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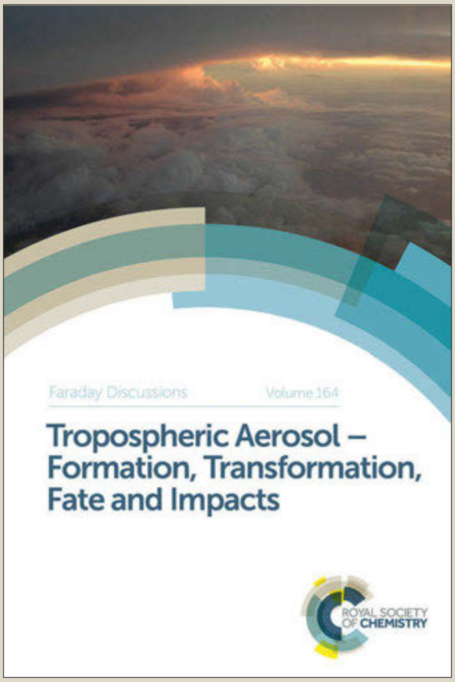

Faraday Discussions Volume 164

Tropospheric Aerosol – Formation, Transformation, Fate and Impacts

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Mechanochemical Synthesis of an Organometallic Compound: A High Volume Manufacturing Method

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Chemical vapor deposition (CVD) precursor chemicals are held to some of the highest purity levels in industry. Many metal reagents form stable, unbreakable adducts with the coordinating solvents that are necessary for solvating highly polar reagents. These adducts are undesirable and must be removed prior to usage. Herein we describe a mechanochemical approach to the synthesis of bis(n-propyltetramethylcyclopentadienyl)strontium that eliminates the use of strongly coordinating solvents. This method overcomes the solubility problems of the two reagents without the formation of stable, unbreakable adducts. We utilize a unique reactor geometry that facilitates mechanochemical syntheses while simplifying handling and allowing for “one pot” production. The synthesis was scaled to five hundred gram lot sizes in a six liter reactor. This technique is applicable to many syntheses and is linearly scalable - limited only by reactor size.

Introduction

Strontium-based semiconductors may be a key material for the production of several types of advanced memory devices. Thin films of the strained strontium titanate ($SrTiO_3$) perovskite structure can be used in ferroelectric memory devices such as smart cards and may pave the way for hybrid transistors that would allow for “Instant on” computers.[1] Barium Strontium Titanate (BST, $Ba_xSr_{1-x}TiO_3$) is a promising high K dielectric material for advanced DRAM capacitors. In MIM capacitors, the dielectric constant (K) for BST can be tuned from under 100 to over 1000 by varying the ratio of barium to strontium.[2] In addition, it also enjoys high breakdown strength, small dielectric loss, and good thermal stability. Furthermore, strontium ruthenium oxide (SRO, $SrRuO_3$) is the one of the best conductive materials available for use as electrodes in these ferroelectric capacitors.

Although these materials can be synthesized by sol gel methods[3-9] and deposited via solution deposition[10, 11] or sputtered from metal targets,[12-14] the aggressive geometry and high aspect ratios of these cutting edge devices will likely require the material to be deposited by chemical vapor (CVD) or atomic layer (ALD) deposition. These methods require a precursor that is volatile yet thermally stable at the process temperatures. Several organometallic precursors for deposition of strontium metal are known in the art but are not ideal.[15-20] The beta-diketonate based precursors are solids and, due to the strong metal-carbon bond, result in carbon contamination of the films[21]. The cyclopentadiene based ligands have a weaker metal-carbon bond, but are solids with low vapor pressures. It is desirable to have a liquid precursor for ease of handling and delivery. By using the bulky ligand n-propyltetramethylcyclopentadiene (Cp') the liquid, bis(n-propyltetramethylcyclopentadienyl)strontium ($SrCp'_2$) can be prepared (Figure 1).

