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Synthesis and Solution Decomposition Kinetics of Flash-vaporizable Liquid Barium Beta-diketonates

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The first room-temperature liquid, flash-vaporizable barium compounds were prepared by reacting barium beta-diketonates with alkyl-substituted triamine and tetramine ligands. For example, barium bis(2,2,6,6-tetramethylheptane-3,5-dionate) ($Ba(thd)_2$) reacts with N,N′,N″-triamyldiethylenetriamine (tadeta) to form a viscous liquid that is miscible with additional amine and organic solvents, forming low-viscosity solutions. Thermal decomposition studies showed that $Ba(thd)_2 \cdot$tadeta is more stable than a similar amine complex of barium 2,2,6-trimethylheptane-3,5-dionate ($Ba(3hd)_2$). This difference in thermal stability can possibly be explained by a beta-hydrogen elimination mechanism operating only in the latter barium compound.

KEYWORDS barium compounds; beta-diketonates; decomposition kinetics; decomposition mechanism; beta-hydrogen elimination; liquid precursors; vaporization; chemical vapour deposition

INTRODUCTION

The development of new precursors for CVD involves the design, synthesis and testing of materials to see if they have the many desired properties necessary for the materials to be vaporized and decomposed under the demanding conditions imposed by this deposition process. In particular, successful operation of a CVD process requires precursors whose vapour can be generated reproducibly at a reasonably low temperature 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, non-reproducible vapour pressures and often leave solid decomposition products after sublimation. Even if the solid decomposes only slightly, the products of decomposition can remain on the surface of the precursor, impeding the free evaporation of the remaining solid. When heated at their sublimation temperature for extended periods, solids may slowly change their state of oligomerization, thereby changing their vapour pressures. Finally, the available surface area from which the solid precursor can evaporate is subject to change during the course of a CVD experiment. This change in surface area can also drastically affect the reproducibility of the vapour pressure. 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 more appropriate for use in almost all practical applications of CVD.

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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, barium bis,2,2-dimethyl-8-methoxyoctane-3,5-dionate, has been reported,[2] but compounds of this type were later found to be non-volatile.[3] A fluorinated barium beta-diketonate, $Ba(C_3F_7(O)CCHC(O)C_3F_7)_2 \cdot$ tetraglyme, 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. Previously we reported room-temperature liquid barium CVD precursors that were mixtures of barium beta-diketonates rather than pure compounds.[5] Analysis of these mixtures can be more difficult than for pure compounds due to the complexity of evaluating a very large number of isomers in the same sample.

In this paper we report the first room-temperature, liquid-barium compounds that are volatile enough to be used for CVD when combined with a rapid evaporation system, such as ultrasonic nebulization or direct liquid injection. These compounds are *n*-alkylated polyamine complexes of barium beta-diketonates and contain no potentially contaminating fluorine. Their viscosities, degree of association in solution, volatility and decomposition rates were also studied. A preliminary account of part of our work has previously been reported.[6]

Similar room-temperature pure liquid precursors can be made for strontium, calcium and magnesium.[7] These new liquid precursors are particularly well suited for CVD of multicomponent materials containing alkaline earth metals because they can be mixed to form a multi-component solution without the components reacting with each other. Of particular current interest are high dielectric constant materials (barium strontium titanate), ferro-electrics (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).

RESULTS AND DISCUSSION

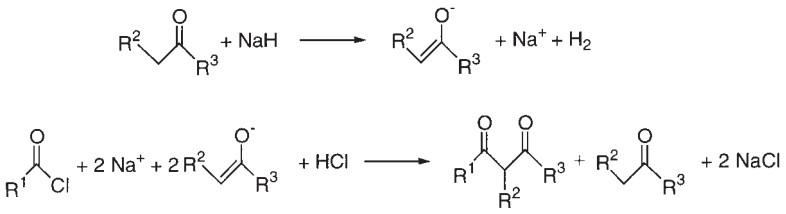
Synthetic Methods

The beta-diketone ligands are synthesized by reaction of an appropriate ketone with sodium hydride in tetrahydrofuran (THF), to form a solution of the corresponding sodium enolate. To form the desired beta-diketone, this enolate is then reacted with an appropriate organic acid chloride, neutralized with a mineral acid and filtered to remove the salt precipitate (Scheme 1). This is an improvement over the traditional Claisen condensation method, which gives impure products in only moderate yields.[8]

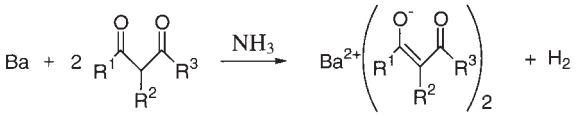
Distillation under reduced pressure than isolates the desired beta-diketone. The excess starting ketone can be recovered and reused for further syntheses. This method is particularly effective when the R^3 group is a tertiary alkyl group, such as tertiary butyl. If the R^3 group is not a tertiary alkyl group, then deprotonation can also take place at the R^3 position, giving a mixture of two beta-diketones rather than a pure product.

