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Lewis Base Adducts of Barium/Copper *tert*-Butoxides: Synthesis and Thermolysis of $[\mathrm{BaCu_2(O^tBu)_4}]_n$ and $[\mathrm{L_2Ba_2Cu_4(O^tBu)_8}]$ (L = $\mathrm{Me_3NO}$ and $\mathrm{Et_3PO}$). X-ray Crystal Structure of $[\mathrm{(Me_3NO)_2Ba_2Cu_4(O^tBu)_8}]$

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Reaction of copper(I) mesityl with $[\mathrm{Ba(O^tBu)_2(t\text{-}BuOH)_2}]_4$ yields insoluble $[\mathrm{BaCu_2(O^tBu)_4}]_n$, which dissolves by adduct formation (L = $\mathrm{Me_3NO}$ or $\mathrm{Et_3PO}$) to form soluble $\mathrm{L_2Ba_2Cu_4(O^tBu)_8}$. For L = $\mathrm{Me_3NO}$, this molecule is shown by X-ray diffraction to have a structure based on a *trans*-$\mathrm{Ba_2Cu_4}$ octahedron, with all Ba/Cu edges bridged by μ_2-$\mathrm{O^tBu}$ units; one L binds to each Ba. Bulk thermolysis, TGA, and product analysis have revealed that $\mathrm{O^tBu}$ units undergo not only O/C cleavage but also C/C cleavage, the latter to form carbonate and nonvolatile hydrocarbon products, in addition to BaO and CuO. The intended oxidant $\mathrm{Me_3NO}$ shows no great tendency to oxidize Cu(I).

Introduction

A pervasive problem of the synthesis of barium alkoxides has been their tendency to form insoluble polymers. This problem stems mainly from the low metal oxidation state (II) on one hand, which would only allow for two anionic ligands, and its large ionic radius on the other hand, which can accommodate and indeed demands a large number of ligands. This is usually met by bridging to a neighboring alkoxide and thus polymer formation. The use of bulky ligands has thus been a method of preventing oligomerization by physically blocking neighboring alkoxide from contacting and thus bridging two barium atoms. Another method has been the use of (neutral) Lewis basic coordinating ligands. Both monodentate (such as THF),[1] multidentate (18-crown-6),[2] and chelating ligands (often as part of the alkoxide)[3] have been employed. This problem also extends to heterometallic alkoxides of barium, $\mathrm{Ba}_m\mathrm{M}_n\mathrm{(OR)}_q$, where the problem with solublity can be overcome in two ways. One method is to have a small (≤0.5) ratio of barium to heterometal, which allows the barium to satisfy its large coordination sphere by bridging to the large number of alkoxides introduced by the several heterometal atoms. Examples are the series of $[\mathrm{M(O^tBu)_3Ba(O^tBu)_3M}]$ (M = Ge, Sn, Pb) alkoxides where the barium is six-coordinate and bridging between two $[\mathrm{M(O^tBu)_3}]^-$ moieties.[4] The second method involves a partner metal with a high oxidation state and thus a large number of alkoxides, which are available for bridging. The barium thus no longer needs to "find" more ligands in a neighboring molecule (forming a polymer) but will form *intra*molecular alkoxide bridges. Examples include $[\mathrm{Ba_2Zr_4(O^iPr)_{20}}]$[5] and $[\mathrm{BaTi_4(OEt)_{18}}]$,[6] which have both a low Ba/heterometal ratio and a heterometal in a high oxidation state. We have been investigating methods of synthesis of soluble heterometallic alkoxides of barium. We here report progress along this theme in form of the depolymerization of a heterometallic barium copper(I) alkoxide by small Lewis basic ligands. For reasons described above, success is especially challenging for heterometallic alkoxides containing a lowvalent (i.e., monovalent) heterometal.

Thermolysis of heterometallic alkoxides has been little investigated, even though their thermolytic behavior is important for an eventual practical use of these compounds. We thus report here our investigation of the thermolysis of homo- (for comparison) and heterometallic alkoxides of barium. Previous observations in this area have established the formation of barium carbonate during thermolysis of alkoxide precursors,[7,8] a result we wanted to examine further.

Experimental Section

Materials and Procedures. All manipulations were carried out under inert atmosphere (argon, nitrogen, helium) or in vacuo using standard Schlenk techniques. All solvents were purchased from Fischer Scientific and dried over alkali metal/benzophenone. They were distilled and stored under nitrogen/argon. In reactions involving monovalent copper, the solvents were degassed in three consecutive freeze−pump−thaw cycles. Barium metal was purchased from Alfa/Aesar Chemicals and was stored in a glovebox under argon. Hexamethyldisilazane was purchased from Janssen Chimica and all other reagents from Aldrich. The starting materials $\mathrm{Ba[N(SiMe_3)_2]_2(THF)_2}$[9]

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and CuMes (copper mesityl)[10] were synthesized according to literature methods. The synthesis of $[BaCu_2(O^tBu)_4]_x$ (**3**) and $[(Et_3PO)_2Ba_2Cu_4(O^tBu)_8]$ (**5**) has already been described, but herein we detail a slightly improved synthesis for the former compound.[11] Elemental analyses were performed by Desert Analytics or in-house using a Perkin-Elmer PE2400 CHN/S elemental analyzer. Copper analyses done in-house used iodometry. A *tert*-butyl alcohol/heptane azeotrope was prepared by refluxing the mixture over calcium hydride and distilling under 1 atm of nitrogen, resulting in a concentration of 5.8 M determined by ^1H NMR.

Instrumental Measurements. ^1H NMR spectra were recorded on a Varian XL-300 spectrometer, and chemical shifts were referenced to residual protio solvent peaks. IR spectra were run as KBr pellets on a Nicolet 510P FT-IR spectrometer (spectral window 4000−400 cm^{-1}). Thermogravimetric analyses (TGA) were carried out on a Dupont 2100 instrument inside a helium-filled glovebox. The TGA profiles were run under a flow of helium (1 atm/70 cm^3/min) at a heating rate of 5 °C/min to a final temperature of 1000 °C. Sample sizes were 7−15 mg. The effluent from the TGA was led into a VG micromass quadrupole mass spectrometer (EGA-300MM) for identification of the volatiles (from 12 to 200 amu), allowing the sequence of products formed in the thermolysis to be determined. *tert*-Butyl alcohol (parent ion *m*/*e* 59) and isobutylene (parent ion *m*/*e* 41) can be easily distinguished. X-ray powder patterns were performed on a Scintag XDS-2000 with a copper source ($\lambda = 154$ nm). X-ray photoelectron spectroscopy (XPS) was performed by the Surface Analysis Center of the University of Minnesota on a Perkin-Elmer Model PHI-5400 instrument. Gas chromatography (GC-MS) was done on a HP 5890 Series II GC with a 5971 mass spectrometer. Helium carrier gas was used (linear velocity: 25 cm s^{-1}). Two columns had been placed in series and connected using a press type connector. The first was a 30 m PLOT (porous layer open tubular) alumina column (J&W, i.d. = 0.53 mm). The second was a 60 m RTX5 (Restek, 5% diphenyl polysiloxane−95% dimethyl, i.d. = 0.25 mm, 0.25 μm stationary phase). Identical conditions were used for all injections (injector temperature 180 °C; sample size 10 μL). The initial temperature of 35 °C was kept constant for 10 min, after which a ramp of 10 °C/min was initiated up to a final temperature of 100 °C. The mass spectrometric detector was set to scan ions from 12 to 300 amu.

