Review

Developments in CVD Delivery Systems: A Chemist's Perspective on the Chemical and Physical Interactions Between Precursors**

By *Paul O'Brien,* Nigel L. Pickett*, and *David J. Otway*

Important factors in considering compounds for use as precursors in CVD techniques are discussed. Conventionally, volatility along with precursor purity and clean decomposition to the desired materials, are all regarded as crucial precursor properties. Recent developments in the way in which precursors are delivered into the vapor phase mean volatility is no longer such an important requirement. Less volatile precursors with better deposition routes are now routinely employed. In this review, a description of the fundamentally new approaches to CVD delivery systems developed in recent years is presented. Examples highlighting the importance of understanding both the chemical and physical interactions between different precursors, and also those between the carrier gases and precursors, are discussed.

Keywords: Delivery systems, MOCVD, Phase rules, Precursors

1. Introduction

Metal-containing precursors for use in CVD techniques encompass a wide range of chemical compounds, from gases through volatile liquids, sublimable solids to relatively involatile solids.[1] Those commonly used in the crystal growth of thin films of functional materials include (Fig. 1), σ-bonded metal–alkyl compounds such as the pyrophoric volatile liquid dimethyl zinc ($ZnMe_2$) and the pyrophoric solid trimethyl indium ($InMe_3$), and π-bonded organometallic compounds, most notably used for otherwise difficult metals such as magnesium or manganese. Coordination compounds such as acetylacetonates and other β-diketonate derivatives have also been used, particularly in the deposition of oxides. To be successful precursors, com-
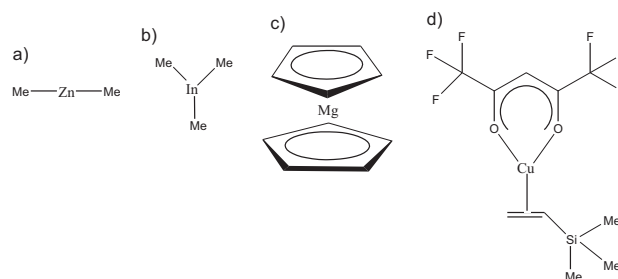

Fig. 1. Some chemical compounds used as precursors in CVD: a) dimethyl zinc, b) trimethyl indium, c) $MgCp_2$, and d) Cu(TMVS)hfac.

pounds must meet a number of requirements such as, high purity, including the exclusion of any extrinsic impurities acquired during precursor synthesis, especially if they can act as dopants,[2] clean decomposition on the substrate surface, without the incorporation of unwanted intrinsic impurities (elements present within the ligands e.g., carbon from an alkyl group or fluoride from a substituted β-diketonate derivative (Fig. 1). The compounds are also required to have moderate vapor pressures, volatilize quantitatively on heating and, at the temperature used for volatilization, remain stable for an adequate period of time in the gas phase, but also decompose cleanly at the temperature of the substrate (this may only be a little higher then the temperature needed to volatilize the precursor).

The purpose of this review is to draw attention to recent developments in precursor delivery methods and to consid-

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er interactions, in terms of their chemical and physical behavior, between precursors, and also between the precursor and the carrier gas.

It is timely to consider that much of the work on precursor design has been driven by attempts to produce precursors of higher volatility, often involving bulky, non-interacting or fluorine-containing, substituent groups so as to decrease molecular interactions. In the light of new delivery methods, the stability of the precursor, its reproducible behavior with respect to the method of delivery, clean deposition, and subsequent levels of impurities and defects within the final grown material are more important than the volatility of the compound.

2. An Overview of Delivery Methods

2.1. The Conventional Approach to Precursor Delivery

2.1.1. Gases

For gases such as phosphine (PH_3), hydrogen sulfide (H_2S), and hydrogen selenide (H_2Se) the conventional method is to use a cylinder containing the correct composition of the precursor(s) in conjunction with a thermal mass flow controller (MFC), to control the vapor phase concentration (Fig. 2).[3] The main criteria for successful and reproducible use are that the inlet pressure is greater than

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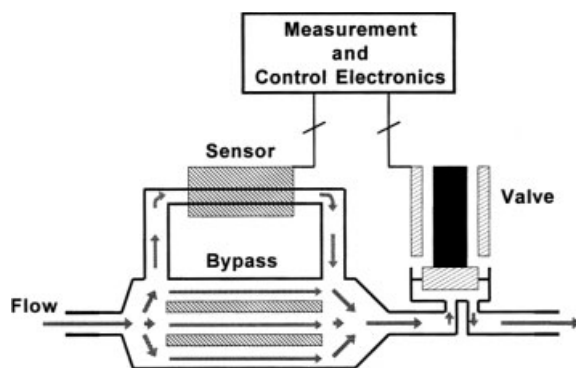
Fig. 2. Thermal mass flow controller.

ca. 50 torr, the operating temperature at the MFC is less than 60 °C, and the flow rate is greater than 0.1 sccm. The vapor can also originate from a liquid source as long as these conditions are met. Special liquid mass flow controllers (LMFC) are available, for the direct control of liquid delivery. The liquid is fed from the LMFC to a vaporizer to produce a vapor of the precursor at the point of use.[4] A further advance in MFC design is the pressure-based MFC, used to deliver precursors from low-pressure sources. Examples of their use include the control of tetraethoxy silane and hexamethyl disilazane for inter-level dielectrics, parylene for thermal polymerization, and metal–organic reactants for MOCVD of II–VI and III–V semiconductor compounds.[5]

2.1.2. Liquids (Entrainment)

Since the time of the original CVD work by Manasevit,[6] the delivery of liquid precursors has been dominated by the use of so-called "bubblers". Typically, these are passivated stainless steel Dreschler bottles (Fig. 3) containing the precursor, ideally a liquid with a significant vapor pressure. The precursor is delivered to the CVD reactor by entrainment with a carrier gas that is fed through the liquid and should become fully saturated with the precursor on passing through the bubbler. There are few problems with the use of modestly volatile liquids, i.e., those with equilibrium
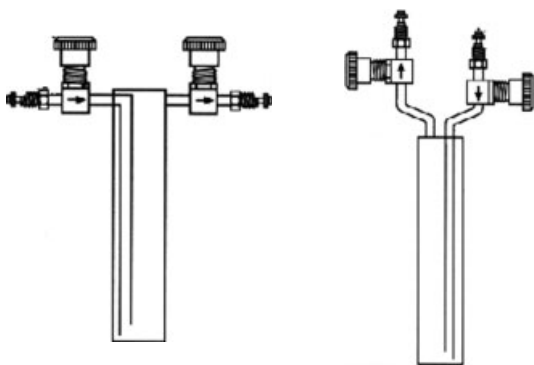
vapor pressures roughly in the range of 5–30 torr at room temperature. There are, however, problems when using materials with very low or high vapor pressures, and with the use of solids. To overcome these difficulties, liquids with low vapor pressures can be heated, using oil baths or thermal tape wrapped around the bubbler to increase the equilibrium vapor pressure within the bubbler. However, there are two problems associated with this technique. Firstly, to prevent condensation of the precursor in other parts of the CVD system, it may become necessary to heat the entire network of feed lines up-stream of the substrate. Secondly, for delivery to be successful, the precursors must have long-term stability at the elevated temperature used. Precursors with high vapor pressures can be difficult to control and in such cases it may be necessary to cool the bubbler. For highly volatile precursors, such as dimethyl zinc, a slight temperature fluctuation can have a significant effect on the gas phase concentration. Most solid precursors have very low volatilities and thus produce similar problems to those of low volatile liquid precursors. Additionally, the surface area of solids in contact with the entraining gas may be insufficient for equilibrium to be established on the passage of the gas. As the solid sublimes, there will be a variation in the surface area leading to a variation in the rate of mass transport over time, so it is more difficult for equilibrium to be established under the dynamic gas flow within a bubbler. One approach which has been used to overcome this problem, notably with trimethyl indium (InMe$_3$), is to use two bubblers in series. This simple method allows more contact between the carrier gas and the precursor so that the carrier gas has sufficient contact time to become fully saturated and equilibrium established before exiting the second bubbler.