Compounds can be formed between the ligands and barium by direct reaction of metallic barium with the appropriate beta-diketone in a hydrocarbon solvent, using ammonia to activate the metal (Scheme 2). Since barium can have greater than eight-fold co-ordination,[9] reaction products of this type are usually oligomeric, typically being tri- or tetrameric. To obtain monomeric species, tridentate or tetradentate amine ligands are added. Several different amine ligands, listed in Table 1, have been found to form monomeric liquid compounds with barium beta-diketonates.

The column defined as '*t*' in Table 1 is the number of angular variables (torsion angles corresponding to 'non-degenerate' rotation around C–C single bonds) in the *n*-alkyl groups of the amine. Angles that only rotate methyl groups about their three-fold axes were not counted, since these 'degenerate' motions do not change the intermolecular interactions as much as the other ('non-degenerate') torsion angles. As *t* increases, the number of configurations available to the alkyl groups on the



Scheme 1. Preparation of a beta-diketone via enolate formation



Scheme 2. Synthesis of a barium beta-diketonate from the zero-valent metal

Table 1. Some tridentate and tetradentate amines. The variable '*t*' in the third column represents the number of 'angular variables' (corresponding to the number of -CH_2-moieties) in the alkyl chains attached to the nitrogen centres)

Name	Nickname	Length of alkyl chain	*t*
N,N′,N″-triethyldiethylenetriamine	tedeta	2	3
N,N′,N″-tripropyldiethylenetriamine	tpdeta	3	6
N,N′,N″-tributyldiethylenetriamine	tbdeta	4	9
N,N′,N″-triamyldiethylenetriamine	tadeta	5	12
N,N′,N″-trihexyldiethylenetriamine	thdeta	6	15
N,N′,N″,N‴-tetrahexyltriethylenetetramine	thteta	6	20

amine increases, frustrating crystallization of the amine adducts.

A typical synthesis for these amines is 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.[8] Then the resulting triamide is reduced with lithium aluminium hydride (Scheme 3).

This procedure results in a compound which has two terminal secondary amines (i.e., has one remaining proton) and one tertiary backbone amine (i.e., has no protons). It is important to note that other alkylation methods are likely to add alkyl groups to the terminal nitrogen atoms. 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 pendant alkyl chain attached per nitrogen.

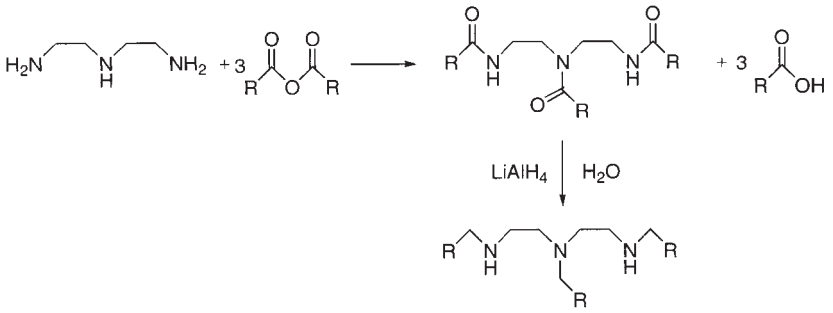
Amine-complexed barium beta-diketonates can be formed by reacting the tri-alkylated triamine with a barium beta-diketonate suspended in hexane, and formation of the adduct is indicated by complete dissolution of the solid. Alternatively, the amine can be added during the initial synthesis of a barium beta-diketonate.

Physical Properties of the Liquids and Solutions

The majority of compounds formed by co-ordination of these rather bulky amines to various barium beta-diketonates are liquids at room temperature. It was determined that, for the barium beta-diketonates tested here, the amines need a pendant alkyl chain of five carbons or longer to form liquids; a shorter chain length results in a solid. These data are summarized in Table 2.

