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# Large- and Small-Scale Syntheses of Donor-Free Rare-Earth Triiodides from the Metals and Ammonium Iodide

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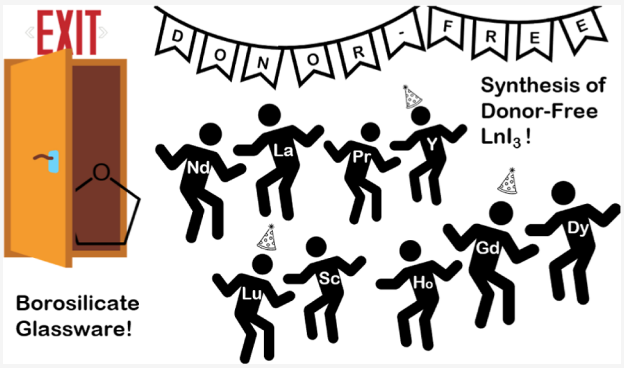
**ABSTRACT:** Rare-earth triiodides free of donor solvents, $LnI_3$ (Ln = Sc, Y, La−Lu), have been prepared in quantities as high as 76 g and in yields between 72% (Sc) and 98% (La) by the reaction between the corresponding metal and excess ammonium iodide in a two-step, one-pot procedure that is conducted in borosilicate glassware at temperatures of 350−430 °C in commercial tube furnaces. Procedures for both large-scale and small-scale syntheses are described, with specific examples for Ln = Sc, Y, La, Pr, Nd, Gd, Dy, Ho, and Lu. While the large-scale synthesis described here utilizes specialized glassware, the small-scale preparation may be performed in commercially available glassware.






## INTRODUCTION

Binary metal halide compounds are among the most useful starting materials in inorganic and organometallic chemistry.[1−3] While the chemistry of the rare-earth elements, Ln (Ln = Sc, Y, and the lanthanides), differs substantially from that of other elements of the periodic table,[4] one significant similarity is that the binary halides were among the first compounds of these elements to be prepared and studied.[5] For these large electropositive elements, major advances in their nonaqueous chemistry have been enabled by the ready availability of anhydrous rare-earth trihalides.[6] Since hydrated rare-earth trichlorides, $LnCl_3(H_2O)_n$ ($n$ = 8−9), are available commercially, methods were developed for their desolvation[7,8] and anhydrous $LnCl_3$ salts have since been extensively used in inorganic and organometallic syntheses.[6,9,10] Since these trichlorides are insoluble in nonpolar organic solvents, syntheses are typically conducted in coordinating solvents, such as tetrahydrofuran and diethyl ether. In these solvents, $LnCl_3L_n$ complexes ($n$ = 3−4, L = donor solvent) which have improved solubility are formed and function as the precursors.[6] Independent syntheses of such solvated halides, $LnX_3L_n$ (X = Cl, Br, I) were subsequently developed and as demonstrated by Deacon and co-workers and other groups, these solvated complexes may be prepared from the elements in an appropriate coordinating solvent.[11−19]

Although reactions of $LnCl_3$ in ethereal solvents have been used extensively, for some rare-earth transformations this protocol is not generally viable because reactive species can cleave the C−O bonds of even residual solvent and form undesirable products. For example, attempts to prepare $(C_5Me_5)_3Ln$ complexes in THF generate alkoxides from the ring-opening of THF[20,21] and more recent studies of the Y(II) complexes $\{Y[N(SiMe_3)_2]_3\}^{1-}$ have shown multiple routes of C−O cleavage for this reactive Ln(II) ion.[22] As early as 1965, E. O. Fischer reported the use of benzene at reflux as the solvent for the synthesis of $(C_5H_5)_3Lu$ from $LuCl_3$ and $NaC_5H_5$,[23] but reactions using $LnCl_3$ are not typically performed in non-coordinating solvents.