The problem of the carrier gas not becoming fully saturated before exiting the bubbler is common when the amount of precursor remaining in the bubbler is low. The solution to this problem, for liquid precursors, is to use a bubbler with a self-metering reservoir (SMR) (Fig. 4). Because of real-time replenishment of the precursor, the volume of precursor stays at a constant level within the bubbler, and so at constant gas flow and temperature, the vapor phase concentration of precursor should also remain constant. When using this conventional approach, only volatile compounds can be considered as precursors. Although these compounds are volatile they do not necessarily lead to clean deposition. New approaches to precursor delivery have allowed a wider range of compounds to be used as precursors.

2.2. Modified Delivery Systems

Each of these new systems has its own advantages for a particular precursor, depending on its physical state. In terms of the physical approach of the delivery part of a CVD system, most of the current systems in use can be

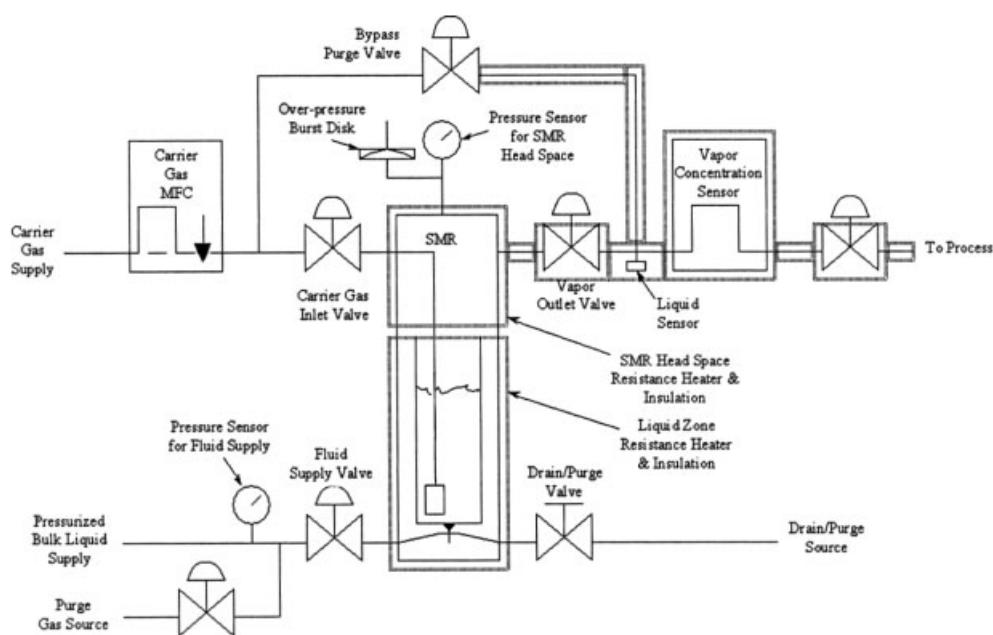
Fig. 3. Two designs of common bubblers.

Fig. 4. SMR self-metering bubbler.

classified within the categories of liquid injection systems (LISs) where a precursor is vaporized directly from a solution, solid delivery systems (SDSs) where the precursor is vaporized directly from a solid, or aerosol-assisted delivery systems (AADSs) where an aerosol containing the precursor is formed prior to delivery.

2.2.1. Liquid Delivery

Direct Liquid Injection (DLI): DLI-MOCVD can be used for liquid precursors or a solution containing all the precursors required. The solution is transported, most often via a syringe, to a vaporization chamber adjacent to the CVD reactor from where it is swept, using a carrier gas, into the reactor (Fig. 5).[7a] It is the speed at which the syringe is depressed that determines the gas phase concentration of precursor. The precursor is maintained at room temperature until just before use, thus reducing the potential for premature decomposition. DLI has been used to grow thin films of single metal oxides of nickel, zinc, and
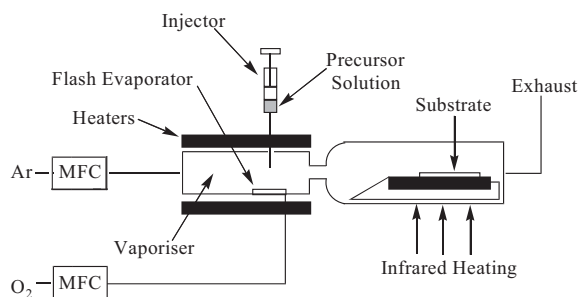
Fig. 5. Schematic diagram of a liquid injection system for MOCVD [7b].

iron along with the binary ferrites (nickel ferrite, zinc ferrite), and the ternary nickel zinc ferrite, from the β-diketonate precursors, Ni(tmhd)$_2$, Zn(tmhd)$_2$, and Fe(tmhd)$_3$, dissolved in THF.[7b] The CVD of lead–scandium–tantalate has also been grown using DLI from Pb(tmhd)$_2$, Sc(tmhd)$_3$, and Ta(OEt)$_2$.[7c]

MKS Instruments Inc.,[7d] developed a DLI system consisting of a high precision two-stage syringe-type liquid pump, an advanced vaporizer with variable temperature zones made up from an array of stacked thin metal disks, and an electronic control unit to regulate the operation of the pump and temperature of the vaporizer. A pressurized liquid precursor is fed into the multistage pump and pumped at high pressure into the evaporator/vaporizer, thus a constant flux of material can be delivered without the use of a solvent. However, as in a conventional bubbler, the precursor must be held above its melting point thus, in some cases, there are potential problems with decomposition of the precursors prior to delivery. Many other modified liquid delivery systems have been designed, some of which are discussed below.

