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SYNTHESIS AND DECOMPOSITION KINETICS OF LIQUID PRECURSORS
FOR CHEMICAL VAPOR DEPOSITION (CVD) OF BARIUM

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ABSTRACT

The first room-temperature liquid compounds useful for the CVD of barium-containing oxides were prepared by reacting barium beta-diketonates with alkyl-substituted triamine ligands. For example, barium bis(2,2,6,6-tetramethyl-3,5-heptanedionate) ($\text{Ba}(\text{thd})_2$) reacts with N,N',N'' -triaryldiethylenetriamine to form a viscous liquid that is miscible with additional amine. The compounds are monomeric in solution and can be completely flash-vaporized in solution with residue undetectable at the parts-per-million level. Thermal decomposition studies of this compound were carried out in a sealed NMR tube. They showed that it is more stable than a similar amine complex of barium 2,2,6-trimethyl-3,5-heptanedionate. This difference in thermal stability can be understood by a beta-hydrogen elimination mechanism operating only in the latter barium compound.

INTRODUCTION

The development of new precursors for CVD involves the design, synthesis and testing of materials to see if they have the many required properties. In particular, successful operation of a CVD process requires precursors with sufficiently high vapor pressures that can be generated reproducibly and without any decomposition to non-volatile residue. Liquid precursors are much more likely to meet these requirements than are solids. Solids tend to have low and non-reproducible vapor pressures, and often leave solid decomposition products after sublimation. Even if the solid decomposes only slightly, the products of decomposition often remain on the surface, impeding the free evaporation of the remaining solid. Solids may slowly change their state of oligomerization, thereby changing their vapor pressures. Liquids have the further advantage over solids in that liquids can be pumped at a controlled rate into a flash vaporizing system, thereby avoiding thermal decomposition during vaporization. Thus liquid precursors (or gaseous ones, when available) are used in almost all practical applications of CVD.

Almost all compounds of alkaline earth metals are solids at room temperature, so it has been difficult to find effective CVD precursors for these metals (1). A room-temperature liquid barium compound has been reported (2), but compounds of this type

were later found to be non-volatile (3). A fluorinated barium beta-diketonate was found to be solid at room temperature, but melted at a low enough temperature so that the molten material could be evaporated from a bubbler (4); however, its CVD products are contaminated by fluorine, which can be deleterious to properties of the deposited material.

In this paper we report the first two room-temperature liquid barium compounds that are volatile enough to be useful for CVD. They are based on amine complexes of barium beta-diketonates and contain no fluorine. We also study their decomposition rates in the liquid phase, and their volatility.

Traditional screening of compounds as potential CVD precursors has been carried out by methods such as thermal gravimetric analysis (TGA). Unfortunately, the weight loss measured using TGA does not distinguish between vaporization and decomposition. Also, TGA also has difficulty detecting small (less than about 1%) but significant percentages of non-volatile residue, which can build up and block a vaporizer, and may incorporate undesirable particles in the product.

We used two different screening techniques that overcome these two limitations of TGA. In order to measure the decomposition kinetics in a liquid without its concurrent vaporization, we collected NMR spectra of the liquid sealed in an NMR tube. In this way we can quantitatively measure decomposition rates of a liquid, and also detect the build-up of its decomposition byproducts and sometimes identify them. In a separate experiment, we found a way to measure extremely small amounts of non-volatile residue from the evaporation of liquid precursors. We use ultrasonic nebulization to break up the liquid into small droplets (typically 20 microns in diameter), which are then flash vaporized within a fraction of a second after mixing with a preheated carrier gas or passing into a heated tube. We then look for light scattering from any tiny droplets or particles of non-volatile residue left in the gas stream by the evaporating droplets. Sensitivities to parts-per-million of non-volatile residue are easily achieved by this light-scattering method.

We have used these techniques to test our two new liquid barium compounds. The more stable of these compounds resisted thermal decomposition for hours at temperatures over 300 °C. Flash volatilization was complete by 250 °C, leaving no detectable non-volatile residue. These are the first reported room-temperature liquid compounds that are useful for transporting barium into CVD systems. Our previously-reported liquid barium CVD precursors are mixtures, rather than pure compounds (5). Thus their purification and analysis can be more difficult than the pure compounds reported in this paper.