Synthesis of $[Ba(O^tBu)_2(HO^tBu)_n]_x$ (1). In an 80 mL Schlenk flask, 4.0 g (6.7 mmol) of $Ba[N(SiMe_3)_2]_2(THF)_2$ was dissolved in 30 mL of pentane. To this solution 2.7 mL (16 mmol) of 5.8 M HO^tBu (in heptane) was added. After several minutes, a large amount of white precipitate had formed. The solution was stirred for another 30 min, and then the solvent was decanted from the white powder. The solid was washed with pentane and dried in vacuo for 1 h, resulting in 1.75 g (82%) of $[Ba(O^tBu)_2(HO^tBu)_n]_x$ ($n = 0.5$). ^1H NMR (C_6D_6) 1.24 (broad, ~1 ppm) and ^1H NMR (d_8-THF) 1.38, 1.28, 1.19 ppm. Chemical shifts (d_8-THF) and integration (~1:1:1) vary slightly depending on the value of *n*. TGA experiments indicate that $n = 0.5-0.7$. The absence of THF is confirmed by an in-line mass spectrometer as well as ^1H NMR spectroscopy. The remaining *tert*-butyl alcohol can be removed by heating the solid in vacuo at 80 °C for 24 h. Elemental analysis calculated for $BaO_2C_8H_{18}$: C 33.89%, H 6.40. Found: C 34.36, H 6.34.

Synthesis of $[BaCu_2(O^tBu)_4]_x$ (3). In an 80 mL Schlenk flask 515 mg (1.6 mmol) of **1** was suspended in 30 mL of toluene. The slow addition of 650 μL of 5.8 M (3.8 mmol) HO^tBu (in heptane) resulted in a clear solution and in situ formation of $[Ba(O^tBu)_2(HO^tBu)_2]_4$ (**2**).[12] A solution of 640 mg (3.5 mmol) CuMes in 10 mL of toluene was added, and the mixture was stirred for 18 h. The solvent was decanted, and the remaining white powder was washed twice with diethyl ether and dried in vacuo for 1 h, resulting in 875 mg (98%) of product. Due to its low solubility, no ^1H NMR signals for this compound can be detected in C_6D_6, d_8-THF, or d_6-DMSO. Elemental analysis calculated for $BaCu_2O_4C_{16}H_{36}$: Cu 22.8%, C 34.51, H 6.52. Found: Cu 22.3%, C 34.28, H 6.55.

Table 1. Crystallographic Data for $(Me_3NO)_2Ba_2Cu_4(O^tBu)_8$

formula	$C_{38}H_{90}Ba_2Cu_4N_2O_{10}$	fw	3172.94 g mol^{-1}
a	25.142(3) Å	space group	$P2_1/c$
b	18.043(2) Å	*T*	−172 °C
c	35.522(4) Å	λ	0.710 69 Å[a]
β	108.43(1)°	ρ_{calc}	1.379 g cm^{-3}
V	15 287.81 $Å^3$	μ	21.5 cm^{-1}
Z	4		
$R(F_o)$[b]	0.0822		
$R_w(F_o)$[c]	0.0801		

[a] Graphite monochromator. [b] $R = \sum||F_o - F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

Synthesis of $[(Me_3NO)_2Ba_2Cu_4(O^tBu)_8]$ (4). In a Schlenk flask 1.5 g of **3** was suspended in 40 mL of toluene. Via a solid addition tube, 200 mg of Me_3NO was added, and the mixture was stirred. Within 4 h the solid had dissolved and a clear solution resulted. From this solution, the solvent was removed in vacuo and the remaining solid was extracted with toluene. The solution was concentrated and placed in a freezer (−15 °C), resulting in 770 mg (45%) of product after in vacuo removal of toluene. ^1H NMR (C_6D_6) 1.81 (72 H, *t*-Bu) 2.06 (18 H, Me) ppm. By ^1H NMR the amount of cocrystallized toluene was determined to be between 3.2 and 4.0 equiv/molecule of **4** depending on the sample. For elemental analysis the cocrystallized solvent was first removed in vacuo. Elemental analysis calculated for $C_{38}H_{126}Ba_2Cu_4N_2O_{10}$: C 36.11%, H 7.18, N 2.22. Experimental: C 36.84, H 7.12, N 2.84.

Bulk Thermolyses. To prepare NMR samples of the volatiles, about 15−20 mg of **1**, **3**, or **4** was thermolyzed in an NMR tube in a Wood's metal bath by submerging the samples into the melted metal at about 120 °C and then heating the samples to 400 °C within the course of 1 h. Volatiles were trapped in a second NMR tube (connected to the first via a short glass vacuum transfer tube) cooled by liquid nitrogen. Immediately after thermolysis, the NMR tubes were flame sealed in vacuo.

To prepare gas samples for GC-MS analysis, 80−150 mg samples were thermolyzed under identical conditions as above, but the receiving vessel in this case was a Schlenk flask submerged in liquid nitrogen.

X-ray Structure Determination of $2[(Me_3NO)_2Ba_2Cu_4(O^tBu)_8]\cdot$7toluene (4). The sample tended to decompose when warmed to room temperature. The flask was stored in the freezer, and during the crystal selection process, it was kept cold (below 0 °C) using dry ice. During transfer to the goniostat, the crystal was kept cold by a stream of dry nitrogen passed through a copper coil immersed in liquid nitrogen. A suitable crystal was obtained by cleaving a larger piece. The crystal selected was a triangular prismatic piece of orange color. A preliminary search for peaks and then analysis using the programs DIRAX and TRACER revealed a primitive monoclinic unit cell. After complete data collection ($6° < 2\theta < 45°$), the systematic extinction of $h0l$ for $l = 2n + 1$ and of $0k0$ for $k = 2n + 1$ uniquely determined the space group $P2_1/c$. Unit-cell dimensions were determined by an unrestrained least-squares fit of the setting angles of 174 carefully centered peaks having 2θ values between 20 and 24°. Details of the data collection are given in Table 1. Due to the large unit-cell dimensions, a quite narrow scan (1.3°) had to be used, and some overlap of neighboring reflections was unavoidable. Initially, the overlap was ignored. Data processing of 26 985 measured intensities produced a unique set of 20 049 reflections and $R_{av} = 0.076$ for the averaging of 4633 redundant data. As the solution of the structure progressed, it became very obvious that many reflections were affected by the overlap: 4713 reflections judged to be affected were removed from the raw data file. Data processing followed by a correction for absorption (range 0.225−0.457) then yielded a unique

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set of 16 757 reflections and $R_{av} = 0.099$ for the averaging of 4027 redundant data. The number of reflections removed corresponds to 16% of the unique data. The structure was solved by a combination of direct methods (SHELXS-86) and Fourier techniques. The asymmetric unit was found to contain two independent molecules of the compound of interest as well as seven molecules of reasonably well-defined toluene, which had been used as a solvent. In molecule A there is a disorder at C(15)A and in molecule B at C(45)B; both disorders refined to 50% occupancy. The least-squares refinement was completed with hydrogen atoms in fixed, calculated positions on the two molecules of interest. The hydrogen atoms were assigned an isotropic thermal parameter equal to one plus the isotropic equivalent of the parent atom. The non-hydrogen atoms on molecules A and B were refined with anisotropic thermal factors, except for the two sets of disordered atoms. Atoms in the solvent molecules were refined using isotropic thermal parameters, and no hydrogen atoms were added. The largest peak in the final difference Fourier was 1.21 e/Å^3 in the vicinity of Ba(1)A, the deepest hole was −1.0 e/Å^3. The results of the structure determination are shown in Table 2 and the Supporting Information.