Liquid Delivery Systems (LDSs): A typical LDS (Fig. 6) consists of a large reservoir containing the precursor(s) dissolved in a suitable solvent. The mixture is vaporized by a flash evaporator matrix. This system allows a constant flux of precursor to be delivered, but only if all the components within the precursor mixture are totally soluble and remain fully miscible. Provided no adverse pre-reactions occur between the precursors and/or the chosen solvent, this system is useful in that it eliminates the need to keep the solution hot, so problems of thermal decomposition are minimized and heating of the feed lines becomes unnecessary. A number of disadvantages are associated with this system.
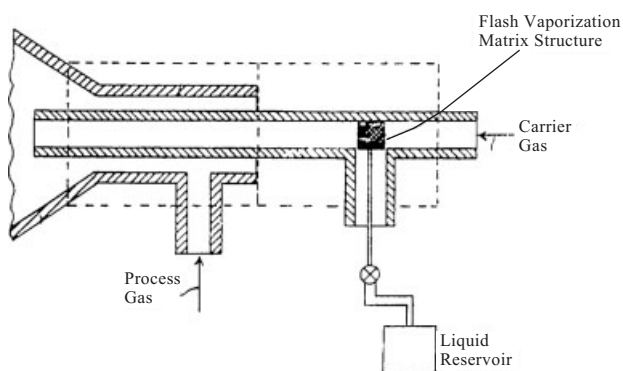
Fig. 6. Scheme of an ATM liquid delivery system (LDS). Reproduced with permission from *US Patent 5 204 314*, 4/20/93.

there is a potential for reactions between precursors in solution, e.g., the hydrolysis of an alkoxide, so both solvent and precursor need to be of high purity. If there is more than one precursor in the solution, any reactions in the source solution between the precursors or solvent can result in the formation of new compounds with different physical properties, which could adversely affect the behavior of the precursors and their delivery. There are also potential problems with the high volume of carrier solvent utilized, which may cause a build-up of flammable vapor within a CVD reactor.

Advanced LDSs: Liquid delivery is now an established technique, with many modifications to this system having been made, depending on the type of material that is being grown. Most of these improvements have been concerned with accuracy, in terms of the quantity of precursor delivered at a specific time, and include methods such as pulsed liquid-injection CVD whereby micro amounts of a precursor dissolved in a solvent are sequentially injected into an evaporator where flash volatilization occurs. The amount of precursor to be deposited is dependent on the volume of precursor evaporated at any given time and this is, in turn, dependent on the length of each injection cycle or "pulse width". Using this method, CVD growth can be precisely controlled by a computer. Thus, intricate and precise heterostructures can be grown by using multiple pulsed injection units, adjusting the injection parameters via the computer program.[8,9]

There is a similar, modified LDS employing a positive displacement pump, again designed to improve accuracy in terms of the amount of precursor delivered at a given time. In this method, multiple precursors are mixed just prior to evaporation. A computer-controlled amount of each precursor solution is delivered into the low-pressure side of a dual-piston pump. When the low-pressure valve of the pump is filled with the required amount of each precursor (as controlled by the computer), the mixed solution is transferred to the high-pressure side where delivery into a vaporizer occurs.[10] These methods have the advantage (over conventional liquid delivery) of being able to deliver precise amounts of precursors at any chosen time.

2.2.2. Aerosol-Assisted Delivery Systems

The widely used aerosol-assisted (AA)CVD has many advantages similar to those of the newer liquid injection systems. Essentially, as in liquid delivery, the method is based on flash evaporation but in this case of an aerosol. A sweep of carrier gas is used to transfer the aerosol of a precursor-containing solution the into the hot zone of a reactor. Again, this method has been designed for compounds with low volatility and thermal stability. The precursor(s) are dissolved in a suitable solvent and the solution is atomized or vaporized into a carrier gas stream. An effective method of producing an aerosol is to use an ultrasonic technique whereby the precursor-containing solution is placed within a vessel fitted with a piezoelectric transducer.[11,12] The advantages and disadvantages of the method are essentially similar to those discussed above for liquid injection. However, when using this method, it is also important that the rate of transfer of the aerosol to the evaporator remains constant, and that the aerosol is of constant composition. One example of the use of AACVD is in the growth of the superconductor YBCO, from the Ba, Y, and Cu precursors, $Ba(tmhd)_2$, $Y(tmhd)_3$, and $Cu(tmhd)_2$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dione), which are dissolved together in a suitable solvent (butylacetate, THF, toluene, decane, and supercritical CO_2) prior to use.[13]

2.2.3. Solid Delivery Systems

Solid delivery systems were developed at Hewlett Packard, and a schematic of this delivery system is shown in Figure 7. This method allows for the delivery of solid-state precursors, which may easily decompose if heated for prolonged periods. The precursors are essentially flash-sublimed into the growth chamber of a CVD reactor. The superconductor YBCuO has also been prepared, from $Ba(tmhd)_2$, $Y(tmhd)_3$, and $Cu(tmhd)_2$, by this method. However, unlike AACVD, the precursors are used as sol-
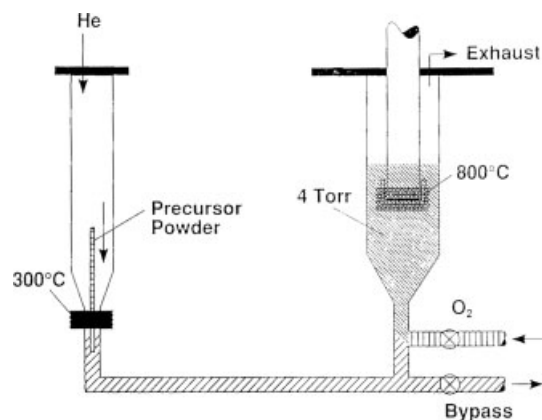

Fig. 7. Scheme of a Hewlett Packard solid delivery system (SDS). Reproduced with permission from [14]. Copyright 1991, the American Institute of Physics.

ids. They are mixed and placed in a Pyrex tube which is then passed through a large temperature gradient (25–300 °C) over a very small distance (2 mm). This initiates vaporization of the precursors, and they are subsequently swept to the substrate by a carrier gas.[14]

Recently, a method combining the principles of both liquid and solid state delivery has been developed whereby droplets of precursor-containing solutions are sequentially injected onto an inert porous conveyer belt. The solvent is removed at room temperature by evaporation into a flowing gas stream (away from the substrate), which is removed from the system via a cold trap. The as-deposited solid is transported, on the porous conveyer belt, into the hot evaporation zone where rapid flash volatilization into an appropriate carrier gas occurs. This then transports the precursor to the substrate, as schematically represented in Figure 8.[15,16]

3. Chemical and Physical Interactions Between Precursors

The methods discussed rely, in principle, on the mechanical delivery of a liquid, solid, or aerosol containing precursor(s) to a hot zone where precursor vaporization quickly occurs. The vaporized precursor is then delivered to the substrate via a carrier gas, as schematically represented below.

$$\text{Precursor Solution} \xrightarrow{\text{Delivery}} \text{Droplets} \xrightarrow{\text{Vaporization}}$$

$$\text{Vapor phase Precursor} \xrightarrow{\text{Transport (Carrier gas)}} \text{Substrate}$$

However, understanding the physical and chemical interactions between precursors, both in the liquid and gas phase, and between that of the carrier gas and precursor(s), is an issue that has been overlooked. In many cases, the actual gas-phase compounds are different to those initially used, and this can seriously affect the quality of the deposited material. An understanding of the chemical and physical interactions can help in modifying the properties of the

precursors and, in turn, result in better delivery with better reproducible mass transport of the precursor. Examples of these issues will be discussed below.