Similar room-temperature liquid precursors can be made for strontium, calcium and magnesium. These new liquid precursors are particularly well-suited for CVD of multicomponent materials containing alkaline earth metals. Of particular current interest are high dielectric constant materials (barium strontium titanate), ferroelectrics (strontium

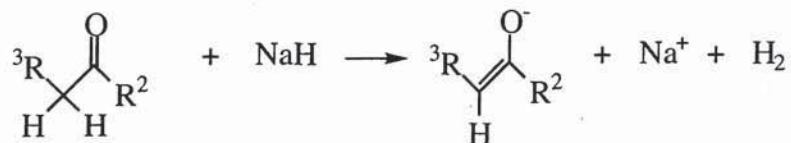
bismuth tantalate, lead magnesium niobate), microwave dielectrics (barium magnesium tantalate), metallic conductors (strontium vanadate, strontium niobate, lanthanum strontium cobalt oxide), phosphors (calcium tungstate), non-linear optical materials (beta-barium borate), magnetic oxides (barium ferrite), colossal magnetoresistive materials (lanthanum strontium manganese oxide) and high T_c superconductors (yttrium barium copper oxide, bismuth calcium strontium copper oxide).

EXPERIMENTAL

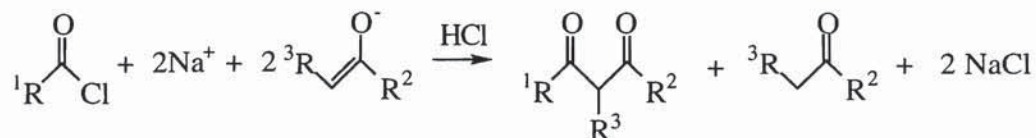
Synthesis of Beta-diketone Ligands

Beta-diketone ligands may be prepared by known methods, such as the Claisen condensation of a methyl ketone and an ethyl ester in the presence of a strong base like sodium hydride (6). These methods, however, give impure products in only moderate yields.

We have found a way to synthesize these beta-diketone ligands in higher yield and with greater purity. We first react an appropriate ketone with a strong base in the presence of a donor solvent, such as sodium hydride in tetrahydrofuran (THF), to form a solution of the corresponding sodium enolate:



This enolate is then reacted with an appropriate organic acid chloride, neutralized with a mineral acid and filtered to remove the salt precipitate, to form the desired beta-diketone:



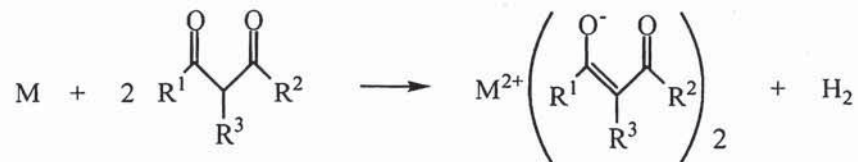
Distillation under low pressure then yields the desired beta-diketone in higher yield and better purity than the traditional Claisen condensation. The excess starting ketone can be recovered and reused for further syntheses. This method is particularly effective when the R^2 group is a tertiary alkyl group, such as tertiary butyl.

As a specific example of this method, the synthesis of the beta-diketone 2,2,6-trimethylheptane-3,5-dione (H3hd) is given as follows. All experimental manipulations were carried out using standard techniques under dry nitrogen either in a glovebox or on a Schlenk line unless otherwise stated. Sodium hydride (NaH) (16.56 g, 690 mmol) was suspended in 400 mL of dry THF and heated to 85 °C. Pinacolone (80.8 ml, 646 mmol) was added at 4.4 mL/min, and vigorous bubbling of hydrogen (H_2) gas began after the first