Since the volatility is highly dependent on the molecular weight of a given compound, it was important to establish the degree of association of the compounds in question. In Table 2, the degree of association is the cryoscopically determined molecular weight divided by the calculated weight of a monomeric compound. All of the degrees of association are unity within experimental error. Thus, the compounds reported are all monomers in paraxylene solution at a dilution of approximately 0.6 M.

When the *n*-alkyl chains in the co-ordinated amine exceed five carbons, the barium compounds are liquids at room temperature. The long alkyl chains can adopt many conformations and make it unlikely for the material to crystallize at room temperature. As the *n*-alkyl chain length is made shorter, the adducts become increasingly likely to solidify at room temperature. Indeed, the adducts



Scheme 3. Synthesis of a trialkyldiethylenetriamine from diethylenetriamine

Table 2. Liquid amine complexes of barium beta-diketonate. The degree of association is the measured molecular weight divided by the calculated monomer molecular weight

β-diketones	Amine	Viscosity (at 40 °C) (centipoise)	Degree of association
3hd	thteta	246	0.85
3hd	thdeta	455	0.93
3hd	tadeta	811	1.00
thd	thteta	1223	0.97
tod	thteta	1236	0.90
tod	thdeta	1861	0.93
thd	thdeta	3292	1.03
tod	tadeta	3845	0.94
thd	tadeta	6782	1.02

with alkyl chains having fewer than five carbons initially formed super-cooled liquids that crystallized after being cooled to −20 °C and then warmed slowly to room temperature. An analogous strontium compound crystallized with three unequivalent molecular units that differ mainly in the torsion angles of the alkyl chains as determined by its X-ray crystal structure. Surprisingly, this indicates that different alkyl group conformations persist even in the solid state.[7]

There appear to be two factors affecting the viscosities of these compounds: the number of angular variables in the amine and the symmetry of the beta-diketonate ligands. For each type of beta-diketonate ligand, the lowest viscosity is found for the tetramine adduct with *n*-hexyl chains, having the most angular variables of these amines. For a given beta-diketonate ligand, the viscosity decreases steadily with increasing numbers of angular variables. The viscosities of the compounds are plotted in Fig. 1. For much longer alkyl chains, we expect that this trend in viscosities will reverse, since the materials should eventually become waxy solids, like paraffin. Thus, it is likely that there will be a minimum viscosity as a function of number of angular variables. However, the amines that we have prepared so far are too short to reach this minimum viscosity.

Asymmetry in the beta-diketone also plays a key role. The most symmetric ligand, thd, has C_{2v} symmetry with two opposing *tert*-butyl groups. The amine adducts of $Ba(thd)_2$ formed the most viscous compounds. The less symmetric ligand, 3hd, has C_v symmetry with an isopropyl group opposing a *tert*-butyl group. The amine adducts of $Ba(3hd)_2$ have much lower viscosities than the corresponding thd analogues, as a result of replacing only one methyl group with one hydrogen. A less significant reduction in viscosity is observed when using the more bulky, asymmetric ligand, tod, in which a larger ethyl group replaces one methyl group in thd. These trends have also been found for magnesium, calcium and strontium analogues.[7]

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. A typical dilution experiment is summarized in Fig. 2. For this dilution experiment, 0.97 g of $Ba(thd)_2 \cdot$ thdeta was used. It was found that only 0.43 g of mesitylene was needed to lower the viscosity below 8 centipoise. Similar trends were found with the other liquid-barium compounds.

