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Short communication

Microscale vacuum distillation apparatus for high-boiling, air- and heat-sensitive liquids

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ABSTRACT

We describe a simple apparatus that enables the vacuum distillation of ~0.2 mL of air- and water-sensitive, high-boiling liquids. The apparatus should be useful in teaching laboratories, and also to practicing chemists.

1. Introduction

The purification of high boiling liquids on the microscale (<0.5 g) can be challenging, especially if they are sensitive to air and moisture and decompose easily when overheated. For such reactive substances, common purification methods such as thin layer or column chromatography often cannot be used. Methods such as sublimation in vacuum or recrystallization under an inert atmosphere can sometimes be adapted for the purification of liquids, specifically by carrying them out below room temperature, but are experimentally challenging and not always applicable. Distillation is an attractive separation method, but conventional microscale techniques such as Kugelrohr distillation [1–3], steam distillation [4], Hickman stills [5–11], Babcock stills [12,13], microfluid distillation [14], and other versions of semi-microscale molecular distillation apparatus [10,15–18] are usually not designed for handling air-sensitive compounds, and the few small-scale distillation methods that can be easily adapted for air-sensitive compounds typically require much more than 0.2 mL of material [19–22].

For organometallic complexes of transition metals, which usually have high densities compared with purely organic liquids, ~0.5 g of distillate corresponds to 0.2–0.4 mL of liquid. We have encountered the need to distill such small quantities of air- and moisture-sensitive organotransition metal compounds in our laboratory-scale research to discover new chemical vapor deposition (CVD) [23–27] and atomic layer deposition (ALD) [28,29] precursors for possible use in the microelectronic industry; the development of volatile precursors has been an important driving force for the advancement of CVD and ALD processes [26,30]. Compared to solid precursors, liquid precursors have one significant advantage in these applications: liquids tend to volatilize at near-constant rates over time, whereas solids often show variable volatilization rates owing to changes in particle size. As a result, the delivery rate of liquid precursors can be more easily controlled and reproduced [25,30,31].

2. Methods and results

We wish to report a simple device that enables the vacuum distillation of ~0.2 mL of air- and water-sensitive, high-boiling liquids (Fig. 1). This apparatus consists of an X-shaped arrangement of 17 mm o.d. glass tubing, equipped with standard 14/20 ground glass joints at the two openings. The two bottom wells serve as source and receiving pots, respectively. The stopcock and the ground glass joints allow the apparatus to be connected to a Schlenk line and maintained at all times either under vacuum or an inert gas. Although we have found that contamination from grease is typically not an issue due to the low volatility of the distillate, the ground glass components may be replaced with greaseless stopcocks and joints (or J. Young valves) if desired. The stopcock is placed on a cross-tube that connects the upper halves of the two legs, so as to provide a good blanketing flow of inert gas when either or both of the two legs is unstoppered. The leg of the X-tube that serves as the receiving pot is fitted with a water-cooled cold finger that extends ca. 100 mm length below the joint; a drip tip at the end of the cold finger is desirable (a convenient commercially available cold finger is Chemglass CG-1222-14).

The dimensions we have used enable heating the neck of the source pot as close to the X-junction as possible so as to minimize the amount of

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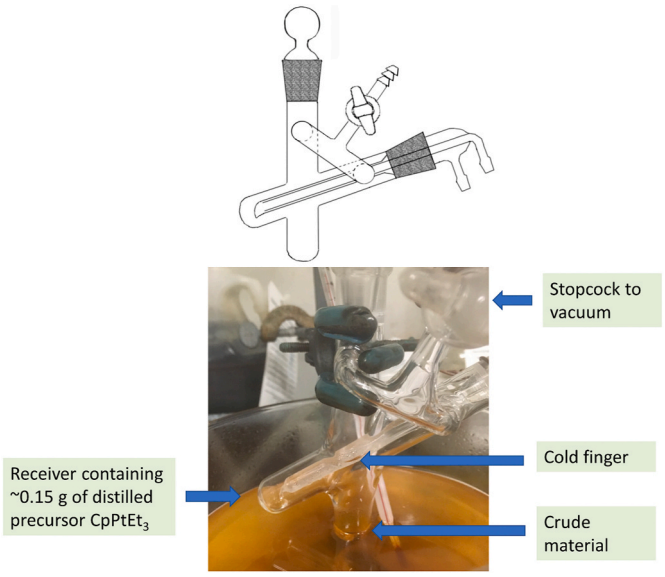

Fig. 1. Top: Drawing of the micro-scale distillation apparatus; Bottom: a picture showing the distillation of ~0.15 g (~0.1 mL) of the organometallic compound $CpPtEt_3$ [32] using the micro-scale distillation apparatus. The isolated yield of this product after distillation was 51% [32]. As judged from comparisons with similar compounds [31], the normal boiling point of $CpPtEt_3$ is estimated to be ~350 °C. The distillation was conducted under ~5 mTorr vacuum and the source pot was heated in an oil bath to ~45 °C. The isolated yield of this product after distillation was 51%. Anal. Calcd for $C_{11}H_{20}Pt$: C, 38.0; H, 5.80. Found: C, 38.2; H, 5.74 [32]. The ^1H NMR spectrum of the distillate shows no impurities above background levels.

condensate that simply returns to the source pot. Although the receiving pot may warm slightly above room temperature, this effect does not impede the distillation. The neck of the source pot is long enough to prevent liquid from easily spattering or bumping into the receiving pot when vacuum is applied.

When carrying out a distillation, the crude product is first dissolved in a minimum amount of a low boiling solvent (such as pentane) to reduce the viscosity and minimize losses during transfer. The resulting solution is delivered under inert gas to the source pot by syringe or cannula through a rubber septum in the upper part of leg that contains the source pot. The septum is replaced with a glass stopper, and the low-boiling solvent is carefully removed by evaporation under vacuum. Then, the leg of the X-tube that serves as the source pot is heated in an oil bath, and the residue is distilled under dynamic vacuum. Any remaining traces of the solvent will be pumped away into the vacuum line, and only high-boiling components will condense onto the cold finger and drip into the receiving pot. When the distillation is complete, the material in the receiving pot can be transferred, either on a Schlenk line or in a glove box, directly to a storage flask by syringe, cannula, or micropipet. With careful control of the pressure and temperature, fractional distillations can in principle be carried out.

The design of this apparatus is similar to but much simpler than the Gould-Holzman-Niemann apparatus [33], in which a well-to-well design is employed to minimize the total volume and inner surface area of the apparatus, and a cold finger is used to condense and direct the flow of the small amount of liquid. A design similar to the present one has been mentioned briefly by King et al. [34].

We have found that this apparatus provides a useful and convenient way to distill a number of high-boiling, air- and moisture-sensitive liquids on scales as small as ca. 100 μL or even smaller (Fig. 1). [32].

Credit author statement

Sumeng Liu: Conceptualization, Methodology, Investigation, Writing – Original Draft. **Gregory S. Girolami:** Conceptualization, Supervision, Funding acquisition, Project Administration, Writing – Review & Editing, Data Curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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