10 mL was added. The addition was continued at a rate of addition low enough to keep the reaction from bubbling too vigorously. After the addition was completed, the reaction was stirred at 85 °C an additional 20 minutes until the bubbling stopped (i.e. when no more bubbles were observed passing through an oil bubbler which was vented to the atmosphere). The pale yellow suspension was then cooled to room temperature and filtered through celite to remove excess NaH. The clear, pale yellow filtrate was cooled to 0 °C and neat isobutyryl chloride (30.8 mL, 294 mmol) was added at 3.1 mL/min giving a very turbid, light yellow suspension. This was removed from the ice bath and stirred for 15 min and again cooled to 0 °C. At this point, the mixture contained 1 eq. NaCl, 1 eq. pinacolone, 1 eq. Na(3hd) and 0.2 eq. Na(enolate). Subsequently, 32 mL of concentrated aqueous HCl was added carefully to give a fluffy, white solid precipitate of NaCl in a clear, colorless solution. Ample MgSO₄ was added to absorb the water, the mixture was stirred for 30 min and then filtered. The solid was washed with 100 mL of hexanes, and the washings were combined with the filtrate. The solvent and excess pinacolone were removed *in vacuo* and the remaining material was distilled leaving a pale yellow liquid (40.50 g, 81%) which was shown to be the desired product, 2,2,6-trimethylheptane-3,5-dione (H3hd), by NMR analysis. The product distilled at 132-133 °C at 150 mbar.

Synthesis of Barium Beta-diketonates

Compounds can be formed between beta-diketonate ligands and most metals. Two ligands can be bound to metal ions in the divalent (+2) oxidation state, including beryllium, magnesium, calcium, strontium and barium. Many different reactions can be used to bind beta-diketonate ligands to metals (7). In particular, alkaline earth metals may be reacted directly with the beta-diketone ligand to form a metal beta-diketonate compound:

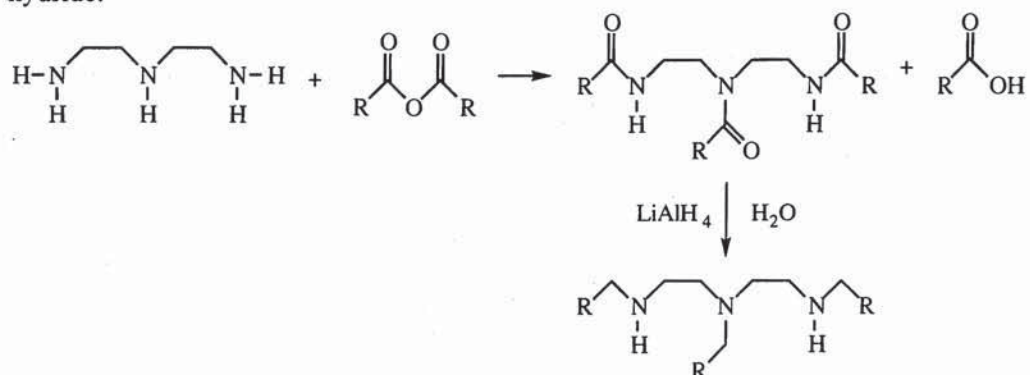


The preparation of barium 2,2,6-trimethyl-3,5-heptanedionate, Ba(3hd)₂, is as follows. Barium metal (1.78 g, 13.0 mmol) and 2,2,6-trimethyl-3,5-heptanedione (H3hd) (4.41 g, 25.9 mmol) were placed together in a flask and immediately bubbles of hydrogen began to form. 30 ml of THF was added and the reaction appeared to slow. After bubbling ammonia gas through the mixture for 2 minutes, the bubbling became vigorous. After 30 minutes, the bubbling slowed, so ammonia was again bubbled for 5 minutes. This procedure was continued for 4 hours until almost no metal remained. Then the mixture was filtered through celite, giving a clear, colorless solution. The THF solvent was removed by evaporation under reduced pressure, leaving 5.01 g (81%) of a solid.

Synthesis of the Triamine Ligands tadeta and d₆-tadeta

We chose to use N,N',N''-triaryldiethylenetriamine (tadeta) to react with the barium beta-diketonates, in order to produce a liquid product. The 5-carbon amyl (or pentyl) groups incorporate enough flexibility and randomness to frustrate the crystallization of the product. The synthesis of this type of triamine can be carried out

as follows. The commercially available unsubstituted triamine, diethylenetriamine (deta), is first acylated with an acid anhydride under conditions in which only one acyl group can attach to each nitrogen. Then the resulting triamide is reduced with lithium aluminum hydride:



This procedure results in a triamine in which the terminal nitrogens have one hydrogen (secondary amines) and the backbone nitrogen carries no directly bonded hydrogen (tertiary amine).

