Inorg. Chem. **1996,** *35,* 6638−6639

Synthesis, Characterization, and Reactivity of Monomeric Strontium and Barium Triphenylsiloxide Compounds: Molecular Structure and Reactivity of $M(OSiPh_3)_2$(15-crown-5)THF, M = Sr (1) and Ba (2)

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Received June 14, 1996

There is currently a great deal of interest in the chemical vapor deposition (CVD) of thin films of materials containing the group 2 elements such as perovskite phase metal oxides,[1,2] ceramic superconductors[3,4] and phosphor materials including group 2 sulfides (MS) and thiogallates MGa_2S_4.[5,6] The development of group 2 compounds which satisfy the design requirements that make them suitable as precursors for CVD of group 2 containing films, including sufficient volatility, solubility, and the presence of ligands which can be eliminated completely during a thermally-induced surface reaction to avoid impurity incorporation, is posing a significant synthetic challenge to inorganic chemists.[7] The strategies adopted to enhance volatility by reducing oligomerization generally involve the use of either sterically demanding or multidentate ligands. The use of sterically demanding ligands, such as $(N(SiMe_3)_2)$, or OC-(*t*-Bu)$_3$, impart a low degree of aggregation but leave the metal center coordinatively unsaturated and so susceptible to reactions with small molecules.[8,9] Group 2 complexes which contain chelating multidentate ligands are amongst the most volatile derivatives of the group 2 elements known, e.g. Ba(hfac)$_2$· 18-crown-6 (where hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato), but multidentate ligands can bridge and this strategy often requires the presence of anionic ligands to form a neutral species.[10−13] In general, both these strategies require the presence of an additional reagent such as H_2O or H_2S, to remove the charged ligands and form the desired product.[10,14,15]

We are interested in developing monomeric (and therefore hopefully volatile) precursors to group 2 element-containing films in which the metal center contains ligands than can be eliminated to avoid impurity contamination in the final film. Here, we report the synthesis and characterization of monomeric strontium and barium siloxide compounds based on a hybrid of the strategies described above. These species are cyclic polyether (L) adducts of strontium and barium siloxides ($OSiR_3$), $M(OSiR_3)_2{\cdot}L$, which we prepared to explore the feasibility of the small molecule ligand elimination reactions shown in eqs 1 and 2. The goal is to derive a better understanding of whether

$$M(OSiR_3)_2{\cdot}L \xrightarrow{\Delta} MO + (R_3Si)_2O + L \qquad (1)$$

$$M(OSiR_3)_2{\cdot}L + M'(OR)_4 \xrightarrow{\Delta} (R_3SiO)_{2-x}M-(O)_x-M'(OR')_{4-x} + xR_3SiOR' + L \qquad (2)$$

ether elimination is a suitable strategy to prepare mixed metal oxide materials containing the group 2 elements using well-defined compounds as models. In this case the cyclic polyether, 15-crown-5, was used because it has been demonstrated that the Sr^{2+} and Ba^{2+} cations are too large to fit in the coordination plane of this ligand which leaves three to five coordination sites available on one side of the cation for other ligands. The number of remaining ligands could be minimized by using large ligands and siloxides were chosen due to their potential to be eliminated as silyl ethers, leaving the metal oxide as the only product.[16,17]

Strontium or barium metal were reacted with 2 equiv of Ph_3SiOH and 15-crown-5 in THF in the presence of an excess of ammonia.[18] The analytical and spectroscopic data of the resulting crystalline solids were consistent with the empirical formula [$M(OSiPh_3)_2$(15-crown-5)THF]THF, M = Sr (**1**) and Ba (**2**).[19] Both compounds were structurally characterized in the solid state by single-crystal X-ray diffraction to determine the degree of oligomerization.[20] The solid-state structures of **1** and **2** are shown in Figure 1 which reveals that each compound is monomeric. Compounds **1** and **2** are rare examples of monomeric Sr(II) and Ba(II) siloxide compounds, the only other examples are Sr(OC_6H_2-*t*-Bu)$_2$(THF)$_3$,[21] and the alcohol adduct, Ba($OC_6H_3Ph_2$)$_2$(18-crown-6)·2$HOC_6H_3Ph_2$(18-crown-6).[22] The structures of **1** and **2** are similar and so only **1** will be described here. The Sr atom in **1** is coordinated to eight oxygen atoms,

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(18) All reactions were carried out under a nitrogen atmosphere with dried and deoxygenated solvents. The metal (M = Ba, 0.412 g, 3.0 mmol; M = Sr, 0.263 g, 3.0 mmol), Ph_3SiOH (1.66 g, 6.0 mmol), and 15-crown-5 (0.60 mL, 3.0 mmol) were transferred to a round bottom flask in a glovebox. The flask was connected to a Schlenk line and 30 mL of THF was added by cannula with rapid stirring. After all the Ph_3SiOH dissolved, the reaction solution was cooled to −50 °C and a large excess of anhydrous ammonia gas was condensed into the flask. The solution was allowed to warm to room temperature over a period of 3 h. When all the metal granules were consumed (*ca.* 3 h) the THF and remaining ammonia were stripped off to yield a waxy white solid. This material was redissolved in 10 mL of fresh THF and left to crystallize in a freezer at −20 °C. The yields were 2.65 g, 83.9% (M = Ba) and 2.42 g, 80.4% (M = Sr).