Results

Synthesis of $[BaCu_2(O^tBu)_4]_x$ (3). $Ba[N(SiMe_3)_2]_2(THF)_2$ is a convenient starting material (it is soluble in hydrocarbon solvents and thus allows for homogeneous reaction conditions) for the synthesis of **2**, a barium alkoxide with hydrogen-bonded alcohol ligands.[12] Other syntheses of barium alkoxides starting from barium metal often yield complexes containing the oxo functionality.[13−15] Hydrocarbon and arene solubility of the hydrogen-bonded product **2** is probably due to the hydrocarbon surface of the molecule. In toluene the reactants CuMes and **2** thus form a yellow solution (due to CuMes, which has a yellow color). As the reaction progresses, first a yellow and then an orange suspension appears. After approximately 4 h the reaction is complete and the final product is colorless. All eight available acidic hydrogens in **2** are replaced by copper(I) in a Brønsted acid/base reaction to form (**3**). No OH stretch is observed in the IR spectrum of the product. Even very Lewis basic solvents such as pyridine, THF, and DME fail to dissolve **3**, which demonstrates the polymeric nature of the white powder. We thus suspect that the very nucleophilic bridging alkoxide oxygens (i.e., $Ba-O^tBu-Cu$) give the compound effective protection against solvent coordination. In d^{10} copper(I), the alkoxide oxygen should be especially nucleophilic, as the copper already has a full d-shell and thus cannot accept further electrons from the oxygen. Deoligomerization by coordination of solvent and thus the rupture of alkoxide bridging would impart solubility to the compound. Some evidence of this is provided by the observation that ethyl acetate (which has a rather nucleophilic oxygen) does dissolve **3** when it is used as a solvent. However, no dissolution is observed when it is added stoichiometrically (up to 4 equiv) to a suspension of the polymer in another solvent (such as THF or benzene). This suggests that the alkoxide bridges could be broken if a sufficiently nucleophilic Lewis base is used. Unfortunately, ethyl acetate slowly reacts to form an insoluble black powder, and we were thus never able to grow crystals from this solvent.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(Me_3NO)_2Ba_2Cu_4(O^tBu)_8$

	molecule A	molecule B
Ba(1)−O(7)	2.527(10)	2.550(18)
Ba(1)−O(17)	2.592(9)	2.623(14)
Ba(1)−O(22)	2.593(15)	2.587(16)
Ba(1)−O(27)	2.616(14)	2.625(10)
Ba(1)−O(32)	2.621(13)	2.627(12)
Ba(2)−O(12)	2.529(12)	2.534(15)
Ba(2)−O(37)	2.599(6)	2.600(16)
Ba(2)−O(42)	2.602(18)	2.622(14)
Ba(2)−O(47)	2.634(10)	2.636(11)
Ba(2)−O(52)	2.577(16)	2.608(8)
Cu(3)−O(27)	1.839(10)	1.829(17)
Cu(3)−O(37)	1.800(9)	1.838(14)
Cu(4)−O(32)	1.827(9)	1.834(19)
Cu(4)−O(42)	1.839(10)	1.838(18)
Cu(5)−O(17)	1.831(10)	1.849(16)
Cu(5)−O(47)	1.850(11)	1.831(17)
Cu(6)−O(22)	1.850(11)	1.849(13)
Cu(6)−O(52)	1.833(11)	1.843(14)
O(7)−N(8)	1.377(15)	1.382(26)
O(12)−N(13)	1.418(21)	1.372(23)
Ba(1)−Cu(3)	3.6254(15)	3.6095(23)
Ba(1)−Cu(4)	3.6262(19)	3.6134(24)
Ba(1)−Cu(5)	3.6479(19)	3.6267(26)
Ba(1)−Cu(6)	3.5994(24)	3.6543(26)
Ba(2)−Cu(3)	3.6321(20)	3.6671(2)
Ba(2)−Cu(4)	3.6187(25)	3.63(3)
Ba(2)−Cu(5)	3.6103(24)	3.6007(22)
Ba(2)−Cu(6)	3.5959(19)	3.5765(20)
Cu(3)−Cu(4)	3.539(3)	3.587(3)
Cu(3)−Cu(6)	3.4349(26)	3.369(3)
Cu(4)−Cu(5)	3.4421(25)	3.521(3)
Cu(5)−Cu(6)	3.360(3)	3.4242(26)
O(7)−Ba(1)−O(17)	108.0(4)	101.8(4)
O(7)−Ba(1)−O(22)	110.7(4)	108.0(5)
O(7)−Ba(1)−O(27)	111.7(3)	115.3(5)
O(7)−Ba(1)−O(32)	108.6(4)	111.9(6)
O(12)−Ba(2)−O(37)	106.2(3)	109.8(4)
O(12)−Ba(2)−O(42)	108.6(6)	103.4(4)
O(12)−Ba(2)−O(47)	112.6(3)	109.2(5)
O(12)−Ba(2)−O(52)	110.8(7)	113.4(5)
O(27)−Cu(3)−O(37)	178.1(8)	177.0(3)
O(32)−Cu(4)−O(42)	178.8(8)	178.8(4)
O(17)−Cu(5)−O(47)	178.7(7)	178.31(22)
O(22)−Cu(6)−O(52)	179.1(5)	179.0(6)
Ba(1)−O(7)−N(8)	174.6(16)	176.0(18)
Ba(2)−O(12)−N(13)	177.82(19)	174.6(5)
Cu(5)−O(17)−C(18)	118.3(8)	122.9(13)
Cu(6)−O(22)−C(23)	118.8(10)	116.3(16)
Cu(3)−O(27)−C(28)	118.8(14)	121.9(13)
Cu(4)−O(32)−C(33)	121.1(9)	119.3(12)
Cu(3)−O(37)−C(38)	121.9(6)	116.9(16)
Cu(4)−O(42)−C(43)	118.6(15)	124.3(25)
Cu(5)−O(47)−C(48)	120.3(9)	118.3(11)
Cu(6)−O(52)−C(53)	116.8(11)	117.9(8)

It is of interest to note that the synthesis of **3** was carried out using excess *tert*-butyl alcohol and CuMes (approximately 8%). Excess $[CuO^tBu]_4$ available is thus not incorporated into the final product and is easily washed away with Et_2O. The preferred stoichiometry for the polymeric solid is thus 1:2 Ba:Cu. Preference for this stoichiometry has already been observed in the synthesis of $[Ba_2Cu_4(OCEt_3)_8]$.[16]