It is important to note that other alkylation methods are likely to add two alkyl groups to each terminal nitrogen. The resulting tertiary amines were found to be too bulky to bind strongly to the barium beta-diketonates. In contrast, the alkylation method that we have used is highly selective, and results in exactly one alkyl chain attached to each nitrogen.

The preparation of d_6 -triamyldiethylenetriamine (d_6 -tadeta) by this method is as follows. Diethylenetriamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, (3.25 ml, 30.1 mmol) was added at 2 drops/sec to a 0°C solution of valeric anhydride, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO})_2\text{O}$, (18.6 ml, 94.1 mmol) in 15 ml diethylether (Et_2O). After addition was complete, the pale yellow solution was then refluxed for 3 hours. The excess anhydride was quenched by adding H_2O (0.15 mL, 8.3 mmol) and then the solution was cooled to 25°C . The Et_2O was removed *in vacuo*, and the valeric acid was distilled off at 110°C under full vacuum leaving a very viscous, light yellow liquid which solidified after cooling to room temperature. This material was dissolved in 40 ml of THF and slowly added dropwise to LiAlD_4 (5.00 g, 119 mmol) in 40 ml THF. The heat of reaction maintained a reflux, and after the addition was complete, the mixture was maintained at reflux temperature for 3 hours. After cooling to 0°C , the mixture was quenched with 5 ml water, 5 ml of 15% aqueous sodium hydroxide (NaOH), and finally 15 ml water. The mixture was filtered, the solid was washed with 30 ml hexanes, and the combined organic liquids were dried with magnesium sulfate. After several hours, the magnesium sulfate hydrate was filtered off and the solvent was removed *in vacuo*, leaving a colorless liquid. Distillation under full vacuum (about 3×10^{-2} Torr) gave the major fraction at $118\text{--}120^\circ\text{C}$ (7.30 g, 77% yield based on diethylenetriamine). NMR confirmed that this product was d_6 -N,N',N''-triamyldiethylenetriamine (d_6 -tadeta).

The partial deuterium substitution of tadeta was done to provide a lock signal for

the NMR without the need to add a volatile deuterated solvent. Such a volatile solvent would have greatly increased the pressure during the thermal decomposition studies that were carried out in NMR tubes sealed under vacuum.

Synthesis and Use of Amine-Complexed Barium Metal Beta-Diketonates Ba(3hd)₂·tadeta and Ba(thd)₂·tadeta

The amine-complexed barium beta-diketonates may be formed simply by reacting the amine with a barium beta-diketonate suspended in hexane until the solid has dissolved. The hexane is then removed by warming the mixture under vacuum. Alternatively, the reaction forming the barium beta-diketonate may be carried out with the liquid amine also present in the reaction mixture.

Apparatus for Nebulization and Vaporization

The liquid precursors were nebulized by pumping them into an ultrasonic nebulizer (Cetac) and carrying the resulting fog with a flow of nitrogen carrier gas. This nebulizer operates at a frequency of 1.4 Mhz, and produces droplets with typical diameters of 20 to 30 microns. The fog was passed through a glass tube in a tube furnace. At the outlet end of the furnace, the vapor mixture was observed with a bright light, to see if the droplets had evaporated. Any non-volatile residue, even with sub-micron diameter, would be seen easily against a dark background.

RESULTS

The compounds Ba(3hd)₂·tadeta and Ba(thd)₂·tadeta were found to be viscous liquids at room temperature, which is surprising since all other known barium beta-diketonates are solids at room temperature. Similar compounds with smaller alkyl groups in place of the amyl (pentyl) groups were found to be solids at room temperature. Thus the long hydrocarbon chains of the amyl groups are essential to keeping the monomeric complexes from solidifying at room temperature.

These liquid barium compounds are miscible in all proportions with additional amine (tadeta), as well as with hydrocarbon solvents, such as mesitylene or dodecane. The solutions have lower viscosity, so that they are more easily pumped and nebulized.