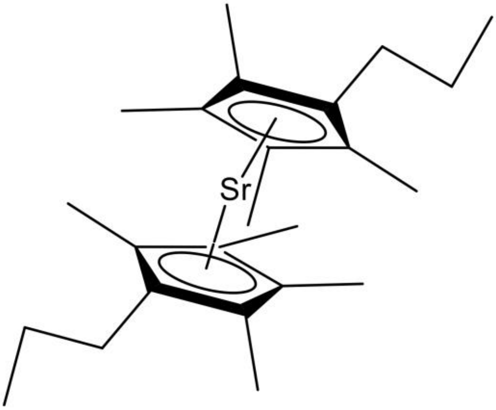

Figure 1. The bulky n-propyltetramethylcyclopentadiene (Cp') ligand forms a sandwich complex with strontium that is liquid at room temperature.

$SrCp'_2$ is an excellent precursor as it is both monomeric and a liquid at room temperature. Typical syntheses of cyclopentadienides utilize alkali metal cyclopentadienides and metal halides to produce the desired product by salt metathesis (Equation 1). However, strontium iodide is poorly soluble in any solvent compatible with the air and water sensitive reagents and final product.

$$SrI_2 + 2\ KCp' \xrightarrow[RT]{\text{Diethyl Ether}} Sr(Cp')_2{:}Et_2O + 2\ KI \qquad \text{(Eq. 1)}$$

The reaction represented in Equation 1 is thermodynamically and entropically favored. But, the low solubility of the precursor halide severely limits the diffusion rate of the precursors. Vigorous stirring and heating can alleviate this problem. However, the density of SrI_2 (5.46 g/cm^3) makes stirring large batches difficult and the maximum reaction temperature is limited to the boiling point of diethyl ether (34.6 ˚C). Mechanochemical methods effectively reduce diffusion barriers and increase reaction rates through attrition, agitation, and localized high-pressure events.[22-25] High energy milling can produce macroscopic temperatures in excess of 200 ˚C.[26] Exothermic processes can also increase the macroscopic temperature. $SrCp'_2$ was chosen as a CVD precursor and high macroscopic and microscopic temperatures would lead to undesirable by-products. In order to minimize any detrimental temperature rise, the mechanochemical synthesis of $SrCp'_2$ was undertaken under solvent or liquid assisted grinding (LAG).[22] Using this approach, the solvent serves to remove product from the surface of the insoluble SrI_2 and also serves as a heat sink. Since chemical reactions only occur during a collision and there is a large liquid heat sink, this approach is easily scaled.

Results and Discussion

Bis(n-propyltetramethylcyclopentadienyl)strontium is readily synthesized in small quantities via standard salt metathesis methods. (Equation 1) The two sparingly soluble reagents are magnetically stirred in an ethereal solvent overnight and worked up via standard methods. More polar solvents such as dimethyl ether (DME) and tetrahydrofuran (THF) are better at solvating the reagents, but are to be avoided as they form stable, unbreakable adducts with the product. The presence of these adducts during epitaxial growth results in carbon and oxygen incorporation and compromises the integrity of the semiconductor device. Additionally, alkali metal salts of the cyclopentadiene (Cp') ligand are highly reactive toward water. Anhydrous diethyl ether forms a Lewis acid/base adduct with the product that can be broken via a high temperature distillation resulting in pure (solvent-free) product. (Equation 2)

$$Sr(Cp')_2{:}Et_2O \xrightarrow{\Delta} Sr(Cp')_2 + Et_2O \qquad \text{(Eq. 2)}$$

This synthesis does not scale readily since neither the strontium iodide nor the potassium salt of the Cp' ligand are readily soluble in diethylether. Strontium iodide is a very dense material (5.46 g/cm^3) and large quantities cannot be stirred magnetically. Larger scale reactions therefore require overhead stirring with a motor and a PTFE paddle to move the reagents in the reactor. However, none of the synthetic attempts utilizing overhead stirring produced any measureable yield of the desired product. Smaller scale syntheses with magnetic stirring always generated product, although yields did vary. Serendipitously, we discovered that a combination of magnetic and overhead stirring would, eventually, produce the desired product. This method, however, suffered from low yields and was very difficult to set up. The magnetic stir plate and the overhead stirrer had to be synchronized or the reaction failed. In addition, reaction times were inconsistent, varying from three to seven days. We observed that repeatable yields could be obtained if the same glassware, paddle and stir bar were used, but only then. Heating of the reactions did not accelerate the reaction nor did it improve yield.