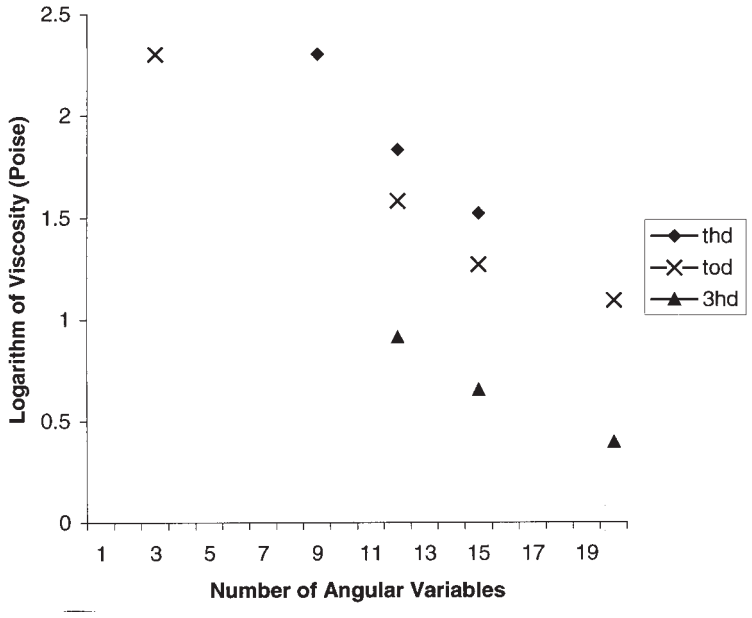


Fig. 1. Viscosity of barium beta-diketonate polyamine adducts as a function of the number of N-alkyl torsion variables in the polyamine

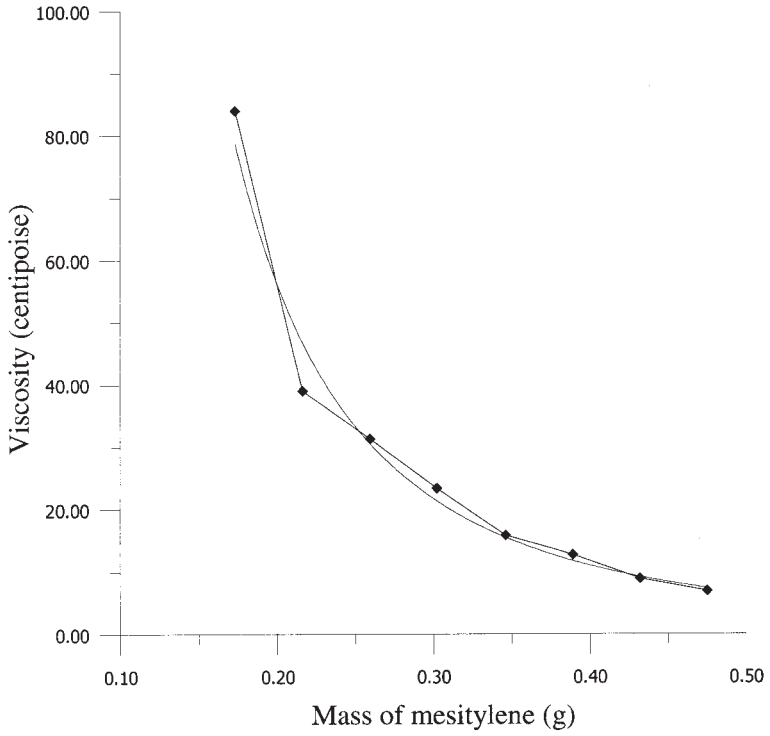


Fig. 2. Viscosity of $Ba(thd)_2 \cdot$ thdeta at 40 °C with increasing dilution by mesitylene

Thermal Stability and Volatility

Traditionally, thermal gravimetric analysis (TGA) has been used for screening of potential CVD precursors for volatility and thermal stability. Unfortunately, the weight loss measured using TGA does not distinguish between vaporization and decomposition. Also, TGA has difficulty detecting small (less than about 1%), but significant percentages of non-volatile residue that can clog a vaporizer and can produce undesirable particles that can contaminate a deposited film.

We used two different screening techniques to overcome these limitations of TGA. Firstly, 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 using a deuterated triamine as an NMR active solvent. In this way we can quantitatively measure decomposition rates by detecting the loss of precursor and build-up of decomposition by-products. Sometimes it is possible to identify individual by-products using this method. Secondly, in order to determine the volatility of the liquid precursors, we entrain nebulized liquid into nitrogen gas flowing into a glass tube in a heated tube furnace and observe whether or not the fog has evaporated by the exit end of the tube.

The ^{1}H NMR spectra of $Ba(3hd)_2 \cdot$tadeta and $Ba(thd)_2 \cdot$tadeta (with d_6-tadeta as a solvent: see Experimental) each show a distinct resonance due to the bridge carbon between the two carbonyl groups, appearing at 5.60 ppm for $Ba(3hd)_2 \cdot$tadeta and 5.42 ppm for $Ba(thd)_2 \cdot$tadeta. The thermal decomposition of these compounds was monitored by the disappearance of this unique resonance line. At a temperature of 310 °C, the intensity of the $Ba(3hd)_2 \cdot$tadeta resonance nearly disappears in about 1 hour, while the resonance for $Ba(thd)_2 \cdot$tadeta does not decrease significantly in intensity during the same time-frame (Fig. 3). Under these conditions, control experiments show that the amines do not decompose. Thus, the amine resonances are used as internal standards for integration in the NMR decomposition studies.