The ¹³C{¹H} NMR spectra of Ba(3hd)₂·tadeta and Ba(thd)₂·tadeta each show distinct singlet due to the bridge carbon between the two carbonyl groups, appearing at 90.5 ppm for Ba(3hd)₂·tadeta and 87.1 ppm for Ba(thd)₂·tadeta. The thermal decomposition of these compounds was monitored by the disappearance of this unique resonance line. At a temperature of 310 °C, the Ba(3hd)₂·tadeta resonance nearly disappears in about an hour, while the resonance for Ba(thd)₂·tadeta does not decrease significantly. This decomposition data is plotted in Figure 1.

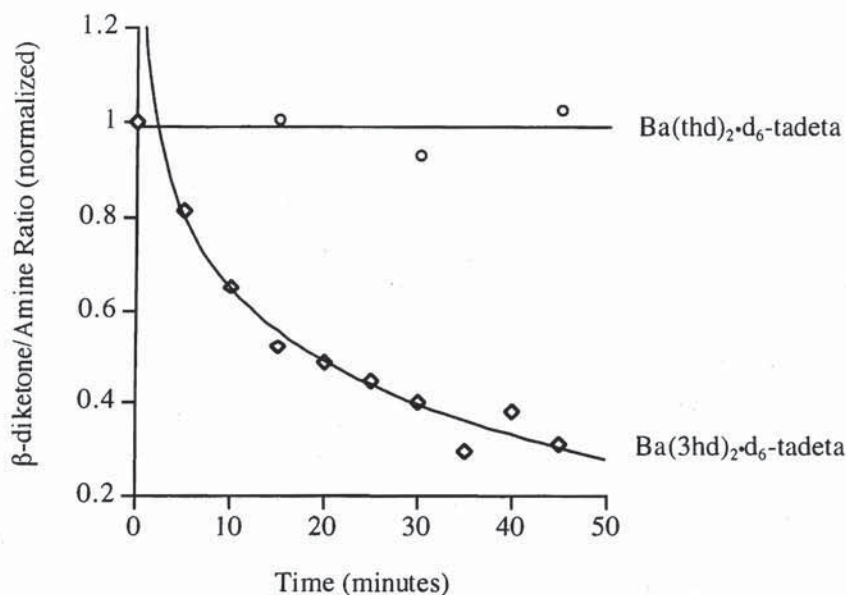


Figure 1. A graph of the concentrations of Ba(thd)₂·d₆-tadeta and Ba(3hd)₂·d₆-tadeta after heating at 310 °C for the indicated times. The abscissa represents the normalized ratio of the areas of a β-diketone ¹³C resonance to a d₆-tadeta ¹³C resonance.

Thus the Ba(thd)₂·tadeta is significantly more stable than the Ba(3hd)₂·tadeta. Additional measurements at a higher temperature, 360 °C, do show decomposition of the Ba(thd)₂·tadeta over the period of an hour. During the decomposition reactions, a white, gel-like precipitate appeared in the NMR tubes, while the liquid turned yellow, then orange and finally brown.

GC mass spectra of the decomposition products from Ba(3hd)₂·d₆-tadeta showed three peaks, with highest masses 170, 184 and 230 amu, and GC retention times of 7.15, 7.50 and 15.04 minutes, respectively. The lightest of these materials was found to be 2,2,6-trimethyl-3,5-heptanedione (H3hd). The GC retention time and the fragmentation pattern in the mass spectrum match those of an authentic sample of this ligand. The last of these compounds to elute corresponds to the amine d₆-tadeta, and its assignment was also confirmed by comparison of its GC and mass spectrum with an authentic sample of the amine. A possible identification of the remaining peak is discussed in the following section.

Vaporization of these compounds was tested by nebulization of mesitylene solutions and passage of the resulting fog through a tube furnace held at 250 °C. The gas mixture exiting from the furnace was clear and no scattered light could be seen. Thus the Ba(3hd)₂·tadeta and Ba(thd)₂·tadeta vaporize completely at this temperature.

DISCUSSION AND CONCLUSIONS

Our observations show that thermal decomposition of barium beta-diketonates is much faster when there is a hydrogen atom that lies beta to the diketone chelate ring. One likely decomposition pathway is sketched in Figure 2.