Synthesis of $[L_2Ba_2Cu_4(O^tBu)_8]$ (4) and (5). In light of our experience with ethyl acetate, we were surprised that the *stoichiometric* (1 equiv of base/barium) addition of trimethylamine *N*-oxide or triethylphosphine oxide would react with **3** to form arene-

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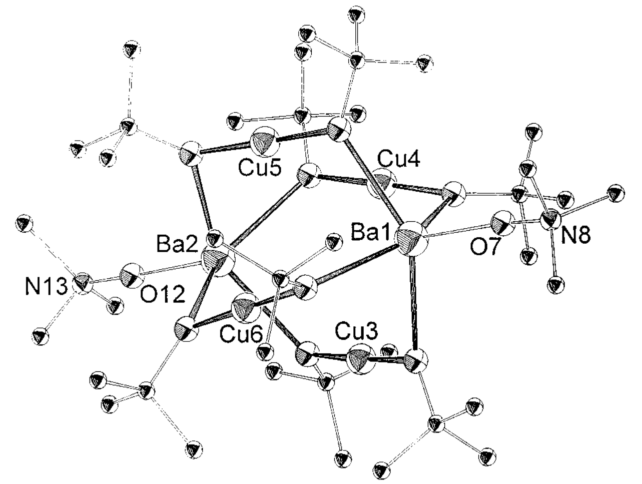

Figure 1. ORTEP drawing of the non-hydrogen atoms of $(\mathrm{Me_3NO})_2\mathrm{Ba_2Cu_4(O}^t\mathrm{Bu)_8}$ showing selected atom labeling. Unlabeled atoms are carbons.

soluble products. Reactivity of each of these two ligands in THF (these ligands do not break up the polymer **3** in benzene) is markedly different, as the amine *N*-oxide reacts within about 20 min to form a yellow solution, whereas the phosphine oxide reacts much more slowly (usual reaction time is about 4 h). The difference in reactivity in the two solvents may be explained by slight solubility of the polymer in THF even though no protio signal for **3** is visible in d_8-THF. The stoichiometry of the final products **4** and **5** (i.e., four alkoxides/neutral donor ligand) is further confirmed by ^{1}H NMR integration of the *tert*-butyl to the alkyl groups of the amine or phosphine oxide.

Solid-State Structure of $2[(\mathrm{Me_3NO})_2\mathrm{Ba_2Cu_4(O}^t\mathrm{Bu)_8}]\cdot 7$toluene (4). Seven toluene molecules cocrystallize with two crystallographically independent molecules of formula $[(\mathrm{Me_3NO})_2\mathrm{Ba_2Cu_4(O}^t\mathrm{Bu)_8}]$. Even though the two molecules of interest are crystallographically independent, the bond lengths and angles in the two are essentially the same. Both molecules also have a similar disorder in the methyl group of one of their trimethylamine oxide ligands.

The six metals and eight oxygens in the central structure are joined together to form a structure resembling a two-ended obelisk (Figure 1). Whereas the barium atoms are located at the square pyramidal ends, the copper atoms form the body of the bipolar obelisk. The alkoxide oxygens complete the structure by bridging the metals in a μ_2 fashion, accommodating the different coordination requirements of the two different metals. Monovalent copper often has a linear coordination environment, which is also observed here (O−Cu−O angles range from 177.0(3) to 179.1(5)°). Four μ_2-alkoxides bridging to the barium form the base of the obelisk's square-pyramidal end; the coordination sphere around the barium is completed by amine oxide in the apical site. This amine oxide is approximately linear with Ba−O−N angles ranging from 174.6(16)° to 177.82(19)°. It is noted here that the NO distance in the free ligand (1.388(5) Å) is the same as those found in this structure (1.372−1.418 Å, average 1.387 Å).[17] Another way to view the structure is that the metals are the vertexes of an octahedron, eight of whose 12 edges are bridged by μ_2-alkoxide ligands.

Thermolysis of $[\mathrm{Ba(O}^t\mathrm{Bu)_2(HO}^t\mathrm{Bu)}_n]_x$ (1). The TGA profile of this homometallic compound indicates that its decomposition occurs in three temperature regimes. Over an extended temperature range (70−150 °C) some of the coordinated *tert*-butyl alcohol is lost. The observed mass loss is not large enough to account for all of the coordinated alcohol. At 330 °C both isobutylene and some *tert*-butyl alcohol (determined by an in-line mass spectrometer) are lost with concurrent formation of $\mathrm{BaCO_3}$ and BaO. The presence of $\mathrm{BaCO_3}$ in the gray solid was confirmed by IR (KBr), with peaks at 1443 (s, asymmetric stretch), 858 (m, out-of-plane bending), and 694 cm^{-1} (w, in plane bending).[18−20] A peak was also present in the C−H region (2956 cm^{-1}), indicating the carbon (3.14%) (combustion analysis for hydrogen 0.69%) found by elemental analysis is not purely graphitic. The intermediate isolated at 400 °C is gray. A ^{1}H NMR spectrum of the volatiles (recorded at room temperature) showed only isobutylene and *tert*-butyl alcohol. Between 650 and 900 °C (the third mass loss), $\mathrm{CO_2}$ (mass spectrometry) is evolved, resulting in colorless solid (BaO). The final % mass is about 44.5−45.5, indicating that *n* in the formula of **1** has a value of 0.5−0.7. A rough estimate of the amount of $\mathrm{BaCO_3}$ present in the intermediate can be made by using all data obtained. The mass lost in the final step is between 6.0 and 6.1% (depending on the amount of *tert*-butyl alcohol present initially). This limits the amount of $\mathrm{BaCO_3}$ to 47% if no "C−H" type carbon was present in the intermediate. With the amount of carbon and hydrogen, determined by elemental analysis, included in the calculation (total of 3.83%) the amount of barium present as $\mathrm{BaCO_3}$ is approximately 25%.[21]

During the final mass loss some of the "C−H" carbon must be lost, in addition to loss of $\mathrm{CO_2}$. A gray-black deposit detected in the furnace tube (but physically remote from the sample holder) after thermolysis of the compound may explain why no other products were detected in the mass spectrum. This deposit was previously not present in the furnace tube and only appeared *after* heating above 400 °C (i.e., the deposit had not formed below 400 °C) and thus is a direct result of thermolysis of the intermediate.

Thermolysis of $[\mathrm{BaCu_2(O}^t\mathrm{Bu)_4}]_x$ (3). Thermolytic decomposition of this heterometallic compound occurs in three steps (Figure 2). A small feature visible in the TGA (mass loss about 2%) above about 80 °C occurs concurrently with the detection of a small amount of *tert*-butyl alcohol (determined by an in-line mass spectrometer). During the second step, at 290 °C, again, only *tert*-butyl alcohol and isobutylene are lost resulting in a black powder containing CuO, Cu metal, BaO as major, and $\mathrm{BaCO_3}$ (vide infra) as the minor barium-containing product. $\mathrm{CO_2}$ loss (mass spectrometry) occurs during the third mass loss, resulting in BaO and

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[17] Caron, A.; Palenik, G. J.; Goldish, E.; Donohue, J. *Acta Crystallogr.* **1964**, *17*, 102.

[18] Nyquist, R. A.; Kagel, R. O. *Infrared Spectra of Inorganic Compounds*; Academic Press: New York, 1971; p 79.