Based on the above information, $Ba(thd)_2 \cdot$tadeta was found to be significantly more stable than the $Ba(3hd)_2 \cdot$tadeta. At 360 °C, $Ba(thd)_2 \cdot$tadeta did show decomposition over the period of 1 hour. During the decomposition reactions, a white, gel-like precipitate formed in the NMR tubes, while the liquid turned yellow, then orange and finally brown.

GC-MS of the decomposition products from $Ba(3hd)_2 \cdot d_6$-tadeta showed three peaks, with parent masses of 170, 184 and 230 amu, respectively. The lightest of these materials was found to be 2,2,6-trimethylheptane-3,5-dione (H3hd). The fragmentation pattern in the mass spectrum matched that of an authentic sample of the ligand. The last of these compounds to elute corresponds to the amine d_6-tadeta, and its assignment was also confirmed by comparison of its mass spectrum with an authentic sample of the amine.

The data support one possible decomposition mechanism where removal of the hydrogen atom in the position beta to the diketone chelate ring may activate thermal decomposition (Scheme 4). In the case where the alkyl group '*R*' is a proton, the hydrogen shifts to oxygen, forming an enol tautomer, with the bonding electron pairs shifting around the four-membered transition state. Subsequently, bonding electron pairs further shift around a six-membered transition state to form a metal hydroxide, releasing the remaining part of the beta-diketone ligand as a ketone conjugated with an allene. In the final step, hydrogen transfer from the hydroxide gives barium oxide as another decomposition product with the release of the second beta-diketone ligand. BaO is presumably the white precipitate seen during the decomposition studies *vide supra*. The free 2,2,6-trimethylheptane-3,5-dione (H3hd) ligand that is released in the last step accounts for the parent mass 170 peak observed in the mass spectrum.

In the thermolysis of $Ba(3hd)_2$, a decomposition by-product with a parent mass peak at 184 amu cannot be explained by the above mechanism. However, it might be accounted for by a similar decomposition mechanism for $Ba(thd)_2$, in which the alkyl group '*R*' is a methyl group. With respect to the above mechanism, the decomposition byproduct 2,2,6-trimethyl-5-methoxy-hept-4-ene-3-one would result if '*R*' were methyl. This would be a less facile decomposition than when '*R*' is a proton, but it would also explain the relative stability of $Ba(thd)_2 \cdot$tadeta compared with $Ba(3hd)_2 \cdot$tadeta.

In a separate experiment, we found a way to qualitatively observe even extremely small amounts of non-volatile residue from the evaporation of liquid precursors. We use ultrasonic nebulization to break up the liquid into a fog of small droplets, which are then flash vaporized within a fraction of a second after mixing the fog with a preheated car-

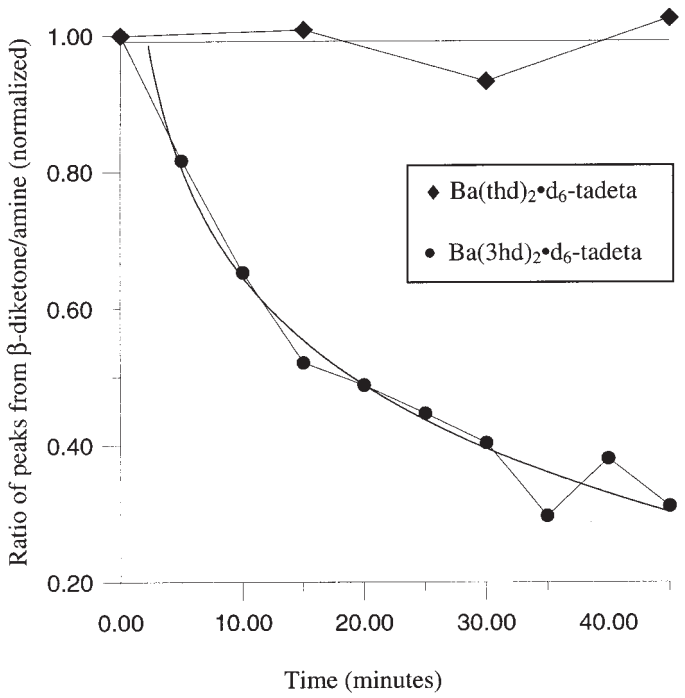
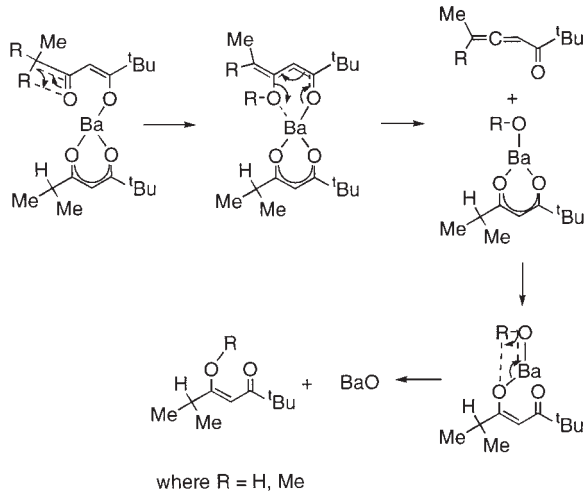