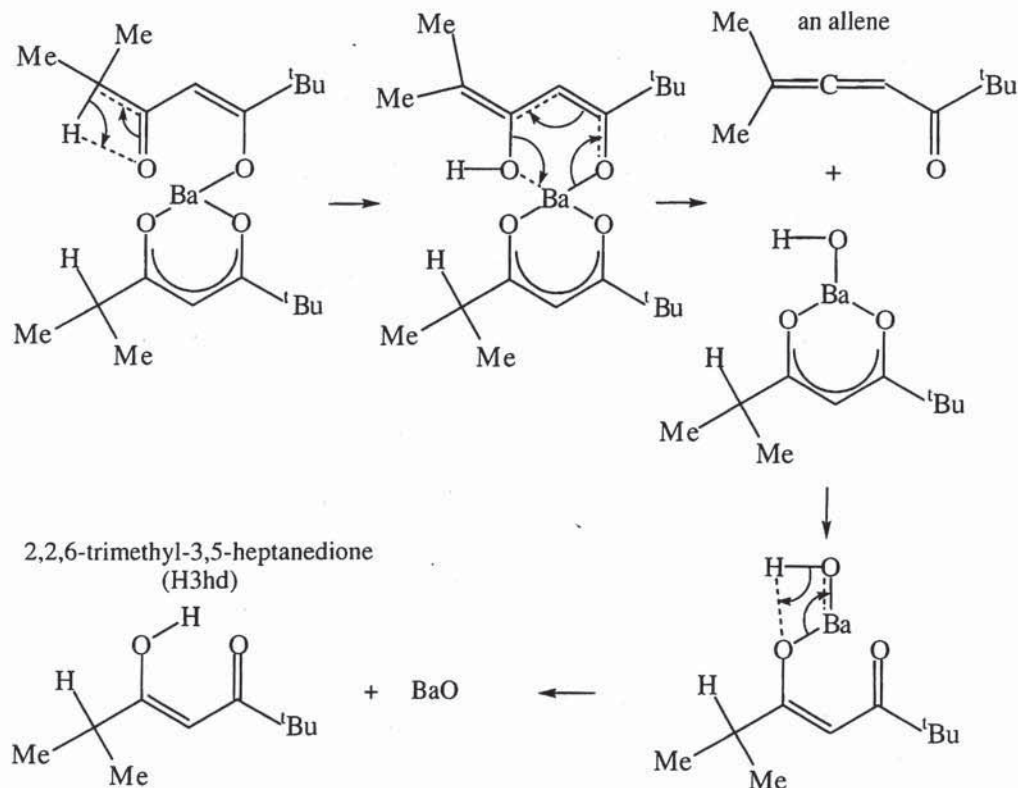


Figure 2. A beta-hydrogen decomposition pathway for barium bis(2,2,6-trimethyl-3,5-heptanedionate), $\text{Ba}(\text{3hd})_2$.

Initially, the hydrogen shifts from the alkyl substituent to an oxygen, forming an enol structure, with the bonding electron pairs shifting around the four-membered transition state in the manner indicated by the curved arrows. In the second stage of the reaction, bonding electron pairs further shift around a six-membered transition state to form a metal-hydroxide, releasing the remaining part of the beta-diketonate ligand as a ketone conjugated with an allene. This keto-allene is likely to absorb blue light, giving the yellow-orange transmitted color to the decomposed liquid. In the last step, the second beta-diketonate ligand is released by hydrogen transfer from the hydroxide, giving barium oxide as another decomposition product, which is presumably the white precipitate seen during the decomposition studies. The free 2,2,6-trimethyl-3,5-heptanedione ligand that is released in the last step accounts for the parent mass 170 peak in the mass spectrum.

The decomposition byproduct with parent mass peak at 184 amu cannot be

explained by the mechanism shown in Figure 2. However, it might be accounted for by a similar decomposition mechanism, in which a methyl group is transferred initially, as shown in Figure 3.