It was theorized that the magnetic stir bar was not aiding in the stirring of the insoluble reagents but was grinding the two together and that the physical grinding was the force driving the reaction. This hypothesis explained why overhead stirring with a paddle alone did not result in a chemical reaction but coupling with a magnetic stir bar did. As there is necessarily a minimal amount of force between the glass reactor and the PTFE coated magnetic stir bar (by design) we set out to increase the force generated. This was expected to decrease the reaction time and increase the yield.

A commercially available vertical geometry filter reactor was chosen. This allowed for an increase in the stirring friction and for easy reagent filtration. In the filter reactor, KCp' was prepared from HCp' and a potassium salt followed by removal of the solvent and by-products via the bottom frit. Strontium iodide, 12.7 mm 316 stainless steel balls, and solvent were added to the KCp' in the reactor. The media:reagent ratio was 0.05:1. Once the reaction was complete, the product was removed from the insoluble by-product through the same bottom frit.

Initially, the glass frit at the bottom of the reactor was expected to provide a rough surface for the steel balls to grind against. It became apparent that the stirring speed needed to be high enough that the ball bearings did not remain on the frit but instead were forced against the sides of the reactor. This still provided enough friction that the reagents ground together and the reaction was complete in twenty-four hours. This suggests that there is a minimum impact force required to induce the reaction. This force would be related to the fracture toughness of SrI_2 and KCp'.

With only a PTFE paddle, stirring the reagents in solvent produced no measureable reaction, even with additional heating. Both reagents are effectively insoluble in diethyl ether and remain, unreacted, on the bottom of the flask. No color is observed in the solvent even after days of stirring via the PTFE paddle. Upon the addition of milling media reaction products were observed and high yields were obtained after twenty-four hours. A distinct yellow color is observed in the solvent after just a few hours of stirring. The insoluble solid remains white and quickly settles to the bottom of the reactor when stirring is stopped. In this liquid assisted mechanochemical reaction, the grinding action of the steel balls on the insoluble reagents improves the reaction kinetics. Although substantially more solvent is used than in typical liquid assisted grinding[22] the principle is the same.

The solvent is serving at least three functions. It acts as a carrier, removing the soluble product from the reaction area, as a suspending agent for easy intermixture of the two insoluble reagents, and as a heat sink limiting the reaction temperature to the boiling point of the solvent (34.6 ˚C). Even though this synthesis is slow and the rate is determined by the grinding action, it is still an exothermic reaction. This heat, coupled with the heat of grinding, could exceed the thermal stability of the reagents or product at a local level. The solvent carries away the excess heat and radiates it to the atmosphere through the glass walls of the reactor. A fourth function may be to serve as a lubricant. Media wear is an important issue when a mechanical attrition process is implemented. It can be a major expense when operating large-scale solutions. The use of a solvent can serve as a lubricant and reduce media wear. Additionally, cyclopentadienides readily form from the metals found in the steel milling media (Fe, Cr, Ni, Mo, Mn). Metal impurities would make the product unsuitable for CVD application. Although wear was observed on the steel media, reactor sides (Figure 2), and stirrer paddle, no appreciable amounts of these metals were found in the final product.

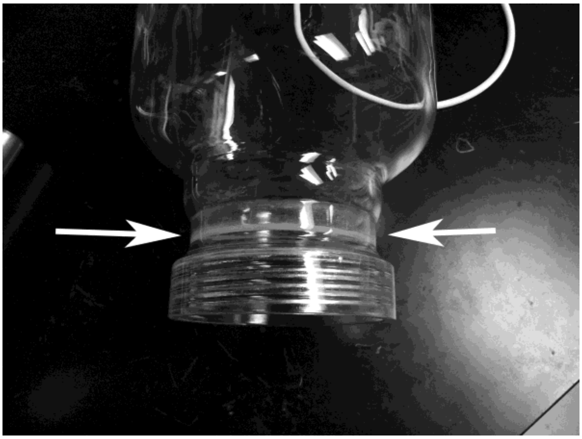

Figure 2. Although wear (arrows) from the media is evident on the sides of the glass reactor, no metals were found in the product.

Although other researchers have reported the synthesis of metal – cyclopentadiene complexes via mechanochemical salt metathesis [27], we believe this is the first report of a preparative scale synthesis using these methods. The use of larger quantities of solvent may play an important part in scaling up mechanochemical syntheses.