3.1. Modifying the Properties of Precursors to Improve Delivery: Application of the Phase Rule to Precursor Design

As mentioned in the introduction, forming mixtures with other precursors, solvent (if present), and an added coordinating compound or carrier gas, can modify the physical properties of a precursor. This, in turn, can have an advantageous effect on the delivery of the precursor(s) to the CVD reactor. The phase rule is often written in the following simple form (for systems composed of reactive components):[17]

$F = (N - R) + 2 - P$ or $F = C + 2 - P$, where

- F = number of degrees of freedom or variance of the system (the number of variables which can be chosen by the experimenter, and must be chosen to define the system).
- $C = (N - R)$ is the number of distinct chemical entities (N) minus the number of independent reactions between them (R) (it is the minimum number of substances that must be mixed to form the system).
- P = number of phases present (liquid, gas, etc.).

There are many important conclusions to be drawn from this law, e.g., the number of phases available cannot exceed the number of components by more than two. This is classically illustrated by the triple point of water, i.e., there is a specific temperature and pressure at which the three phases coexist (ice, water, steam), so there can be no degrees of freedom.[17] This approach can be applied to the delivery of a precursor from a bubbler to the reactor chamber of a CVD system. Crucially, if we assume that, as the entraining gas passes through the bubbler equilibrium is established between the gas and the material within the bubbler, reproducible and time independent behavior is observed. For the classic single component in a bubbler, at any instant in time, assuming equilibrium is established then:

- $C = 2$ precursor and carrier gas (no chemical reaction between the two).
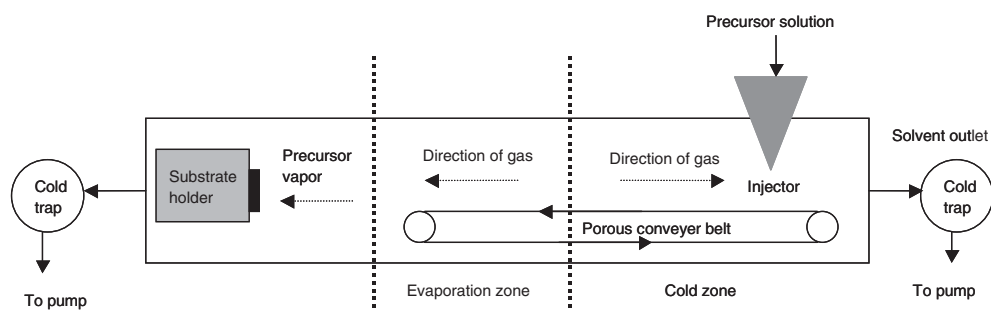

Fig. 8. Injection CVD reactor with solvent-eliminating porous belt [15,16].

- $F = 2$ temperature and pressure (the former may be selected at any value below the boiling point of the precursor under the pressure chosen).
- $P = 2$ vapor and liquid.

The same will be true for a bubbler containing a volatile solid material, such as trimethyl indium. Depending on the rate at which the carrier gas passes through the bubbler, mass transfer can easily become kinetically controlled. In considering this approach, we will be interested in several different systems. In the next section we shall consider some of these cases in more detail.[18]

3.1.1. Two-Component Precursor Systems

For two-liquid component systems in a bubbler, at any instant in time, assuming equilibrium has been established and there is some interaction between the liquids:

- $C = 3$ the two precursor species and carrier gas (with a chemical reaction in the bubbler).
- $F = 2$ pressure and temperature.
- $P = 2$ vapor and liquid.

The consequences of the phase rule, as it governs the separation of liquids by distillation, are familiar to all chemists. Many mixtures distill with constant composition (azeotrope), with perhaps the most familiar example being that of water–ethanol. The use of metal–alkyl Lewis base adducts such as $Me_2Zn \cdot NEt_3$ or $Me_2Cd \cdot S(CH_2)_4$ was first seriously studied by Wright et al.[19] These adducts are now well-documented, commercially available precursors,[20–23] and have several advantages over the base-free metal–alkyls, including greater ease of handling (the adducts are not pyrophoric liquids), fewer premature homogeneous reactions between the precursors (up stream of the substrate),[24–26] and greater purity.[2,27] In addition, a lower vapor pressures makes the flow rates into the reactor easier to control (particularly important when such compounds are used as dopants). In many cases, the presence of a Lewis base compound also improves the quality of the semiconductor layers grown. Recent work has shown that Lewis base adducts of dimethyl zinc are particularly useful in the doping of III/V materials with zinc.[28,29] Figure 9 represents the crystal structure of the dimethyl zinc bistriazine adduct, with many monodentate amines forming similar "bis" coordinating adducts in the solid state with group 12 alkyl compounds.[30] Dimethyl zinc has a high vapor pressure and is used either at low temperatures or diluted in hydrogen. However, the latter method tends to give non-reproducible results.

There are a number of observations concerning the chemistry of this system that are helpful in interpreting the physical properties of mixtures of amines with metal–alkyls in terms of their use as precursors. The commonly used mixture of dimethyl zinc–triethylamine (DMZ–TEAM) adduct is a liquid at room temperature but in the vapor phase the components are fully dissociated.[30] Moreover, one important feature of the system is that the vapor above a 2:1
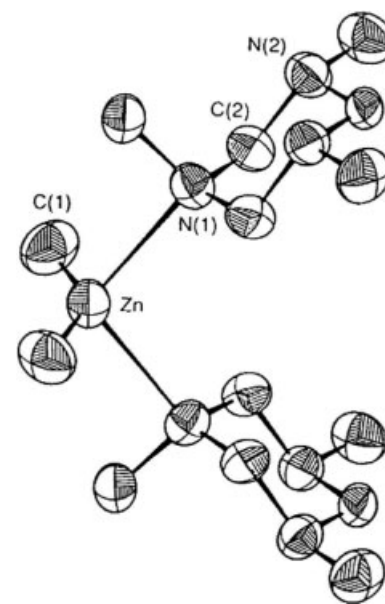