Although rare-earth *triiodides* are also insoluble in nonpolar solvents, the weaker Ln−I bond[24] allows $LnI_3$ to function as a good starting material in arene solvents at elevated temperature. For example, Nief and co-workers reported that while $(Cp^{ttt})_2TmI$ ($Cp^{ttt} = C_5H_5(^tBu)_3$) could not be prepared from the reaction of $KCp^{ttt}$ or $NaCp^{ttt}$ with $TmI_3$ in THF, it may be prepared from $KCp^{ttt}$ and $TmI_3$ in toluene.[25] More recently, McClain, Harvey, Long, and co-workers have shown that $(Cp^{iPr5})_2LnI$ ($Cp^{iPr5} = C_5(^iPr)_5$) complexes are accessible by the reaction between $LnI_3$ and $NaCp^{iPr5}$ in toluene at 160 °C and reduction of these complexes can be accomplished in benzene to form $(Cp^{iPr5})_2Ln$ compounds (Ln = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er).[26,27] For scandium, the smallest rare-

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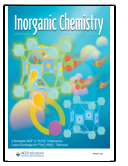

earth metal, use of the triiodide in nonpolar solvents allowed for the isolation of $(Cp^{ttt})_2ScI$, the precursor to the first scandium(II) metallocene, $(Cp^{ttt})_2Sc$.[28]

Thereare also cases where the identity of the halide ligand is critical to the formation of reduced rare-earth complexes. For example, reduction of the iodide $(Cp'')_2ScI$ ($Cp'' = C_5H_3(SiMe_3)_2$) forms the Sc(II) complex, [K(2.2.2-cryptand)][$(Cp'')_2ScI$], but the analogous chloride complex could not be obtained by this method.[28] Recently we reported the synthesis of the Ln(II) terphenylthiolate complexes $Ln(SAr^{iPr6})_2$ ($Ar^{iPr6} = C_6H_3$-2,6-($C_6H_2$-2,4,6-$^iPr_3$)$_2$) by reduction of the Ln(III) iodides, $Ln(SAr^{iPr6})_2I$, which were prepared by the reaction of $LnI_3$ and $KSAr^{iPr6}$ in toluene at 120 °C.[29] For these studies, we needed a convenient and cost-effective[30] source of donor-free $LnI_3$ starting materials which led to the development of the methods reported here.

There are several established routes to prepare donor-free rare-earth triiodides and these have been compiled in a recent review of rare-earth starting materials.[6] These include reactions between (1) a rare-earth metal and iodine or hydrogen iodide, (2) a rare-earth metal and mercuric iodide, (3) a rare-earth oxide ($Ln_2O_3$) and ammonium iodide, and (4) $LnI_3(H_2O)_x$ and ammonium iodide.[7] However, each of these methods has drawbacks. Method 1 must generally be conducted at very high temperature (>700 °C) which may not be readily accessible in many laboratories. Furthermore, a specialized apparatus is required because molten $LnI_3$ reacts with typical borosilicate glassware. A tungsten or molybdenum crucible must therefore be used and the apparatus must be carefully constructed to prevent overpressurization of the gas phase iodine used in the synthesis.[9,31] It is possible to prepare $LnI_3$ at lower temperatures from lanthanide "metal" powder and elemental iodine, but this relies on the presence of at least a catalytic amount of lanthanide hydride either prepared in advance of the $LnI_3$ synthesis or present as an impurity from the manufacture of the metal powder.[9] Method 2 requires the handling and separation of elemental mercury by distillation during the purification of the $LnI_3$ and mercury contamination can remain in the product.[31] The major shortcoming of methods 3 and 4 is the potential for the formation of LnOI that can occur if the temperature program of the synthesis is not carefully followed.[8,32] Method 4 has the additional drawback of requiring the initial synthesis of $LnI_3(H_2O)_x$ from the reaction between Ln metal or $Ln_2O_3$ and hydroiodic acid, a chemical which is inconvenient to obtain due to its potential for illicit use and the resulting restrictions on its sale.