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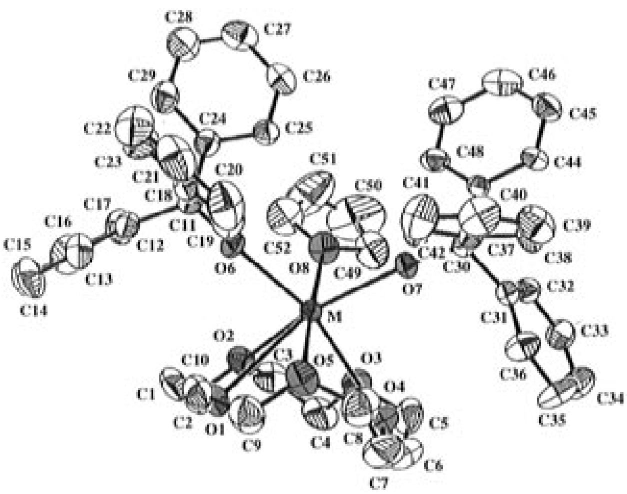

Figure 1. Molecular structure of **1** and **2**. Relevant bond lengths for **1**, Å: Sr−O(1) = 2.833(7); Sr−O(2) = 2.803(7); Sr−O(3) = 2.737(6); Sr−O(4) = 2.751(7); Sr−O(5) = 2.790(5); Sr−O(6) = 2.363(5); Sr−O(7) = 2.322(6); Sr−O(8) = 2.640(8). Relevant bond lengths for **2**, Å: Ba−O(1) = 2.943(6); Ba−O(2) = 2.971(7); Ba−O(3) = 2.887(6); Ba−O(4) = 2.888(6); Ba−O(5) = 2.909(5); Ba−O(6) = 2.482(4); Ba−O(7) = 2.466(6); Ba−O(8) = 2.809(8).

five from the crown ether ligand, two from the $OSiPh_3$ ligands, and one from coordinated THF. In addition there is a second THF molecule incorporated into the crystal structure but not coordinated to the metal. The 15-crown-5 ligand is coordinated to one side of the metal atom resulting in a *cis*-relationship of the $OSiPh_3$ ligands with an O(6)−M−O(7) angle of 104.7(2)° for **1** and 105.6(2)° for **2**. The angles at O in the siloxide ligands are similar to the values observed in other barium siloxide compounds, being 168.2 and 167.3° for **1**, and 166.9 and 160.5° for **2**.[23,24] Other bond lengths and angles are in the ranges expected.

As a result of the monomeric nature of these compounds in the solid state, their volatility was examined by sublimation at 10^{-5} Torr and 200 °C. The compounds do not sublime intact: the crown ether and THF ligands are dissociated leaving "$M(OSiPh_3)_2$", probably as a polymer which was previously reported for the case of M = Ba.[23] The thermal reactivity of these compounds was then studied in the solid state and in solution. Thermogravimetric analyses, conducted in dry N_2 with a heating rate of 10°/min, exhibit similar trends for each compound through the loss of the THF ligands (79.5 °C (2 THF) for **1**; and 85 °C (1 THF), 148 °C (1 THF) for **2**), followed by loss of the remaining ligands at 220 °C for **1**, and 215 °C for **2** to give the solid-state product MSi_2O_5 as determined by weight loss and elemental analysis. This observation was somewhat unexpected since it shows that the stoichiometry of the metal atoms is retained in the final solid-state material in contrast to the solution experiments described below.

Thermally-induced reaction of **1** and **2** in refluxing toluene solution results in elimination of approximately one-half for **1** and one quarter for **2** of the siloxide ligands with formation of the crystalline solid, $(Ph_3Si)_2O$, as determined by NMR spectroscopy, with concomitant formation of a metal−oxo species which as yet we have been unable to unambiguously characterize. When a similar experiment is carried out in either THF or pyridine solution, no reaction is observed. We speculate that silyl ether elimination may be preceded by dissociation of the coordinated THF ligand.

The reaction of **2** with $Ti(O\text{-}i\text{-}Pr)_4$ (1:1) in toluene solution at 60 °C results in quantitative elimination of 2 equiv of the unsymmetrical ether Ph_3SiO-*i*-Pr, which has been unambiguously identified by spectroscopic and analytical methods[25] as well as single-crystal X-ray diffraction.[25] We have been unable to unambiguously characterize the metal-containing product of this reaction, thought to be $BaTiO_2(O\text{-}i\text{-}Pr)_2$•15-crown-5 based on mass balance and ^1H and ^{13}C NMR spectroscopy. However, on TGA analysis under N_2, thermolysis of this species results in formation of crystalline $BaTiO_3$.