[19] Pouchert, *The Aldrich Library of FTIR Spectra*, 1st ed.; Aldrich Chemical Co.: Milwaukee, WI, 1985; Vol. 2, p 1273.

[20] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons: New York, 1970; pp 96−98.

[21] Calculation (X = % mass loss due to carbonate; the ratio 12/44 is the % mass of carbon in $\mathrm{CO_2}$): $X + 0.0383 - (12/44)X = 0.061$. This results in $X = 0.0312$, which allows the amount of barium that is present as $\mathrm{BaCO_3}$ to be determined.

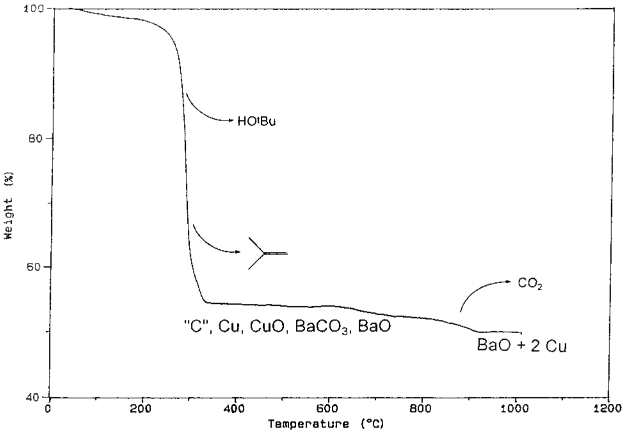

Figure 2. Thermogravimetric profile of $[BaCu_2(O^tBu)_4]_x$ under He gas flow.

Cu; two separate distinguishable high-temperature CO_2 evolution stages can be detected, one at about 700 °C and the other at about 900 °C.

Investigation of the intermediate formed after the second mass loss (isolated at 400 °C) revealed it to be a mixture of several different products. The presence of Cu metal and $BaCO_3$ could be confirmed by X-ray powder diffraction. Carbonate type carbon is substantiated by XPS analysis and IR.[18,19] The IR spectrum of the intermediate again shows peaks at 1443(s), 865(m), and 694(w) cm^{-1} (similar to the intermediate formed at 400 °C in the thermolysis of **1**). In addition, several peaks are present at 1415(s), 1262(m), 1096(m), 1021(m), and 803(m) cm^{-1}. The peaks at 1415 and 803 cm^{-1} are probably due to carbonate that is in an environment slightly different from that of "pure" $BaCO_3$.[22] Assignment of the three other peaks is not possible at this point. XPS analysis also confirmed graphitic or "C−H" type carbon; these two types of carbon are indistinguishable by XPS. The C−H (2956 cm^{-1}) stretch indicates that the carbon (4.09%) and hydrogen (0.49%) found by elemental analysis is present as mostly nonvolatile (polymeric) hydrocarbon chains. The XPS energy shows that some of the copper must be in an oxidation state of +2. This is confirmed by the black color of the intermediate, indicating CuO. The Scherrer method[23] was used to determine that the average size of the metallic copper particles was 400 ± 100 nm.

During the final mass loss (occurring between 700 and 900 °C), which proceeds in two distinct steps, the color of the solid changes from black to a red-brown color. Excellent agreement is found for the expected final % mass (found 50.2%, calcd 50.6%) indicating that Cu metal and BaO are the only products at 1000 °C. X-ray diffraction confirms the presence of Cu metal, whereas hydrolysis of BaO to $Ba(OH)_2$ (after removal of the powder sample from a helium glovebox containing the TGA) prevented the observation of BaO in the powder pattern. The loss of the black color (probably due to CuO) that was present in the intermediate isolated at 400 °C is consistent with the loss of oxygen from CuO. This leads to the question of how the oxygen leaves the sample. An explanation may be the reduction of CuO by carbon, a process thermodynamically favored above room temperature. Ample "C−H" carbon is available in the solid intermediate intimately mixed with the copper oxide. Thus the reactions with negative ΔG found[24,25] in the Ellingham diagram ($CuO + {}^1/_2C \rightarrow Cu + {}^1/_2CO_2$, $\Delta G = -100$ kJ mol^{-1} at 500 °C; $CuO + C \rightarrow Cu + CO$, $\Delta G = -75$ kJ mol^{-1} at 500 °C) can proceed without great kinetic barriers. As in the case of the thermolysis of **1**, there is the question of the fate of the "C−H" carbon. Here again a gray-black deposit is observed in the furnace tube. It is only observed after the thermolysis of the intermediate (formed at 400 °C). Formation of CO_2 from CuO and "C−H" type carbon would go far in explaining the two-step mass loss during each of which CO_2 is lost. As the decomposition temperature of $BaCO_3$[26] is around 1000 °C, it is reasonable to assign the first step to the decomposition of CuO and the second to decomposition of $BaCO_3$.

tert-Butyl alcohol is the *first* product observed by mass spectroscopy in the initial mass loss at 290 °C. Only *later* during this same mass loss is isobutylene detected in the mass spectrum. As the amount of isobutylene in the mass spectrum increases, the amount of *tert*-butyl alcohol decreases, until, at the end of this mass loss, only isobutylene is detectable in the mass spectrum. ^1H NMR spectra (recorded at room temperature and −50 °C) of the volatiles shows only *tert*-butyl alcohol and isobutylene. The ratio of isobutylene to *tert*-butyl alcohol over this entire mass loss was determined as 1.07 ± 0.06 by ^1H NMR integration.

Using all data obtained allows us to make an estimate of the amount of $BaCO_3$ and CuO present in the intermediate. An upper limit to the amount of barium present as $BaCO_3$ in the intermediate (formed at 400 °C) is 50% if neither CuO nor "C−H" type carbon were present in the intermediate. If neither "C−H" type carbon nor $BaCO_3$ (but only BaO) was present in the intermediate, then the amount of the total copper present as CuO would be 72%. If the 4.09% carbon and 0.49% hydrogen that were found by elemental analysis were present only[27] as "C−H" type carbon, the two maxima must be revised to 28% for CuO and $BaCO_3$. The actual amount of each of the two must lie somewhere in between.

Thermolysis of $[(Et_3PO)_2Ba_2Cu_4(O^tBu)_8]$ (5). Below 90 °C, loss of lattice solvent (0−5%, depending on sample) is observed (mass spectrometry). Subsequently (at 152 °C), loss of Et_3PO is detected, consistent with the volatility of this ligand (it can be distilled at 50 °C at 1 Torr). This leaves **3**, which proceeds to decompose as already described (vide supra). This loss of ligand to give the polymeric alkoxide is very different from the thermolysis of the amine oxide analogue, which cannot decompose in such a manner due to the nonvolatile nature of the ligand (vide infra).

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[22] Under high pressures, such as those employed in making KBr pellets, counterion exchange has been observed. Also, different structures of the same compound often display somewhat different IR peaks. See, for instance, refs 18 and 20.

[23] Weller, M. T. *Inorganic Materials Chemistry*; Oxford Science Publications: New York, 1994; p 25.

[24] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; University Press: New York, 1994; p 327.

[25] Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; W. H. Freeman and Co.: New York, 1990; p 230.

[26] A sample of $BaCO_3$ (Aldrich), thermolyzed under identical conditions, decomposed at 950−1010 °C with loss of CO_2.