Functioning as a carrier, the solvent removes the product from the reaction area which allows for a localized application of Le Chatelier's principle. In addition, by removing the product from the reaction area, the solvent effectively prevents mechanochemical destruction of the product due to excessive grinding, a problem encountered by Makhaev *et al.*

Conclusion

The mechanochemical synthesis of bis(n-propyltetramethylcyclopentadienyl)strontium is six times faster than the standard method and produces a 90 percent yield. The synthesis can be performed using reactors and stirring apparatus developed for traditional solvent-based chemistry. This effectively reduced the capital expenditures needed for implementing this approach. It also allows air and moisture sensitive reactions to be carried out using proven reaction apparatus. Consistent, high yields were obtained on the pre-pilot plant scale (500 g). This yield should scale linearly with the size of the reactor. We have been very conservative in our experiments and limited the overall reaction scale to that of the first step – generating the KCp' by standard solvent based techniques. As long as the stirring system has sufficient torque to move the solid reagents and the steel balls, a higher concentration of reagents could be placed in the reactor and more product could be generated in the same volume and with the same amount of solvent. An attrition mill modified for inert atmosphere use could grind many times the amount of solid we used with a minimal amount of solvent.

Since this approach scales linearly, the need for extensive reaction engineering as production needs increase is reduced. As we have shown, existing batch reactors can be readily converted to mechanochemical reactors. The use of liquid solvents in a mechanochemical reactor enhances mixing, reduces media wear, and improves thermal regulation. The use of a liquid carrier facilitated the reduction in media mass needed. In fact, the media loading for this reaction is almost two orders of magnitude lower than typical mechanochemical reactions (0.05:1) Previous reports of LAG have focused on the minimal amount of solvent needed[22]. Although it is true that less solvent results in a greener process, there are potential benefits to the use of larger quantities of less aggressive and more environmentally friendly solvents especially for larger scale reactions. This synthesis may be further improved by replacing the low-boiling, peroxide forming solvent diethyl ether with toluene. The toluene would solvate the product and aid in suspension but would not form an adduct with the product, eliminating an energy intensive processing step.

Experimental

General Considerations

All manipulations were performed using standard Schlenk and dry box techniques under an atmosphere of nitrogen[28]. Anhydrous solvents and reagents were purchased from catalog vendors and used without further purification. Deuterated solvents were dried over 4Å sieves prior to use. NMR spectra were referenced to residual protium in the solvent. The filter reactor used is an ACE 6384-137 heavy wall reactor with a medium glass frit. All glass, steel and PTFE parts are dried overnight in a 120° C oven and purged with nitrogen prior to use.

Reactor Assembly

The reactor is assembled hot from the oven following the manufacturer's instructions. Kalrez® O-rings are used in place of the encapsulated ones supplied. The reactor is placed in a ring stand and secured with a chain clamp. It is purged with nitrogen through the gas inlet in the top and out the bottom valve. (Figure 3.)