In principle, the formation of LnOX contaminants (X = halide) may be avoided by using a rare-earth metal as the starting material rather than the $Ln_2O_3$ oxide. Indeed, the reaction of excess ammonium chloride with Ln metal has been previously shown by Meyer to afford rare-earth trichlorides of high purity.[8] In *Synthesis of Lanthanide and Actinide Compounds*, Meyer even suggested this method for the preparation of lanthanide triiodides: "with the realization that hydrogen iodide (even catalytically) does react much better [with rare-earth metals] than iodine itself, it appears that ammonium iodide might be an easily accessible alternative reagent."[9] In 1985, Meyer also reported the preparation of $(NH_4)_3YI_6$, which is potentially a precursor to $YI_3$ (vide infra), by the reaction between Y metal and ammonium iodide.[33] Despite this, and to our surprise, reports of the synthesis of rare-earth triiodides by this method in the peer-reviewed literature are scant. An unclassified report from the U.S. Atomic Energy Commission by Spedding et al. in 1959 indicated that yttrium triiodide may be prepared from yttrium metal and ammonium iodide at 700 °C under a stream of helium.[34] This method has the limitations described above for method 1. A 1995 study of the thermal decomposition of $(NH_4)_3YI_6$ briefly mentions that $YI_3$ can be prepared from yttrium metal and ammonium iodide, although preparative conditions were not given.[35] Highlighting the potential drawbacks of method 3, the authors of both of these reports assert that $YI_3$ cannot be prepared from $Y_2O_3$ and ammonium iodide, and Meyer also confirms this in his aforementioned 1985 report.[33]

We report here a general synthetic protocol for the preparation of donor-free rare-earth triiodides, $LnI_3$, by reaction of the corresponding Ln metal with excess ammonium iodide. The syntheses may be carried out in typical borosilicate glassware at large- or small-scale and at easily accessible temperatures. In the case of the small-scale synthesis, commercially available glassware may be used. We have successfully carried out this synthesis for the rare-earth elements Sc, Y, La, Pr, Nd, Gd, Dy, Ho, and Lu to demonstrate the efficacy and generality of the method.

## EXPERIMENTAL SECTION

**General Considerations.** All rare-earth metals (Sc, Y, La, Pr, Nd, Gd, Dy, Ho, Lu) were purchased as ingots of 99.9% purity from Stanford Advanced Materials and used without further purification. Ammonium iodide (99%, bottled under argon) was purchased from Oakwood Chemical and stored in an argon-filled glovebox until use. The solid−state reactions were all performed in borosilicate glassware under UHP (99.9999%) argon gas and heated using ThermoScientific Lindberg/Blue M electric furnaces of the appropriate diameter and length for the scale of the synthesis.

The purity of the lanthanide triiodide complexes was established through complexometric titrations in deionized water using xylenol orange tetrasodium salt, disodium EDTA, and hexamethylenetetramine as described previously.[36−38] These reagents were purchased from Sigma and used without further purification. In a typical experiment, ca. 20 mg of $LnI_3$ was dissolved in ca. 50 mL of deionized water. 1,3,5,7-Tetraazaadamantane (hexamethylenetetramine, ca. 0.5 g) was then added to this solution and dissolved with stirring. Xylenol orange indicator (ca. 0.5 mL of 0.1% solution) was added and the pH was adjusted to between 4 and 5 by addition of dilute HCl (3 M, ca. 0.5 mL). This solution was then titrated with a 3.79 mM solution of disodium EDTA dihydrate until the violet/pink color of the solution had vanished, leaving a persistent yellow color. In every case, a 1:1 ratio of metal to EDTA was assumed in determining the total metal content.

The purity and identity of the $LnI_3$ reagents were also demonstrated in subsequent reaction chemistry. For example, $Cp^*_2ScI$ was prepared by the overnight reaction between $ScI_3$ (0.61 g, 1.43 mmol) and KCp* (0.5 g, 2.87 mmol) in toluene at 100 °C in a yield (70%) and purity ($^1$H NMR) consistent with the literature.[39]

**Synthesis of Yttrium Triiodide (Small Scale).** Yttrium metal pieces (1.0 g, 11.2 mmol) and ammonium iodide (13.0 g, 90.0 mmol) were combined in air in a cylindrical borosilicate glass sublimation tube 30 cm in length and 3 cm in diameter with a 24/40 female ground glass joint at the top, Figures 1 and 2. The vessel was sealed using a 24/40 ground glass gas adapter equipped with a threaded Teflon valve (see Figure 1 for more detail). All ground glass joints were greased with a thin layer of Apiezon H grease. An inert atmosphere was established within the vessel by using a Schlenk line to evacuate ($10^{-3}$ Torr) and refill the vessel with argon 3 times. The apparatus was then kept under a gentle flow of argon and mounted vertically in an 800 W electric tube furnace (Lindberg/Blue M model TF55030A-1) with the top 2 cm of the tube raised above the furnace such that the vacuum grease would not liquefy during the reaction.