[27] This calculation takes into account that some of the carbon found in the elemental analysis must be present as $BaCO_3$ (see ref 21 for a sample calculation). The % weight lost in the final step (600−900 °C) is too large to correspond only to the carbon and hydrogen found by elemental analysis.

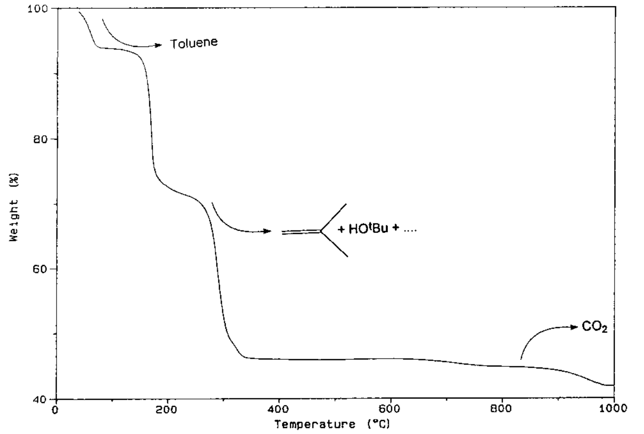
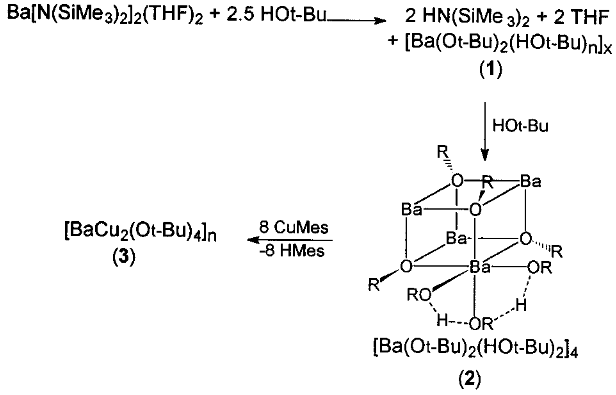


Figure 3. Thermogravimetric profile of $(Me_3NO)_2Ba_2Cu_4(O^t\text{-}Bu)_8$ under He gas flow.

Thermolysis of $[(Me_3NO)_2Ba_2Cu_4(O^tBu)_8]\cdot n$(toluene) (4). Again, loss of lattice solvent is observed first (below 90 °C, Figure 3). Depending on the amount of toluene present in the crystals, the mass lost varies from sample to sample (about 2−7%). Mass loss can be observed even in the absence of heating, indicating facile loss of solvent from the lattice which complicated the X-ray diffraction structure determination. Next, all organic ligands are lost in two distinct steps, the first of which occurs at 168 °C and the second at 290 °C. Loss of *tert*-butyl alcohol and isobutylene as well as trimethylamine is observed during the mass loss at 168 °C. This is confirmed by the % mass lost, which is 13% larger than would be expected for loss of Me_3NO alone; thus some of the *tert*-butoxide ligands must leave in this decomposition. This intermediate (formed at 180 °C) further decomposes (when heated to 290 °C) to give the intermediate formed (as determined by weight) in the thermolysis of **3**. ^1H NMR and ^{13}C NMR spectra of all volatiles indicate that trimethylamine, *tert*-butyl alcohol, and isobutylene are the only volatile products observed up to 400 °C. The subsequent decomposition resembles that of **3**, with loss of CO_2 above 750 °C (in two distinct steps) to leave BaO and copper metal. (The final mass of the sample, when the mass of the sample after loss of lattice solvent is taken to be 100%, was 44.6%; calculated 44.4%.) Solution thermolysis of **4** in a sealed NMR tube in d_8-toluene at 120 °C resulted in a black precipitate and a plethora of products as evident by a large number of ^1H NMR chemical shifts. Only Me_3N could be identified in the mixture.

GC-MS Analysis. ^1H NMR spectra (at room temperature and −50 °C) of the volatiles from the thermolyses of **1** and **3** indicate that *tert*-butyl alcohol and isobutylene are the volatile products. The formation of $BaCO_3$ might suggest the formation of other carbon (C_1, C_2, or C_3) products from the C_4 *t*-Bu group. If C_3 products (propylene and propane, bp −47 and −42 °C, respectively) were produced in the thermolysis, they would certainly be visible in the ^1H NMR spectrum at −50 °C. This may not be the case for ethylene and methane with boiling points of −104 and −164 °C, respectively. We therefore performed gas chromatographic analysis of the evolved volatiles. Separation of isobutylene from C_1, C_2, and C_3 products was facile under the conditions (see Experimental Section) used. Retention time for isobutylene was 15.3 min, whereas those for propylene, ethylene, and methane are 8.4, 5.75, and 5.6 min, respectively. While the parent ion of methane (16) overlaps with the oxygen peak (i.e., the retention time of methane and oxygen were the same), several runs with a methane standard showed that the peak at 15 (oxygen does not overlap with this peak) is about 80% of the peak at 16 and thus can be used for the detection of methane.

Scheme 1



Mass spectral ion chromatograms of the thermolyzed samples of **1** and **3** showed only two peaks. One of them is at 15.3 min and the other at 5.6 min. The ions present in the peak at 5.6 min were mostly due to air (32, 28, 16, and 14). A very small peak at 15 was also present, indicating that a small amount of methane is a product of the thermolysis. The peak at 15.3 min was readily identified as isobutylene. The ion intensity of *m*/*e* 41 (room temperature, 15.3 min) is more than 2 orders of magnitude larger than the peak at 15 (room temperature, 5.6 min).[28] We can thus conclude that isobutylene is the major gaseous product and that methane is only a very minor product of the thermolysis reaction. Most importantly, neither ethylene (room temperature, 5.75 min) or propylene (room temperature, 9.4 min) were products of the thermolysis. We conclude that any *t*-Bu group which is degraded to form carbonate is either totally converted to carbonate or contributes to the nonvolatile aliphatic species detected.

Discussion

Alcoholysis of $Ba[N(SiMe_3)_2]_2(THF)_2$ with 2.5 equiv of HO^tBu in pentane results in the formation of **1**, a hydrocarbon-insoluble product (Scheme 1; for simplicity, **2** is drawn with terminal ligands on only one Ba; dashed lines indicate hydrogen bonding).[29] This compound is not even soluble upon addition of 5 equiv of THF; solubility can only be observed when THF is used as solvent. However, the addition of more *tert*-butyl alcohol (to make a total of 4 equiv) results in a very (>500 mg in 2 mL at 25 °C) pentane-soluble compound (**2**) which has eight hydrogen-bonded protons available for further reactivity.[12] Two factors account for the stability of this Lewis base adduct. First, the Lewis basicity of the alcoholic oxygen, but this may not be enough, as THF does not form a stable adduct. Second, hydrogen

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(28) The ionization efficiencies of these two molecules cannot differ by 2 orders of magnitude.

(29) In benzene and toluene, in a concentration of about 30%, it forms a gel of such high viscosity that a magnetic stirrer can no longer stir the solution. Suspensions at lower concentration form less viscous gels.

bonding of the alcoholic protons to the terminal alkoxide adds to the stability of **2**.