Fig. 3. A graph of the concentrations of $Ba(thd)_2 \cdot$ tadeta (diamonds) and $Ba(3hd)_2 \cdot d_6$-tadeta (dots) after heating at 310 °C for the indicated times. The abscissa represents the normalized ratio of the areas of a β-diketone ^{13}C resonance to a d_6-tadeta ^{13}C resonance



Scheme 4. Proposed decomposition pathway for barium bis(2,2,6-trimethylheptane-3,5-dionate), $Ba(3hd)_2$

rier gas or passing it 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.

In order to demonstrate flash volatility of these new liquid compounds, a fog of a precursor/mesitylene mixture was carried from the nebulizer of a dry N_2 stream through a glass tube in a tube furnace. At the outlet end of the furnace, the vapour mixture was observed with a break light, to see if the droplets had evaporated completely. Any non-evaporated residue should be visible against a dark background. The flow rate of the nitrogen carrier gas was increased until the fog at the outlet disappeared. Under these conditions, a saturated vapour exists, and the vapour concentration can be calculated from the measured flow rates of the liquid and the nitrogen gas. We are currently working to develop a quantitative detection system for this method.

Nebulization of mesitylene solutions of the compounds, and subsequently passing the resulting fog through a tube furnace held at 250 °C, showed complete vaporization of these compounds. The gas mixture exiting from the furnace was clear and no scattered light could be seen. Thus, both $Ba(3hd)_2 \cdot$tadeta and $Ba(thd)_2 \cdot$tadeta flash vaporize completely at this temperature. In contrast, slow vacuum distillation resulted in dissociation of the compounds, with the intact amine ligand distilling out.

CONCLUSIONS

Novel, flash-vaporizable, barium compounds were found to be liquids at room temperature. These pure, non-fluorinated compounds are easily synthesized in high yield by reaction of barium betadiketonates with certain *n*-alkylated polyamines. The liquids are thermally stable up to temperatures well above those needed for complete vaporization using ultrasonic nebulization techniques. We have also found that similar chemistry can provide pure liquid CVD precursor compounds for the other alkaline earth metals.[7] Their use should greatly facilitate the CVD of materials containing alkaline earth metals.

EXPERIMENTAL

General Considerations

All syntheses were performed using standard Schlenk techniques. All NMR spectra were taken on either a Bruker AM 500 MHz or a Bruker AM 300 MHz NMR spectrometer. Desert Analytics Laboratory in Tucson, AZ performed combustion analyses. Solvents were dried with either Na/benzophenone (THF) or Na/K alloy (diethylether) and distilled onto molecular sieves. Sodium hydride, lithium aluminium hydride, lithium aluminium deuteride, pinacolone, isobutyryl chloride, 2-ethylbutyryl chloride, barium metal, valeric anhydride and hexanoic anhydride were used as purchased from Aldrich Chemical Company. Diethylenetriamine and triethylenetetramine were purchased from Aldrich, dried over magnesium sulphate and distilled before use. Ammonia gas was 99.99% pure and used as purchased from Matheson Gas Company.

