cation $[(MeZnOMe)_3]^+$ prefers a roof-like structure but with one particularly long ZnC bond prone to eliminate a methyl group on electron impact as has been observed mass spectrometrically.

The thermal dissociation of the tetramers $(MeZnOMe)_4$ (**1**) and $(MeZnO^tBu)_4$ (**4**) to the trimers is endothermic and endergonic, but the Gibbs energies of the dissociation reactions are quite different and demonstrate a destabilizing effect of the *tert*-butyl groups on the larger molecule. Extrapolation to the all-*tert*-butyl derivative $(^tBuZnO^tBu)_4$ (**6**) leads to the prediction that tetramer **6** and the related trimer may be of almost equal stability and may therefore exist in equilibrium in solution.

Supporting Information Available: Figure S1: structure of $(MeZnOMe)_4$ (**1**); Figure S2: space filling model of $(MeZnO^tBu)_4$ (**4**); Figure S3: structure of $(MeZnO^tBu)_3$ (**5a**); Figure S4: structure of $(MeZnO^tBu)_3$ (**5b**); Figure S5: structure of $[(MeZnOMe)_4]^+$ (**1$^+$**); Table S1: thermodynamic data of Me_2Zn; atomic coordinates of all novel species. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For selected examples, see: (a) Auld, J.; Houlton, D. J.; Jones, A. C.; Rushworth, S. A.; Malik, M. A.; O'Brien, P.; Critchlow, G. W. *J. Mater. Chem.* **1994**, *4*, 1249–1253. (b) Hambrock, J.; Rabe, S.; Merz, K.; Birkner, A.; Wohlfart, A.; Fischer, R. A.; Driess, M. *J. Mater. Chem.* **2003**, *13*, 1731–1736. (c) Polarz, S.; Neues, F.; van den Berg, M. W. E.; Grünert, W.; Khodeir, L. *J. Am. Chem. Soc.* **2005**, *127*, 12028–12034. (d) Polarz, S.; Roy, A.; Merz, M.; Halm, S.; Schröder, D.; Schneider, L.; Bacher, G.; Kruis, F. E.; Driess, M. *Small* **2005**, *1*, 540–552. (e) Ischenko, V.; Polarz, S.; Grote, D.; Stavarache, V.; Fink, K.; Driess, M. *Adv. Funct. Mater.* **2005**, *15*, 1945–1954. (f) Polarz, S.; Orlov, A. V.; Schüth, F.; Lu, A.-H. *Chem.–Eur. J.* **2007**, *13*, 592–597.

(2) Coates, G. E.; Ridley, D. *J. Chem. Soc.* **1965**, 1870–1877.

(3) Jana, S.; Berger, R. J. F.; Fröhlich, R.; Pape, T.; Mitzel, N. W. *Inorg. Chem.* **2007**, *46*, 4293–4297. See also: Lewiński, J.; Marciniak, W.; Lipkowski, J.; Justyniak, I. *J. Am. Chem. Soc.* **2003**, *125*, 12698–12699.

(4) Polarz, S.; Strunk, J.; Ischenko, V.; van den Berg, M. W. E.; Hinrichsen, O.; Muhler, M.; Driess, M. *Angew. Chem.* **2006**, *118*, 3031–3035. *Angew. Chem. Int. Ed.* **2006**, *45*, 2965−2969. For an extensive review on the chemistry and physics of ZnO surfaces, see:Wöll, C. *Prog. Surf. Sci.* **2007**, *82*, 55–120.

(5) Steudel, R.; Steudel, Y. *J. Phys. Chem. A* **2006**, *110*, 8912–8924.

(6) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1968**, *12*, 425–431.

(7) (a) The same compound had been reported previously but was considered to be a dimer; see. Coates, G. E.; Roberts, P. D. *J. Chem. Soc. A* **1967**, 1233–1234. (b) Lewiński, J., personal communication of unpublished results (2006−2009).

(9) (a) Miertus, S.; E. Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117–129. (b) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239–245. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327–335.

(10) Schröder, D.; Schwarz, H.; Polarz, S.; Driess, M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1049–1053.

(11) Frisch, M. J., Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford CT, 2004.

(12) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(13) (a) Almenningen, A.; Helgaker, T. U.; Haaland, A.; Samdal, S. *Acta Chem. Scand.* **1982**, *A36*, 159–166. (b) Rao, K. S.; Stoicheff, B. B.; Turner, R. *Can. J. Phys.* **1960**, *38*, 1516.

(14) (a) Jackson, R. L. *Chem. Phys. Lett.* **1989**, *163*, 315. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Smith, G. P.; Patrick, R. *Int. J. Chem. Kinet.* **1983**, *15*, 167.

(15) Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr.* **1980**, *B36*, 2046–2050.

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