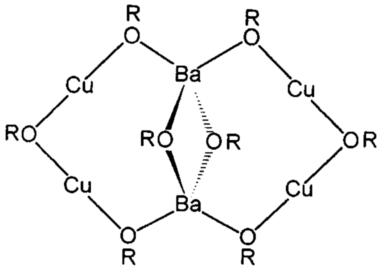
In a Brønsted acid/base reaction, all eight available acidic, alcoholic protons (i.e., two per barium) are replaced by monovalent copper to generate **3**. Further alcoholic protons are no longer present as evidenced by the lack of an OH stretch in the IR spectrum. The resulting colorless compound is striking in its insolubility: all attempts to dissolve it in common coordinating solvents (THF, DME, pyridine, DMSO) were unsuccessful. Also, the addition of coordinating ligands (18-crown-6, Ph_3PO, tetraglyme, TMEDA, PPh_3, PEt_3, and ethylene carbonate) to a suspension of **3** in benzene or THF did not result in soluble products. Most surprisingly, the addition of *tert*-butyl alcohol to a suspension of this compound in benzene did not solubilize this compound, even upon heating. This is in stark contrast to **1**, which dissolves in pentane upon addition of enough *tert*-butyl alcohol to form **2**. Coordination of barium to the strongly Lewis basic alkoxide ligands must be more favorable than coordination to the alcoholic oxygen, even with the potential hydrogen bonding that is possible upon addition of HO^tBu. Addition of stronger Lewis bases finally did allow us to dissolve this compound by its coordination to barium. This lead to the synthesis of $[L_2Ba_2Cu_4(O^tBu)_8]$ (L = Me_3NO, Et_3PO). Deoligomerization of an alkoxo bridge by Me_3NO and Ph_3PO has been demonstrated in one of Feher's aluminosilsesquioxanes.[30] In this case the addition of HO^iPr also could not break up the bridging alkoxides (even with 10-fold excess), and only the more strongly nucleophilic phosphine oxide and amine oxide resulted in a monomer. Two explanations may rationalize why $Ph_3P{=}O$ was ineffective in our case to dissolve **3**. First, the three phenyl groups are too bulky to allow the reaction to proceed, and second, the oxygen is not nucleophilic enough to break the alkoxide bridges. Dissolution of **3** by Me_3NO and $Et_3P{=}O$ was not immediate and did take about 1 h in the case of Me_3NO and 3−4 h in the case of Et_3PO. This can be due to the different nucleophilicity of the oxygen. The resonance structure $Me_3N^+{-}O^-$ should have the largest contribution in the amine oxide, but for the phosphine oxide we can envision that the resonance structure $Et_3P{=}O$ has a major contribution. The larger steric bulk of Et_3PO may also contribute to the longer reaction time than Me_3NO.

One would expect the reaction of Me_3NO with a species containing monovalent copper to lead to the oxidation of the copper to the divalent state, but this does not occur. Oxidation does occur after several weeks (6 weeks) in a sealed NMR tube (C_6D_6 solvent), based on formation of a large amount of insoluble black solid (the ^1H NMR spectrum of the soluble fraction does not reveal any new resonances). An insoluble black solid has also been seen when a solution of **4** is oxidized with N_2O, or by reaction of either **4** or **5** with ^tBuOOH. This suggests that, over an extended period of time, the amine oxide ligand does oxidize the monovalent copper to its divalent state. A solution of **5** remains colorless even over the course of 3 months (no change in the ^1H NMR spectrum), which is readily explained by the more oxidizing nature of the amine oxide as opposed to the phosphine oxide.

Barium can easily accommodate six *tert*-butoxide ligands as exemplified by **2** or in the series of $[M(O^tBu)_3Ba(O^tBu)_3M]$ (M = Ge, Sn, Pb) alkoxides.[4] It is thus surprising to find five coordinate barium in **4** and **5**. This is especially surprising for **4**, as Me_3NO is approximately isosteric with *tert*-butoxide. Five-coordinate (with *tert*-butoxide) barium is not unprecedented,[31] and it does provide enough steric bulk to prevent oligomerization, generating a molecular species with a core structure $Ba_2Cu_4O_8$. One may speculate that this central unit is also present in the polymeric starting material.[11]

Apart from the obviously identical core $Ba_2Cu_4O_8$ and terminal amine or phosphine oxide ligands, both **4** and **5** are similar in a number of detailed points. Both pack with several solvent molecules. One toluene and three THF solvent molecules are packed in one unit cell with two molecules of **5**. A very similar pattern is followed by amine oxide adduct, as there are seven molecules of toluene in each unit cell with two molecules of **4**. Both crystal structures feature an asymmetric unit having two independent heterometallic alkoxide molecules. All four independent determinations of the core structure display a distinct helical twist of the four O−Cu−O vectors. It could be viewed as a quadruple helix (contrast the double helix of DNA). The symmetrical inner core structure might suggest that the molecules would pack together easily in the solid, but this does not seem to be the case, as both of them need an extraordinary number of solvent molecules to fill larger holes in the crystal lattice. Solid **4** and **5** are *not* crystallographically isomorphous.

It is intriguing that even though these two compounds are so similar, a change of the alkoxide to $[Et_3CO]^-$ does not alter the metal stoichiometry but gives a very different structure. The structure of $[Ba_2Cu_4(OCEt_3)_8]$ (**I**) could be described as a butterfly, as it has a central $[Ba_2(OR)_2]^{2+}$ body with two $[Cu_2(OR)_3]^-$ wings attached (R = CEt_3).[16] It differs fundamentally from **4** and **5** in that neither of these has $Ba_2(\mu\text{-}OR)$ bridges. This structure again ensures that the copper(I) has a linear two-coordinate environment, but due to the lack of terminal ligands barium is only four coordinate, in a roughly tetrahedral arrangement. Another way to look at the structure is that, upon removal of the two neutral ligands L (L = Me_3NO and Et_3PO) from **4** or **5**, the structure rearranges to give a pseudotetrahedral arrangement arround barium in lieu of the square-pyramidal structure found in **4** or **5**. This avoids that all ligands lie on one side of the barium. Such versatility in structural types indicates that the energetic



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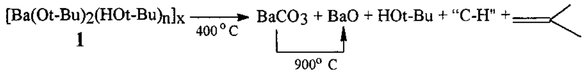
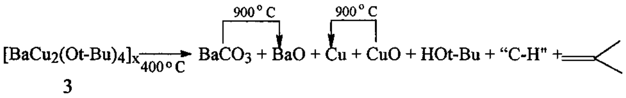
(30) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288.

(31) Borup, B.; Samuels, J. A.; Streib, W. E.; Caulton, K. G. *Chem. Ber.* **1996**, *129*, 1003.

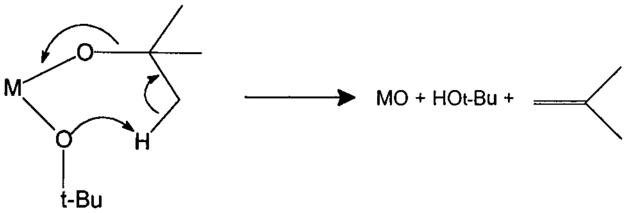
Scheme 2



Scheme 3

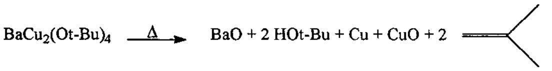


Scheme 4



preference for one structural type over another is small and that small changes in the barium ligand environment can have a fundamental effect on the resulting structure.