Further experiments are in progress to determine the identity and further reactivity of the metal−oxo species and to determine whether **1** and **2** can be transported to surfaces intact in the vapor phase under mild conditions using aerosol assisted chemical vapor deposition. However, this work shows that a new class of monomeric group 2 siloxides can be prepared and that they undergo thermally-induced ether elimination reactions that have potential utility in the synthesis of materials such as $BaTiO_3$.

Acknowledgment. We thank Texas Instruments for financial support of this work, the NSF chemical instrumentation program for the purchase of a low-field NMR spectrometer, and AFOSR and the Camille and Henry Dreyfus Foundation for the purchase of an X-ray diffractometer.

Supporting Information Available: Tables of crystal data, positional and thermal parameters, and complete bond distances and angles for **1**, **2**, and Ph_3SiO-*i*-Pr and ^1H and ^{13}C NMR and melting point data for Ph_3SiO-*i*-Pr and an ORTEP drawing of Ph_3SiO-*i*-Pr (51 pages). Ordering information is given on any current masthead page.

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(19) Characterization data. (**1**) ^1H NMR ([D_8]toluene): 1.45 (m, 8H, THF), 3.34 (s, br, 20 H, 15-crown-5), 3.56 (m, 8H, THF), 7.13, 7.16, 7.18 (s, 3H, Ph), 7.84−7.88 (m, 2H, Ph). ^{13}C NMR ([D_6]benzene): 25.76 (s, THF), 67.78 (s, THF), 68.84 (s, br, 15-crown-5), 127.48 (s, Ph), 128.20 (s, Ph), 136.09 (s, Ph), 142.93 (s, Ph). Anal. Found (calcd for $SrO_9C_{54}Si_2H_{66}$): C, 63.62 (64.67), H, 6.58 (6.63). (**2**) ^1H NMR ([D_8]toluene): 1.44 (m, 8H, THF), 3.04 (s, 20 H, 15-crown-5), 3.56 (m, 8H, THF), 7.18, 7.19, 7.20 (s, 3H, Ph), 7.89 (s, 2H, Ph). ^{13}C NMR ([D_8]toluene): 25.81 (s, THF), 67.75 (s, THF), 69.07 (s, 15-crown-5), 127.50 (s, Ph), 128.03 (s, Ph), 136.02 (s, Ph), 144.26 (s, Ph). ^{29}Si ([D_8]toluene, external TMS standard) in $CDCl_3$: −31.4 (s). Anal. Found (calcd for $BaO_9C_{54}Si_2H_{66}$): C, 60.77 (61.62), H, 6.40 (6.32).

(20) Crystal data for **1**: $C_{54}H_{66}O_9Si_2Sr$, colorless prisms from THF, 0.18 × 0.46 × 0.46 mm, monoclinic, $P2_1/c$, $a = 11.029(1)$ Å, $b = 24.697(4)$ Å, $c = 20.068(2)$ Å, $\beta = 103.00(1)°$, $V = 5350(1)$ Å^3; $Z = 4$; $D_c = 1.245$ g cm^{-3}; μ(Mo Kα) = 1.105 mm^{-1}; $T = 25$ °C, Siemens R3m/v, Mo Kα. Of 12 224 data ($2 \leq 2\theta \leq 47°$), 7840 were independent ($R_{merge} = 2.22$ %), and 4511 were observed [$1.3\sigma(F_o)$]. The structure was solved by the Patterson method. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized, $R(F) = 8.58\%$, $R_w(F) = 5.26\%$, GOF = 0.94, $N_o/N_v = 7.9$. Crystal data for **2**: $C_{54}H_{66}O_9Si_2Ba$, colorless rectangular plates from THF, 0.23 × 0.51 × 0.80 mm, monoclinic, $P2_1/c$, $a = 11.134(1)$ Å, $b = 24.745(4)$ Å, $c = 20.253(2)$ Å, $\beta = 103.30(1)°$, $V = 5430(1)$ Å^3; $Z = 4$; $D_c = 1.288$ g cm^{-3}; μ(Mo Kα) = 0.827 mm^{-1}; $T = 25$ °C, Siemens R3m/v, Mo Kα. Of 24 975 data ($2 \leq 2\theta \leq 53°$), 11 247 were independent ($R_{merge} = 3.16\%$), and 6348 were observed [$2.0\sigma(F_o)$]. The structure was solved by the Patterson method. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized, $R(F) = 5.95\%$, $R_w(F) = 5.18\%$, GOF = 1.07, $N_o/N_v = 11.1$. SHELXL software used for all compounds (Sheldrick, G. Siemens XRD, Madison, WI).

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