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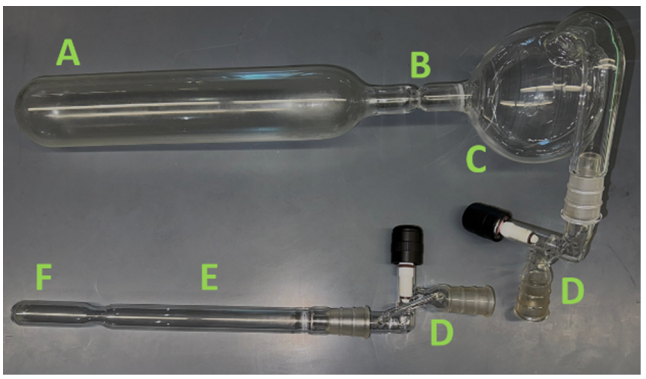


**Figure 1.** Glassware used in the large-scale (top) and small-scale (bottom) syntheses of lanthanide triiodides. (A) Reaction tube into which the rare-earth metal and are placed. (B) Tapered glass region which is scored to break the apparatus when the reaction is complete (note: the inner bore of the glass at this point should be no less than 10 mm to prevent becoming clogged during the sublimation). (C) 1 L receiving bulb into which sublimes under vacuum. (D) Teflon stoppered gas adapters (24/40 ground glass joints). (E) Upper section of sublimation tube into which $NH_4I$ sublimes during small-scale synthesis. (F) Lower section of sublimation tube into which the rare-earth metal and $NH_4I$ are placed in the small-scale synthesis. The constriction between E and F is not necessary for a successful synthesis.

The reaction mixture was then heated to 375 °C over 5 min. The evolution of a colorless gas (ammonia) was observed after ca. 1 h of heating at this temperature as indicated by a substantial increase in the rate of bubble formation in the oil bubbler. After 18 h, the apparatus was sealed and allowed to cool to ambient temperature. The vessel was then raised such that only the lowest quarter of the tube that contained the solid reaction mixture was in the furnace. The apparatus was evacuated ($10^{-3}$ Torr) and heated to 425 °C over a period of 5 min. The mixture was kept at this temperature for 3 h, after which time all of the ammonium iodide had sublimed into the upper portion of the tube and the vacuum manifold pressure had reached a steady minimum (ca. 10 mTorr). The apparatus was allowed to cool and was then sealed under vacuum and transferred to an argon-filled glovebox. The yttrium triiodide in the bottom of the vessel, Figure 2, was poured out, leaving behind the ammonium iodide which had adhered to the wall of the sublimation tube. The recovered pieces of the product were then ground to afford 4.6 g (9.8 mmol, 87%) of yttrium triiodide as a faintly gray powder. The total metal content of the material was assessed by complexometric titration using EDTA.[36−38] Anal. Calcd for $YI_3$: Y, 18.9. Found: Y, 18.1.