The viscosities of the liquids (about 1 ml) were measured with a Cambridge Applied Systems (Medford, MA) Viscolab 3000 viscometer in a glove box over a range of temperatures (typically 30 to 60 °C). Solution molecular complexities were determined by cryoscopy in *p*-xylene (Aldrich, purified by fractional crystallization). Freezing points of the solution (typically 2 mmol of compound in 3 ml of *p*-xylene) were measured with a digital thermistor while cooling the stirred solution with an ice bath (about 5 °C).

An improved synthesis of 2,2,6-trimethylheptane-3,5-dione (H3hd)

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 low enough to keep the reaction from bubbling too vigorously. After the addition was completed, the reaction was stirred at 85 °C for 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). (Caution: H_2 is explosive in concentrations over 4% in air. It is recommended to dilute the evolved H_2 with an inert gas before venting 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 minutes 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, colourless solution. Ample $MgSO_4$ was added to absorb the water, the mixture was stirred for 30 minutes 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 pale yellow, 2,2,6-trimethylheptane-3,5-dione (H3hd) (40.50 g, 81%). The product distilled at 132–133 °C at 150 mbar. ^{1}H NMR (C_6D_6): (δ 5.49 ppm, singlet, 1H), (δ 2.22 ppm, septet, 1H), (δ 1.47 ppm, singlet, 9H), (δ 0.90 ppm, doublet, 6H).

An improved synthesis of 2,2,6,6-tetramethyloctane-3,5-dione (Htod)

Synthesis of 2,2,6,6-tetramethyloctane-3,5-dione (Htod) followed the same preparation using 2-ethylbutyryl chloride with a yield of 75%. The resulting liquid was distilled at 145 °C and 150 mbar. ^{1}H NMR (C_6D_6): (δ 5.63 ppm, singlet, 2H), (δ 1.46 ppm, quartet, 2H), (δ 1.06 ppm, singlet, 9H), (δ 1.03 ppm, singlet, 6H), (δ 0.74 ppm, triplet, 3H).

Synthesis of barium beta-diketonates

The barium beta-diketonates were synthesized using literature methods.[9] By way of example, the preparation of barium 2,2,6,6-trimethylheptane-3,5-dionate, $Ba(3hd)_2$, is as follows. Barium metal (1.78 g, 13.0 mmol) and 2,2,6-trimethylheptane-3,5-dione (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. The mixture was then filtered through celite, giving a clear, colourless solution. The THF solvent was removed by evaporation under reduced pressure, leaving 5.01 g (81%) of solid $Ba(3hd)_2$· ^{1}H NMR (C_6D_6): (δ 5.73 ppm, singlet, 2H), (δ 2.50 ppm, septet, 2H), (δ 1.27 ppm, singlet, 18H), (δ 1.19 ppm, doublet, 12H).

Synthesis of d_6-N,N′,N″-triamyldiethylenetriamine (d_6-tadeta)

Diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$, (3.26 ml, 30.1 mmol) was added at 2 drops/sec to a 0 °C solution of valeric anhydride, $(CH_3CH_2CH_2CH_2CO)_2O$, (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. Adding H_2O (0.15 ml, 8.3 mmol) quenched the excess anhydride 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 sulphate. After several hours, the magnesium sulphate hydrate was filtered off and the solvent was removed *in vacuo*, leaving a colourless liquid. Distillation under full vacuum (3×10^{-2} Torr) gave d_6-N,N′,N″-triamyldiethylenetriamine (d_6-tadeta) at 118–120 °C (7.30 g, 77% yield based on diethylenetriamine). ^{1}H NMR ($CDCl_3$): (δ 2.53 ppm, triplet, 4H), (δ 2.44 ppm, triplet, 4H), (δ 1.37 ppm, triplet, 4H), (δ 1.13 ppm, triplet, 2H), (δ 1.10–1.28 ppm, multiplet, 18 H), (δ 0.79 ppm, multiplet, 9H). Combustion analysis: C: 71.40% calc., 70.75% exp., H: 15.45% calc. 13.77% exp., N: 13.12% calc., 13.12% exp.