Thermolysis of **1** and **3**−**5** proceed to yield the same ultimate products: BaO and Cu metal (except in the case of **1**, which yields only BaO). We commence our discussion with the thermolysis of **3**. A simple approach to this thermolysis would suggest that the thermolysis should proceed via reaction 1. We can envision that the thermolysis should proceed leaving BaO as only barium containing product. On the other hand copper should undergo disproportionation yielding Cu and CuO. This should result in the simultaneous evolution of an equivalent amount of *tert*-butyl alcohol and isobutylene. We indeed find only those volatiles, and in a ratio similar to that shown in eq 1 (1.07 ± 0.06, vide supra). But, to our surprise, in addition to the expected solid-state products we also found $BaCO_3$ in the intermediate (formed at 400 °C), which decomposes only in the ultimate step to form BaO and CO_2. A fundamental problem with $BaCO_3$ as a product is that there is inadequate oxygen in a "$BaCu_2(Ot\text{-}Ba)_4$" species to form carbonate, CuO and leave any (O^tBu).

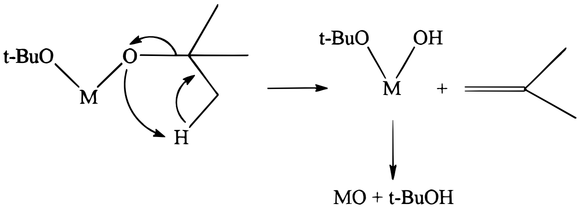


(1)

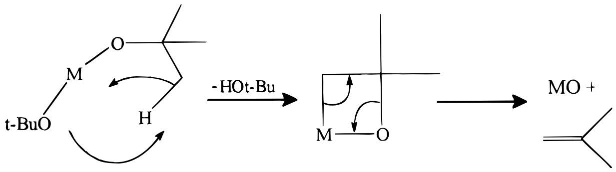
Thermolysis of **1** (Scheme 2) and **3** (Scheme 3) proceed in very similar ways. Loss of *tert*-butyl alcohol and isobutylene are not simultaneous as would have been expected (vide supra); instead *tert*-butyl alcohol is observed first. As there was greater overlap of the evolution of isobutylene and *tert*-butyl alcohol for **1**, its thermolysis was less rigorously investigated.

Before we turn our attention to the mechanistic implications of these data, we first look at the thermolyses of the ligand adducts. Thermal decomposition of **4** and **5** proceed in very different ways. Whereas **5** loses phosphine oxide easily to give **3** (the TGA of **5**, after the loss of Et_3PO, is essentially the same as that of **3**), the amine oxide is not lost as a molecular unit from **4**. As trimethylamine is the only nitrogen-containing product observed in the volatiles, the *N*-oxide oxygen must remain in the solid, either oxidizing some of the copper to copper(II) or incorporated into the carbonate.

Scheme 5



Scheme 6



Three possible mechanisms can be invoked for the decomposition of *tert*-butoxides of barium. Two of these can be ruled out because *tert*-butyl alcohol evolution precedes isobutylene. A concerted mechanism (Scheme 4) can be discounted, as both isobutylene and *tert*-butyl alcohol should form at the same time and would thus reach the mass spectrometer simultaneously. Moreover, if either of the two organic products would be temporarily retained in the residue, it would be the alcohol (not the olefin), since the alcohol has both O-donor and hydrogen-bond functionalities to bond to the residue.

γ-Hydrogen elimination (Scheme 5) is also excluded, as isobutylene would be formed first, whereas the actual order of evolution is reversed.

A mechanism consistent with the formation of first *tert*-butyl alcohol and then isobutylene is one that involves the transient existence of a carbon−metal bond (Scheme 6).

Carbonate formation is difficult to rationalize mechanistically, but three general pathways (Scheme 7) can be envisioned for the decomposition of a *tert*-butoxide ligand to form carbonate. These differ in the fate of the four *tert*-butyl carbons and in particular in the fate of the methyl carbons. It is most reasonable to assume that the quaternary carbon is converted into carbonate, as it already has one oxygen attached and must scavenge only an additional two. Both eqs 2 and 3 imply that the remaining products are some volatile hydrocarbons such as methane (C_1), ethane, ethylene (C_2), or propane, propylene (C_3). Path 4 involves variable amounts of graphitic and polycyclic aromatic products.

Scheme 7

$$O^tBu \rightarrow CO_3^{2-} + C_3 \qquad (2)$$

$$O^tBu \rightarrow CO_3^{2-} + C_1 + C_2 \qquad (3)$$

$$O^tBu \rightarrow a\ CO_3^{2-} + (4\text{-}a)\ \text{“C−H”} \qquad (4)$$

A priori, neither of these pathways can be excluded, as there is enough oxygen in neighboring *tert*-butoxide ligands, as long as only *some* of the *tert*-butoxides are converted to carbonate. Also, the amount of isobutylene is larger than the amount of *tert*-butyl alcohol, thus some of the oxygen is left behind in the solid. GC-MS analysis allows us to discount (2) and (3), as all of the volatile products are observed to have four carbons. Evidence from XPS analysis (indicating carbonate and "C−H" type carbon) and IR spectroscopy (where prominent C−H stretches are present) shows that (4) may be a more realistic way to view the decomposition. We suggest that the metallacycle in Scheme 6 could also cleave a C−C bond and thus lead to carbonate and nonvolatile hydrocarbon products.

Conclusions

Lewis basic reagents can break up polymeric alkoxides of barium. Whereas in some cases the energetics of such a breakup can be helped by hydrogen bonding to an alcohol, this is not always sufficient. Reagents having very nucleophilic oxygen atoms (such as amine *N*-oxide) need to be used for the more robust polymers encountered here.

Heterometallic alkoxides of barium often display very different structures even though the ligand set has not changed considerably. This study reveals the ease with which they change their structure in response to a slightly different ligand set.

Each *tert*-butoxide ligand can decompose in one of two different ways. Either it forms isobutylene and *tert*-butyl alcohol as volatile products or the ligand is completely dismembered to form CO_3^{2-} and "C−H" type carbon. The formation of $BaCO_3$ indicates that an important mechanism of thermolysis is one that involves C−C bond cleavage.

The sequence of products formed, (first HO^tBu, then isobutylene) and also the formation of $BaCO_3$ are characteristic of the thermolysis of both **1** and **3**. Hence the formation of barium carbonate is independent of the presence of copper, which is present only in **3**. Similarly, the sequence of product formation is independent of the presence of copper as both compounds decompose in the same manner. Thus copper is unlikely to be involved in the mechanism of carbonate formation or in the mechanism that generates the sequence of products; this is apparently controlled by the electropositive metal ion Ba^{2+}. Consequently, it may be that the metallocycle in Scheme 6 is also central to the C/C bond cleavage which "dismembers" ^tBuO to nonvolatile hydrocarbon products.

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Supporting Information Available: Full crystallographic details and atom positional and thermal parameters for $(Me_3NO)_2Ba_2Cu_4(O^tBu)_8$ (8 pages). Ordering information is available on any current masthead page.

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