Fig. 9. Crystal structure of dimethyl zinc bistriazine.

mixture of DMZ and TEAM consists mainly of TEAM, with little or no evidence (from vapor phase infrared spectra) of the presence of DMZ. In fact the mixture is effectively air stable, suggesting very low volatility for any zinc-containing species. This observation indicates that the vapor pressure of TEAM is very much greater than that of any adducts with DMZ. Indeed, the vapor pressure of a 2:1 mixture of TEAM/DMZ very closely resembles that of the pure amine.[31] A second important feature of the chemistry of zinc–alkyl compounds is their relatively weak Lewis acidity. As a consequence, they have a low degree of association with Lewis base compounds such as amines. This lack of association in non-coordinating solvents is supported by ebulliostatic measurements on 1:1 mixtures in benzene.[32]

Taking into account the above points, the total vapor pressure of any mixture of DMZ and TEAM (ignoring the adduct, as its vapor pressure is low) is (approximately) given by Equation 1.

$$p_{obs} = x_{DMZ}\, p_{DMZ} + x_{TEAM}\, p_{TEAM} \tag{1}$$

x_{DMZ} is the true mole fraction of DMZ, as given by Equation 2.

$$x_{DMZ} = N_{DMZ}/(N_{DMZ} + N_{TEAM} + N_{ADDUCT}) \tag{2}$$

N_{DMZ} is the number of moles of DMZ, with similar relationships for TEAM. We consider only the formation of 1:1 adducts to be significant in this analysis. Two measurements are particularly useful in defining the system. The first is the vapor pressure of a 1:1 mixture of TEAM and DMZ, which we have measured on several occasions,[33] and is ~11.4(3) at 0 °C (4 measurements, different sets of appara-

tus).[34] At this composition the equilibrium can be expressed as shown in Equation 3.

$$DMZ(\alpha) + TEAM(\alpha) \rightleftharpoons DMZ/TEAM(1-\alpha) \tag{3}$$

Consequently, the approximate vapor pressure should be as given in Equation 4.

$$p_{obs} = p_{DMZ}(\alpha/(1+\alpha)) + p_{TEAM}(\alpha/(1+\alpha)) \tag{4}$$

The equilibrium constant (expressed in mole fractions) is given by Equation 5.

$$K = (1-\alpha)(1+\alpha)/\alpha^2 \tag{5}$$

The fractional dissociation can be readily calculated from the observed vapor pressure and the known equilibrium vapor pressures of the components, thus the equilibrium constant estimated in this way is 152.

A second important experiment is concerned with measuring the equilibrium vapor pressure of a mixture entrained with dry nitrogen for a period of time. Such solutions were found to reach a stable, and limiting stoichiometry, in which the ratio [DMZ]/[TEAM] was 1:1.5 ($x = 0.4$), with a vapor pressure of 10.4 torr at 0 °C. The composition was assessed from proton nuclear magnetic resonance (NMR) spectroscopy (likely accuracy, within 5 %); the vapor pressure may be affected slightly by dissolved nitrogen. As this stoichiometry is stable, i.e., in equilibrium, the chemical potential of all components must be the same, and the composition of the vapor containing DMZ and TEAM must reflect that of the liquid. In order to make further progress, an expression of the relationship between the vapor pressure of the mixture and its composition is needed. The derivation of such a relationship depends on the difference between the value x, calculated from the amount of material added (composition of the solution), and the true mole fractions, e.g., x_{DMZ} (taking into account association). The equation is a quadratic of the form shown in Equation 6.

$$-xK(x_{DMZ})^2 + (2xK - K - 1)x_{DMZ} + x = 0 \tag{6}$$

Using this equation it is possible to calculate the variation of vapor pressure as a function of the equilibrium constant. Typical plots using different values of K are shown in Figure 10, and it is immediately apparent how well the quadratic equation reproduces the pattern of the variation of vapor pressure. The nature of the formation of these relatively weak complexes makes it hard to refine the measurement much further. However, it is worth noting that the behavior of the plot is relatively insensitive to the value of K chosen, other than in the region $0.4 < x < 0.6$, and that in this region, the variation of the vapor pressure is small, i.e., the observed minimum is broad and flat. Another problem in the further refinement of any value of K is that
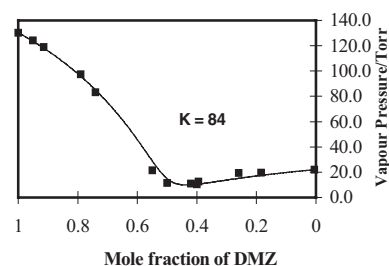

Fig. 10. Variation of the vapor pressure of a mixture of dimethyl zinc and triethylamine as a function of the mole fraction of the alkyl.

it would be expected to vary with the component composition of the mixture. Moreover, the number and type of molecular interactions are likely to be quite different for a solution of DMZ in TEAM than for a solution of TEAM in DMZ. However, the results are useful in explaining a number of perplexing apparent anomalies in the literature.

We have noted a need (indeed, it is recommended) to precondition bubblers of DMZ/TEAM 1:1 adduct before use. Moreover, this procedure allows excess DMZ to be blown out of the bubbler and a stable DMZ/TEAM stoichiometry to be achieved. It is now apparent that the partial pressure of DMZ at the entrained composition is not half the total pressure, as would be expected, but a more complex function. Using the vapor pressure of a 1:1 mixture to calculate K, the minimum vapor pressure of the system is predicted to have a total pressure of 7.7 torr, and a partial pressure for DMZ of 3.5 torr, at $x = 0.46$. The results from the entrained mixture give an empirical value of 3.2 torr for the partial pressure of DMZ.

Recent measurements by an ultrasonic method (using an Epison)[34] have also led to the suggestion that the partial pressure of DMZ in these mixtures is lower than expected for a simple 1:1 eutectic, with a value of 1.7 torr being quoted for the vapor pressure of DMZ.[32] This value is in reasonable agreement with our estimates of the equilibrium vapor pressure for DMZ above the mixture which, depending on the value of K and the method used, puts the partial pressure of DMZ in the range 2.5–3.5 torr. There are further possible explanations for these differences, including the effect of dissolved gas, the absolute calibration of the Epison, the temperature of evaporation, and measurement in the entrained system.[34] However, these discrepancies cannot simply be explained away as due to differences in stoichiometry as had earlier been suggested.[34]

3.1.2. More Complex Systems

The interpretation of the DMZ/TEAM system as functioning as a reproducible precursor because it forms a stable eutectic, may have some general implications for other mixtures of precursors, such as the reproducible behavior observed for mixtures of triisopropyl gallium with TEAM in metal organic molecular beam epitaxy

(MOMBE) growth,[35] or using ethyldimethyl indium (EDMIn),[36] and may provide a route for the design of improved systems for the delivery of oxides.