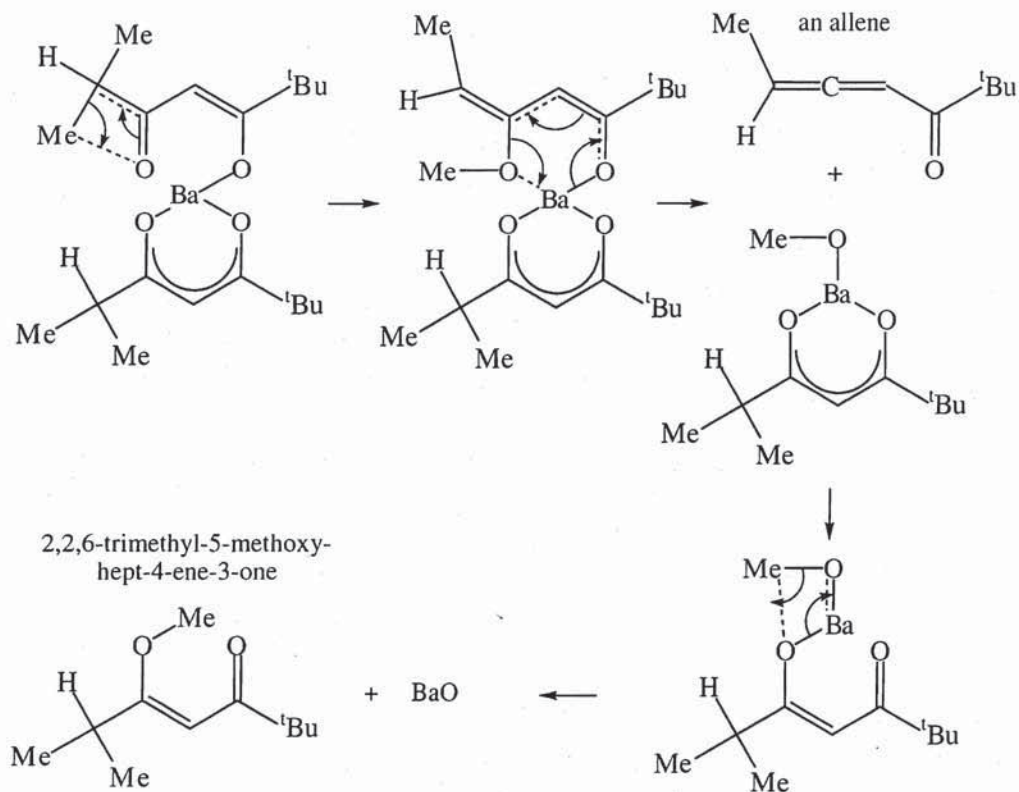


Figure 3. A beta-methyl decomposition pathway for barium bis(2,2,6-trimethyl-3,5-heptanedionate), Ba(3hd)₂.

The decomposition byproduct 2,2,6-trimethyl-5-methoxy-hept-4-ene-3-one may account for the parent mass peak at 184 amu in the mass spectrum, as well as some likely fragments, such as tert-butyl. An authentic sample of this material was not available to provide its unambiguous identification. Its retention time is slightly longer than that of the slightly lighter byproduct, 2,2,6-trimethyl-3,5-heptanedione, lending some support for this identification.

Ba(thd)₂ has available only the beta-methyl decomposition pathway of Figure 3, and lacks the more facile beta-hydrogen pathway of Figure 2. This difference may explain the greater thermal stability of Ba(thd)₂·tadeta. However, GC-mass spectra of the decomposition products from Ba(thd)₂·tadeta at 360 °C did not include any mass peak at 198, which would be expected from this beta-methyl mechanism. The only decomposition byproduct identified from Ba(thd)₂·tadeta was 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd).

Even if these decomposition mechanisms are incomplete or wrong, we can still

conclude that the most thermally robust beta-diketone ligands have no hydrogens beta to the diketone chelate ring. In particular, Ba(thd)₂·tadeta is a more stable CVD precursor for barium than is Ba(3hd)₂·tadeta.

Although Ba(thd)₂·tadeta is a viscous liquid at room temperature, adding small amounts of the high-boiling parent amine greatly reduces its viscosity and makes a solution that is very well suited for flash vaporization and use in CVD systems. No volatile solvents are used, so premature evaporation and consequent blockage of direct liquid injection systems can be avoided.

We have also found that similar chemistry can provide liquid CVD precursor compounds for the other alkaline earth metals. Their syntheses easily produce high yields of pure precursors. Their use should greatly facilitate the CVD of materials containing alkaline earth metals.

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