**Synthesis of Scandium Triiodide (Large Scale).** Scandium metal (7.25 g, 0.16 mol) was cut into pieces of ca. 0.5 g in mass and combined with ammonium iodide (187 g, 1.29 mol) in air in a borosilicate reaction vessel consisting of a reaction tube (7 cm diameter, 35 cm length) which was attached to a 1 L round receiving bulb equipped with a 24/40 female ground glass joint attached at a 90° angle to the reaction tube, Figure 1. The vessel was shaken until all of the reagents were collected in the bottom of the reaction tube. An inert atmosphere was then established within the vessel by using a Schlenk line to evacuate ($10^{-3}$ Torr) and refill with argon three times. The vessel was sealed with a threaded Teflon valve and placed horizontally in a 5400 W electric tube furnace (Lindberg/Blue M model HTF55342C). The vessel was then connected through a 24/40 ground glass adapter to a three-way gas adapter with the remaining two tubes connected to an argon gas cylinder and a mineral oil bubbler. The vessel was then opened to the argon gas flow and the flow rate was adjusted such that ca. 2 bubbles per second were observed in the mineral oil bubbler. The neck joining the reaction tube and the receiving bulb was wrapped in an electric heating tape and the reaction tube was wrapped with enough glass wool to fill the void space between the furnace and the apparatus. The heating tape around the neck of the vessel was then adjusted to a temperature of ca. 350 °C and the furnace was closed and slowly heated to 350 °C over a period of 45 min. After ca. 2 h at this temperature, the reaction between the metal and the ammonium iodide was observed to occur as evidenced by a substantial increase in the flow rate of gas (ammonia) through the mineral oil bubbler. After 18 h of heating at this temperature, the flow of argon was increased to maintain the argon atmosphere in the vessel during cooling and the apparatus was allowed to cool to room temperature. The vessel was evacuated to a pressure of $10^{-4}$ Torr using an oil diffusion pump. The reaction tube was then heated to 430 °C under dynamic vacuum to separate the ammonium iodide. Heating was continued until all volatile material had sublimed into the receiving bulb (about 2 h) to afford large pieces of a pale yellow/green solid that were loosely adhered to the wall of the reaction tube (see Note below). The vessel was then allowed to cool to ambient temperature and sealed under vacuum. The apparatus was then taken into an argon-filled glovebox, the neck was scored with a glass cutting tool, and the vessel was broken to separate the reaction tube from the receiving bulb. The contents of the reaction tube were

**Figure 2.** Images collected from the small-scale synthesis of yttrium triiodide. Left: the mixture of yttrium metal pieces and ammonium iodide before heating under argon. Center: large pieces of yttrium triiodide after the decomposition of $(NH_4)_3YI_6$ under reduced pressure. Right: Excess ammonium iodide collected in the upper part of the apparatus and completely separated from the yttrium triiodide.



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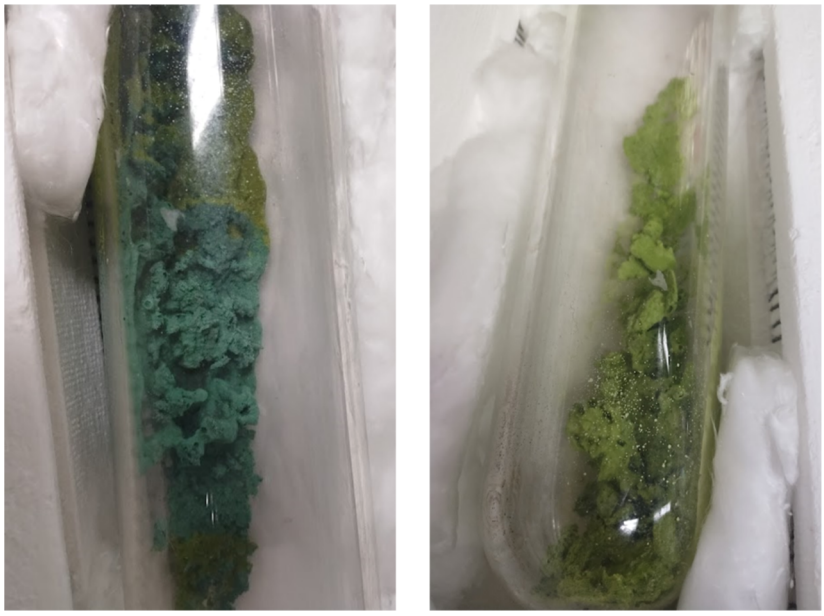

**Figure 3.** Images collected from the large-scale synthesis of neodymium triiodide. Left: A mixture of the putative $(NH_4)_3NdI_6$ (blue) and $NdI_3$ (green) showing the incomplete formation of the triiodide product. Right: the same reaction vessel after a full 2 h of heating at 430 °C under reduced pressure showing complete conversion to neodymium triiodide.

then collected to afford 60.74 g (0.12 mol, 72%) of scandium triiodide as a pale, yellow/green powder. The total metal content of the material was assessed by complexometric titration using EDTA.[36−38] Anal. Calcd for $ScI_3$: Sc 10.6. Found: Sc 10.6.