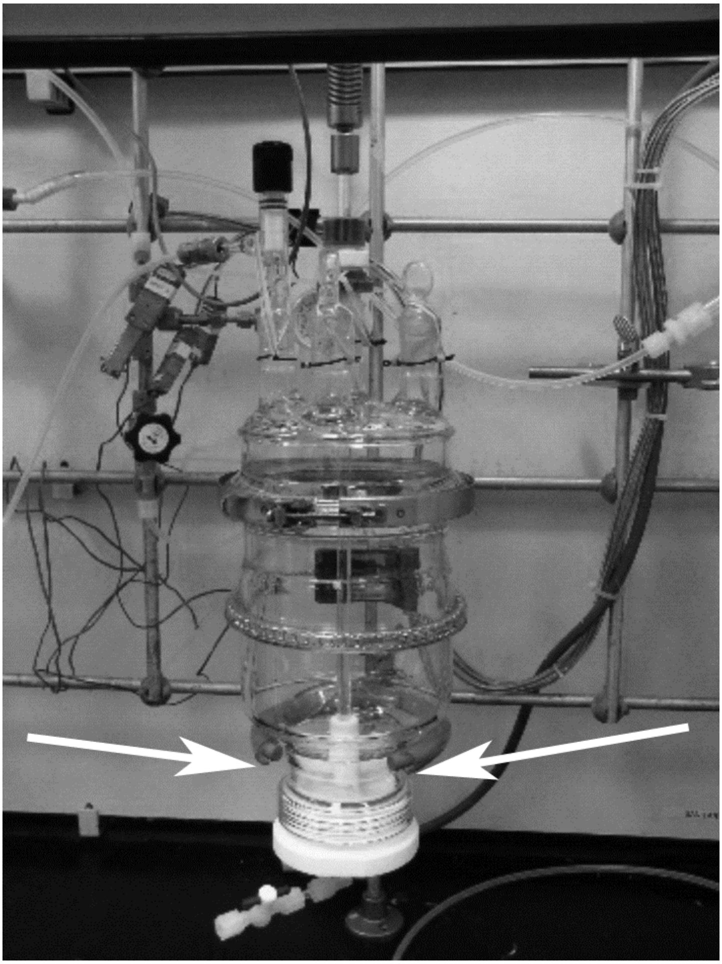

Figure 3. The reactor assembly is based on commercially available large-scale glassware. The media rides in the region indicated by the arrows.

Synthesis of KCp'

Approximately 500ml of toluene was added to the reactor to leak check the reactor and dilute the $KN(SiMe_3)_2$. To this 3600g of a 15% solution of $KN(SiMe_3)_2$ in toluene (550g, 2.28 mol of $KN(SiMe_3)_2$) was added. The mixture was stirred via an overhead stirrer @300 rpm and 392g (2.38 mol) of Cp'H was transferred to the reactor using 6.35 mm PTFE tubing under a positive pressure of nitrogen. Addition rate is not critical. The reaction mixture was stirred overnight at room temperature under nitrogen and yielded a yellow solution with a white solid (KCp'). The solid was isolated by removing the solvent through the bottom valve and washed with three 500 ml portions of toluene. Quantitative yield for the KCp' was assumed for the calculations utilized for the remainder of the synthesis.

Mechanochemical Synthesis of Sr(Cp')$_2$:OEt$_2$

SrI_2 powder (380 g, 1.12 mol) was loaded into a solid addition Schlenk flask inside a glove box and connected to a Schlenk line. Four liters of diethyl ether was added to the KCp' in the reactor. Six 12.7 mm stainless steel ball bearings (316) were added to the reactor. The stirring speed was adjusted so that the ball bearings remained on the bottom of the reactor. Once stirring has been established, the solid SrI_2 powder was added using a flexible PTFE solid-addition adapter. The reaction was stirred for twenty-four hours at room temperature under a nitrogen overpressure.

The product was collected by filtering through the frit at the bottom of the reactor. The filter cake is washed with three 500 ml portions of diethyl ether and added to the product flask. The filtrate was concentrated under reduced pressure yielding approximately 492 grams of Sr(Cp')$_2$:OEt$_2$ as a waxy oil (88% yield).

Isolation of Sr(Cp')$_2$

Vacuum distillation of Sr(Cp')$_2$:OEt$_2$ affords the base free compound. In a typical distillation Sr(Cp')$_2$OEt$_2$ was distilled using a jacketed short path distillation head. Once the pressure was below 750 microns, the source flask was heated to 145 °C. After 30 minutes the temperature was increased to 160 °C to break the adduct and remove diethyl ether from the material. After 3 hours, all of the ether has been removed and the apparatus can be transferred to the product flask. The external temperature of the source flask was increased to 230° C in 20° steps. The product begins to distill at a head temperature of ~165° C. Distillation was carried out until no more material came over. Yield: 380 grams of pure material. ^{1}H NMR (C_6D_6, 15 °C): δ 0.907 triplet, 1.31 multiplet, 1.96 singlet, 2.001 singlet, 2.39 multiplet.

Characterization

Organic purity was determined by NMR. The spectrum was integrated and peaks not assignable to Sr(Cp')$_2$ were integrated and found to be less than 1% of the total spectrum. Metallic purity was determined by ICP-MS. All lots were examined for the presence of elements found in 316SS – iron, chromium, manganese, molybdenum, and nickel. In two of the six lots iron was detectable at 1ppm and 1.09ppm. The other four lots had no detectable iron and none of the other elements were detectable in any of the six lots made by this method. Non-volatile residue was determined by simultaneous thermal analysis and all lots showed less than 2.5% NVR.

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