Some years ago there was considerable interest in the use of heteroleptic metal–alkyls such as EDMIn, EtMe$_2$In, as a liquid precursor for the delivery of indium in thin film CVD techniques.[35] Early reports claim reproducible growth results were possible,[37] and that EDMIn has a stable vapor pressure over a long period of time.[38] Initial investigations, by mass spectrometry (MS), indicated that EDMIn consisted of only the single compound, EtMe$_2$In.[35,39] Other studies by Raman spectroscopy,[40] and more recent studies, again by NMR spectroscopy, suggest that EDMIn undergoes ligand exchange. However, as long as equilibrium is established, the phase rule can also be applied to heteroleptic metal–alkyl systems. The composition of the system will be close to the stoichiometry EtMe$_2$In, with the predominant equilibrium as in Equation 7 below, with the formation of trimethyl indium (TMIn) and diethymethyl indium (DEMIn).

$$2\,Me_3In + Et_2MeIn \rightleftharpoons 3\,EtMe_2In \tag{7}$$

If this is the only formal equilibrium in the system i.e., disproportionation as far as Et$_3$In does not occur, the system is formally equivalent to the DMZ/TEAM system and so:

- $C = 3$ the two precursor species and carrier gas (with a chemical reaction in the bubbler).
- $F = 2$ temperature and pressure (which may be selected at any value below the boiling point of the precursor).
- $P = 2$ vapor and liquid.

If the equilibrium lies largely to the right (Eq. 7), the solution is likely to behave as a stable source. However, we know that alkyl scrambling, with the formation of TMIn, DEMIn, and even some triethyl indium (TEIn) does occur, Equation 8.

$$2\,Me_2InEt \rightleftharpoons Me_3In + MeInEt_2 \tag{8a}$$

$$3\,Me_2InEt \rightleftharpoons Me_3In + 2\,InEt_2 \tag{8b}$$
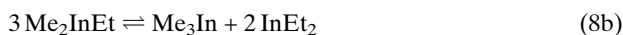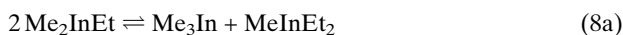
Neglecting the formation of TEIn, an azeotrope will form if there is a minimum in the vapor pressure composition curve, such that

$$x_{TMIn}\,p_{TMIn} = x_{EDMIn}\,p_{EDMIn} = x_{DMEIn}\,p_{DMEIn} \tag{9}$$

The fact that delivery is consistent and reproducible suggests that, at low temperatures, an azeotrope is indeed formed. It has been noted that, at higher temperatures, growth results using EDMIn become less reproducible,[35] suggesting that one component, TMIn, distils out preferentially. The stability of the system may well depend on the temperature of delivery and whether an amine is added to form Lewis base complexes, as these may, to an extent, inhibit ligand exchange.

These systems sometimes give poor growth results, with poor elemental stoichiometry in the as-grown semiconduc-

tor layers. This has been attributed to ligand exchange. Unlike the previous cases, ligand exchange produces new compounds (TMIn, EDMIn, and TEIn in the case of EDNIn), that have quite different properties from the originally designed precursors. Moreover, due to ligand exchange being a common phenomenon in main group metal–alkyls, when a heteroleptic metal–alkyl, or a number of metal–alkyls possessing different alkyl groups are used, after equilibrium is established, a complex mixture of labile (in this case indium) alkyl compounds are formed[41] (Eq. 8). The indium alkyl compounds possess different physical properties from one another, including the temperatures at which they decompose. Thus different species decompose at different temperatures via different mechanistic pathways. When preparing ternary main group semiconductors this can become a severe problem.

Thin film metal–organic vapor phase epitaxy (MOVPE) growth of InGaAs from a mixture of the metal–alkyls, triethyl gallium (GaEt$_3$), trimethyl indium (InMe$_3$), and *tert*-butyl arsine (As^{t}Bu$_3$), as attained from on-line IR monitoring, shows ligand exchange between the three precursors in the feed lines of the reactor, upstream of the substrate. The composition of the resulting product consisted of trimethyl gallium (GaMe$_3$), dimethylethyl gallium (Me$_2$GaEt), methyldiethyl gallium (MeGaEt$_2$), dimethylethyl indium (Me$_2$InEt), and methyldiethyl indium (MeInEt$_2$). Ligand exchange has a profound effect on the composition of precursors in the reactor feed, as shown in Figure 11, with the relative concentrations of the exchange products being dependent on the initial ratio of precursors
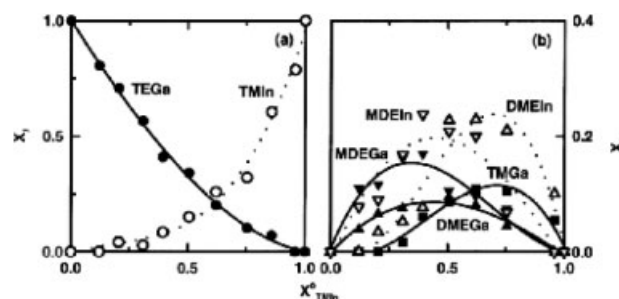
Fig. 11. The dependence of the relative partial pressures of each component compound in the gas on the initial relative pressure of TMIn fed at 80 °C.

used. Again, the thermal stability of these resulting compounds varies over a wide temperature range,[42] with the indium species decomposing in the order MDEIn > DMEIn > TMIn. The gallium species tend to decompose at higher temperatures, but in a similar order. This, in turn, can result in inhomogeneous element distribution (indium and gallium) in the as-grown InGaAs layers, with the film near the reactor inlet being rich in indium, while that near the reactor outlet is rich in gallium.

For main group alkyl precursors, ligand exchange appears to be a common occurrence and has been observed in hydrocarbon solutions of trimethyl gallium, trimethyl

indium, and trimethyl aluminum at temperatures as low as –65 °C.[43] Rapid ligand exchange was also observed in cold (–60 °C and –85 °C) hydrocarbon solutions, between trimethyl gallium and triethyl gallium,[44] along with mixtures of group 12 alkyls and trimethyl indium or trimethyl gallium.[45] More recently, with advances in in-situ monitoring techniques, a number of studies have demonstrated the occurrence of ligand exchange in the gas phase. Kappers et al.,[46] when growing CdZnTe in a MOVPE reactor, observed that the precursors diethyl zinc and dimethyl cadmium rapidly exchange their alkyl ligands to produce methylethyl zinc, dimethyl zinc, methylethyl cadmium, and diethyl cadmium. This was also the case for a study on the gas phase mixing of trimethyl gallium, trimethyl indium, and trimethyl amine alane, $[AlH_3\text{-}N(CH_3)_3]$, which produced methyl aluminum, alkyl gallium hydride, and alkyl indiumhydride compounds in the feed lines of a MOVPE reactor.[47,48] The use of sterically bulky ligands, such as ^tBu groups and σ-donor coordinating complexes to form Lewis acid–base mixtures may reduce or even inhibit ligand exchange between these compounds. This may be a factor in why precursor-amine mixtures, in general, give better growth results.