Synthesis of N,N′,N″-triamyldiethylenetriamine (tadeta)

Synthesis of triamyldiethylenetriamine (tadeta) followed the same preparation using $LiAlH_4$ with a yield of 78%. The resulting liquid was distilled at 111–116 °C and $<$50 mTorr. ^{1}H NMR ($CDCl_3$): (δ 2.52 ppm, triplet, 4H), (δ 2.46 ppm, triplet, 4H), (δ 2.42 ppm, triplet, 4H), (δ 2.28 ppm, triplet, 2H), (δ 1.37 ppm, multiplet, 4H), (δ 1.13 ppm, multiplet, 2H), (δ 1.10–1.28 ppm, multiplet, 18 H), (δ 0.79 ppm, multiplet, 9H). Combustion analysis: C: 72.78% calc., 72.89% exp., H: 13.82% calc., 14.05% exp., N: 13.40% calc., 13.40% exp.

Synthesis of N,N′,N″-trihexyldiethylenetriamine (thdeta)

Synthesis of trihexyldiethylenetriamine (thdeta) followed the same preparation using hexanoic anhydride and $LiAlH_4$ with a yield of 80%. The resulting liquid was distilled at 142–145 °C and $<$50 mTorr. ^{1}H NMR ($CDCl_3$): (δ 2.54 ppm, triplet, 4H), (δ 2.49

ppm, triplet, 4H), (δ 2.44 ppm, triplet, 4H), (δ 2.30 ppm, triplet, 2H), (δ 1.38 ppm, multiplet, 4H), (δ 1.33 ppm, multiplet, 2H), (δ 1.14–1.24 ppm, multiplet, 24H), (δ 0.78 pp, multiplet, 9H). Combustion analysis: C: 74.30% calc., 74.30% exp., H: 13.89% calc., 14.14% exp., N: 11.82% calc., 11.75% exp.

Synthesis of N,N′,N″,N‴- tetrahexyltriethylenetetramine (*thteta*)

Synthesis of tetrahexyltriethylenetetramine (thteta) followed the same preparation with triethylenetetramine, hexanoic anhydride and $LiAlH_4$. The resulting liquid was distilled at 240 °C and <50 mTorr, and the yield was 50%. ^{1}H NMR (C_5D_5N): (δ 2.77 ppm, multiplet, 4H), (δ 2.66 ppm, multiplet, 12H), (δ 2.51 ppm, triplet, 4H), (δ 1.48–1.62 ppm, multiplet, 8H), (δ 1.15–1.45 ppm, multiplet, 24H), (δ 0.90 ppm, multiplet, 12H). Combustion analysis: C: 74.62% calc., 73.88% exp., H: 13.77% calc., 13.46% exp., N: 11.60% calc., 11.61% exp.

Measurement of Volatility

Two types of ultrasonic nebulizers were used. The smallest droplets, typically 20 to 30 microns in diameter, were obtained by pumping the liquid at a controlled rate from a syringe pump onto a quartz plate driven to vibrate at 1.4 MHz by a transducer (Cetac Technologies, Inc., Omaha, NE). The resulting fog was entrained by nitrogen gas flowing upward toward a tube at a speed such that droplets larger than 20 microns in diameter fell back to the plate on which they were broken up again. In this way, the liquid was completely nebulized into a fog of droplets that were all less than 20 microns in diameter. This system works well for liquids or solutions with relatively low viscosities, less than about 5 centipoise.[10] For liquids or solutions with higher viscosities, material tends to accumulate on the quartz plate and nebulization stops.

Liquids with higher viscosities can be nebulized with an ultrasonic spray nozzle (Sono-Tek Corporation, Milton, NY), modified with a flange so the spray is confined to a closed tube. This nozzle vibrates at a lower frequency, 125 kHz, and thus produces larger droplets, typically about 40 microns in diameter. This ultrasonic nebulizer operates successfully with liquids up to at least 100 centipoise.

Thermal Decomposition Studies by NMR

Partial deuterium substitution of tadeta was done to provide a lock signal for the NMR experiment without the need to add a volatile deuterated solvent. When d_6-tadeta is used as the solvent, its boiling point is high enough to allow thermal decomposition studies to be carried out in a closed tube, sealed under vacuum. NMR evidence dramatically supported the deuteration of the α-carbon of the alkyl chain by the absence of the triplets at 2.46 ppm (i.e., those attached to secondary nitrogens) and 2.28 ppm (i.e., those attached to the tertiary nitrogen) when compared with tadeta.

In a typical experiment, 0.015 g of barium betadiketonate and 0.300 g of d_6-tadeta were sealed in a normal NMR tube. The tube was heated at temperature for 5 minutes in a tube furnace, cooled and then an ^{1}H NMR was taken at room temperature. This was sequentially repeated until the loss of a measurable signal.

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