3.2. Solution Sources

TMIn is probably the most commonly used solid precursor in semiconductor deposition. As is typical for a solid, the delivery of material from a bubbler can become time dependent, due to the kinetic constraints on mass transfer between the solid and vapor phase. One commonly used approach, as mentioned before, is to use two bubblers in series since this allows for greater contact time between the entraining gas and the solid precursor and can, hence, lead to more reproducible mass transport results. Another approach, initially developed by Frigo and co-workers,[49,50] is to use a saturated solution of TMIn in a non-volatile coordinating solvent that is in contact with the solid precursor, Figure 12. The advantage of this approach is that the carrier gas passes through a solution containing dissolved precursor, making equilibration easier than for the solid vapor contact. Moreover, by placing the liquid in direct contact with excess solid, and providing the rate at which TMIn dis-
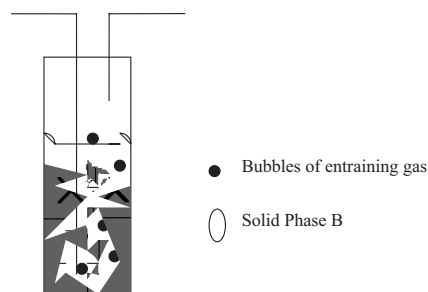
Fig. 12. A saturated solution of TMIn in a non-volatile coordinating solvent in a conventional bubbler.

solves is greater than the rate at which it evaporates, the solution remains fully saturated so the gas-phase concentration should remain constant over prolonged periods. The situation should be as illustrated in Figure 13, and the aim is to facilitate equilibrium by providing a kinetically more favorable transfer (solution to vapor) process. We
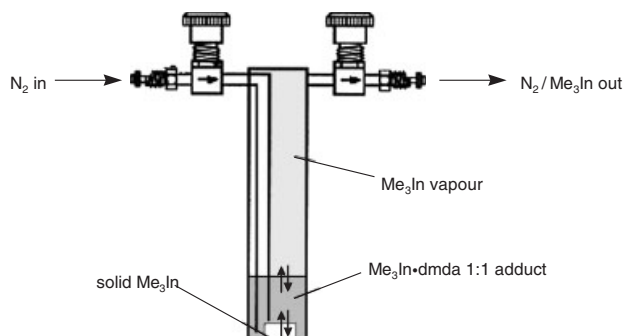
Fig. 13. Bubbler containing a solution of TMIn in dmda and solid TMIn.

now have a three-phase situation and at any instant in time, assuming equilibrium:

- $C = 3$ precursor, solvent, and carrier gas.
- $F = 2$ temperature and pressure (which may be selected at any value below the boiling point of the precursor – significantly $F = 3$; once the solid phase is consumed, compositional variations would be predicted once the solid material has been consumed).
- $P = 3$ vapor, liquid, and solid.

The partial pressure of TMIn above the mixture will be that of the solid. The situation is analogous to the determination of a solution concentration by an insoluble phase. Several solvent-TMIn combinations have been investigated but N,N-dimethyldodecylamine (dmda) has proved to be particularly useful. Excess TMIn is added to the initially formed 1:1 TMIn-dmda adduct-solution.[49,50] Even when only 5 g of solid TMIn remains, the performance of the system is satisfactory. This method is of renewed interest as it may provide a source of very low oxygen-containing TMIn. The dependence of this method on the phase rule has not been fully appreciated. In later work on this system, emphasis has been placed on the fact that coordination between the precursor and dmda is not important. For a system of this type to function successfully, it is important that the kinetics of transfer are improved, and there must be three phases present to define a system with only two degrees of freedom (temperature and pressure). This was proved by using a non-coordinating solvent, hexadecane, which dissolves only a negligible amount of TMIn but gives relatively constant delivery rates comparable to the dmda system.[51]

Figure 14 shows the calculated vapor pressure as a function of the total mole fraction of amine or TMIn at 20 °C (main graph) using $p = 1.7$ torr (20 °C) and the solubility of TMIn in the amine as 1.63 mol/mol. Inset is the phase diagram for this system showing the invariant region (shaded dark gray) in which all three phases are present.
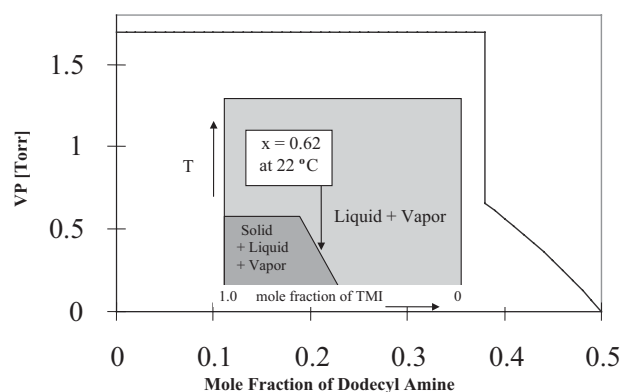
Fig. 14. Calculated vapor pressure as a function of total mole fraction of amine or TMIn at 20 °C (main graph), using $p = 1.7$ torr (20 °C) and the solubility of TMIn in the amine as 1.63 mol/mol [36,37]. Inset is the phase diagram for this system showing the invariant region (shaded dark gray) in which all three phases are present.

### 3.3. The Ammonia Method: Delivery Using a Reactive Gas

Compounds containing the β-diketonate ligand tmhd, or its derivatives (Fig. 1) have been widely used as precursors in CVD applications. Many commercially used derivatives contain fluorinated ligands as these have the effect of increasing volatility. However, because of the presence of fluorine, thermally stable fluorides such as BaF_2 can be formed on deposition, and this, in turn, can lead to fluoride being incorporated into the growing thin films, or etching of the films. To prevent the formation of fluorides, water vapor is added to the reactor chamber and/or a higher temperature used, however, for many materials this is undesirable. Buriak et al. have developed a route to depositing group 2 oxide materials that utilizes ammonia gas, NH_3, to increase the transport of non-fluorinated β-diketonate compounds, e.g., $[Ba_4(tmhd)_8]$, to the reactor chamber and substrate.[52] Recent investigations show that delivery from the system can be made to be very reproducible. Thus using the phase rule, for a reactive carrier gas with a single solid component in a bubbler interacting with two component single-phase vapor streams, e.g., ammonia in argon:

- $C = 2$ precursor and two carrier gases ($N = 3$), and one chemical reaction between the second carrier gas and the precursor.
- $F = 2$ temperature and pressure (which may be selected at any value below boiling point or sublimation point of the precursor).
- $P = 2$ vapor and solid.

This approach allows the use of less volatile precursors such as $[Ba(acac)_2]_n$ [acac = acetylacetonate] to deposit thin films of BaO. As no functional substitutions are required on the diketonate ligand, there is no potential for contamination in the resultant films, especially crucial in superconducting structures. One drawback is that this method can produce a buildup, within the CVD system, of NH_3 gas, which is extremely reactive and corrosive, and has, in some cases, resulted in spectacular explosions.

A similar approach was employed to prepare films of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_x$, from $Sr(tmhd)_2$, $Ca(tmhd)_2$, $Cu(acac)_2$, and triphenyl bismuth $[Bi(Ph)_3]$ by low-pressure CVD. The strontium and copper precursors only attain sufficient volatility at temperatures in excess of 200 °C, which can lead to premature precursor decomposition and oligomerization, thus making the stoichiometry in the as-deposited films difficult to reproducibly control.[53] Using a mixture of anhydrous ammonia and argon as the carrier gases improved the volatility and the thermal stability of both $Sr(tmhd)_2$ and $Ca(tmhd)_2$. Thus the source temperatures for both precursors could be lowered by ca. 40–50 °C. There was also enhanced source volatility for the copper precursor, $Cu(acac)_2$ when in the presence of pyridine.

The improvements in effective volatility are, to date, not yet fully understood. However, to attain a fully saturated coordination sphere at the central metal atom, precursors such as $Sr(tmhd)_2$, $Ca(tmhd)_2$, and $Cu(acac)_2$ are polynuclear in the solid state (Fig. 15). Heating at or before volatilization leads to dissociation into molecular monomers. Thus equilibrium is established at the surface of the solid or the melt, between monomers in the gas phase and higher oligomers in the bulk solid. In the gas phase, when monomer dimerization occurs, the resulting oligomers precipitate out, thus the overall equilibrium (Equation 10) would lie over to the left, with little precursor remaining in the gas phase for any prolonged period of time.

$$Ca_3(tmhd)_6(s) \rightleftharpoons 3\,Ca(tmhd)_2(l) \rightleftharpoons 3\,Ca(tmhd)_2(g) \qquad (10)$$
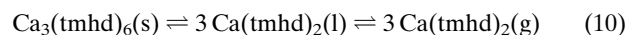
In the presence of ammonia, ammonia gas may coordinately saturate the metal center, via nitrogen–metal Lewis acid–base bonds. This reaction may have the effect of inhibiting, or at least slowing down, gas-phase oligomerization, shifting the overall equilibrium to the right (Equation 11) thus increasing the volatility of the precursors.

$$Ca_3(tmhd)_6(s) \rightleftharpoons 3\,Ca(tmhd)_2(l) \overset{NH_3}{\rightleftharpoons}$$
$$3\,Ca(tmhd)_2(NH_3)_n(g) \qquad (11)$$
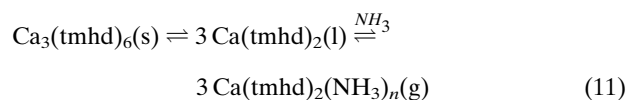
An example is provided by $[Ca_3(tmhd)_6]$. The crystal structure (Fig. 15a) consists of trimeric calcium units with inter-coordinating tmhd ligands.[54] One method of achieving monomeric calcium compounds, albeit in the solid phase, is to use additional σ-donor compounds, such as chelating amines, to prevent tmhd ligands from inter-molecular coordination, as in the case of $[Ca(tmhd)_2(tetraen)]$, tetraen = tetraethylenepentamine, where the chelating amine completes the coordination sphere about the metal center (Fig. 15b). The adduct molecule $[Ca(tmhd)_2(tetraen)]$ has a higher vapor pressure than the non-adducted parent complex $[Ca_3(tmhd)_6]$.[55]
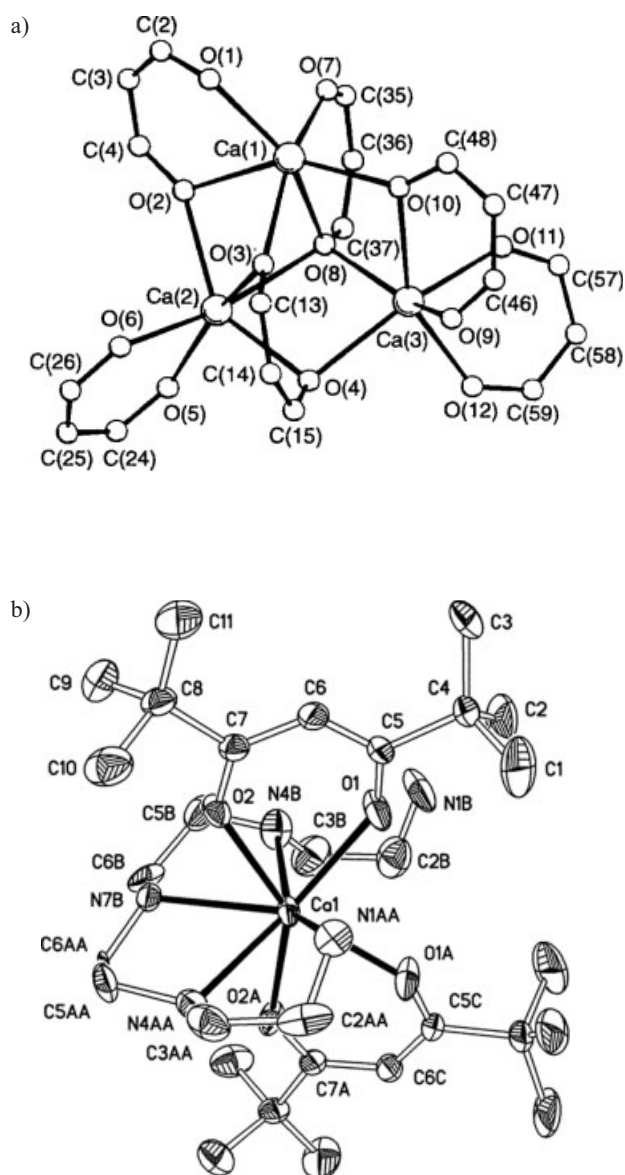
a)

b)

Fig. 15. a) Crystal structure of [Ca₃(tmhd)₆] reproduced from the literature [54]. b) Crystal structure of [Ca(tmhd)₂(tetraen)] reproduced from the literature [55].

4. Conclusion

Although, to date, volatility, along with purity, and clean decomposition routes have been the fundamental requirements for precursors used in CVD, advances in the design of precursor delivery systems now mean that many compounds that only fulfill the latter two requirements can successfully be used as precursors. This situation means that the chemist can now concentrate on the design of precursors with clean decomposition mechanisms, without the added problem of volatility. Many more compounds that would otherwise not be considered as precursors can now be used in CVD. One problem that should be taken into account is the interactions and reactivity of a precursor with the carrier gas and other precursors present in the solution and gas phase. These can drastically affect the physical and chemical nature of the precursor(s) and thus, the as-grown film.

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