Note: In some instances, a dark gray or brown material was present in the reaction tube after the sublimation of colorless ammonium iodide was complete. In these cases, the vessel was allowed to cool to ambient temperature and, without breaking the tube, an additional 80 g portion of ammonium iodide was added under an argon atmosphere. The apparatus was then reheated to a temperature of 350 °C under an argon atmosphere as described above until all of the material in the reaction tube became yellow in color, usually 3 to 5 h. The sublimation step (430 °C, $10^{-4}$ Torr) was then repeated to afford scandium triiodide as a yellow/green solid. The necessity of this step has not been encountered in any of our syntheses of the remainder of the triiodides described here.

This large-scale procedure was also used successfully to prepare donor solvent-free triiodides of yttrium, lanthanum, praseodymium, gadolinium, dysprosium, holmium, and lutetium using the amounts and in the yields and purities described below.

**Yttrium Triiodide.** Following the procedure above, yttrium metal pieces (5.56 g, 0.063 mol) were treated with ammonium iodide (72.51 g, 0.50 mol) to yield $YI_3$ as a faintly gray powder (26.66 g, 0.057 mol, 90%). Anal. Calcd for $YI_3$: Y, 18.9. Found: Y, 19.4.

**Lanthanum Triiodide.** Following the procedure above, lanthanum metal pieces (20.89 g, 0.15 mol) were treated with ammonium iodide (174.32 g, 1.20 mol) to yield $LaI_3$ as a yellow/gray powder (76.03 g, 0.14 mol, 98%). Anal. Calcd for $LaI_3$: La, 26.7. Found: La, 27.0.

**Praseodymium Triiodide.** Following the procedure above, praseodymium metal pieces (5.44 g, 0.039 mol) were treated with ammonium iodide (44.74 g. 0.31 mol) to yield $PrI_3$ as a pale green powder (18.03 g, 0.035 mol, 89%). Anal. Calcd for $PrI_3$: Pr, 27.0. Found: Pr, 28.3.

**Neodymium Triiodide.** Following the procedure above, neodymium metal pieces (18.45 g, 0.13 mol) were treated with ammonium iodide (148.00 g, 1.02 mol) to yield $NdI_3$ as a green powder (64.49 g, 0.12 mol, 96%). Anal. Calcd for $NdI_3$: Nd, 27.5. Found: Nd, 27.6.

**Gadolinium Triiodide.** Following the procedure above, gadolinium metal pieces (10.63 g, 0.068 mol) were treated with ammonium iodide (78.38 g, 0.54 mol) to yield $GdI_3$ as a white/gray powder (31.27 g, 0.058 mol, 86%). Anal. Calcd for $GdI_3$: Gd, 29.2. Found: Gd, 29.9.

**Dysprosium Triiodide.** Following the procedure above, dysprosium metal pieces (6.2 g, 0.038 mol) were treated with ammonium iodide (44 g, 0.30 mol) to yield $DyI_3$ as a white/gray powder (20.0 g, 0.037 mol, 97%). Anal. Calcd for $DyI_3$: Dy 29.9; Found: Dy 28.6.

**Holmium Triiodide.** Following the procedure above, holmium metal pieces (4.22 g, 0.026 mol) were treated with ammonium iodide (29.7 g, 0.20 mol) to yield $HoI_3$ as a pink/gray powder (11.6 g, 0.021 mol, 83%). Anal. Calcd for $HoI_3$: Ho, 30.2; Found: Ho, 30.3.

**Lutetium Triiodide.** Following the procedure above, lutetium metal pieces (12.0 g, 0.069 mol) were treated with ammonium iodide (79.5 g 0.55 mol) to yield $LuI_3$ as a white/gray powder (36.6 g, 0.066 mol, 96%). Anal. Calcd for $LuI_3$: Lu, 31.5. Found: Lu, 31.3.

## RESULTS AND DISCUSSION

The synthesis of donor-free $LnI_3$ reported here is accomplished using the procedure in reaction 1. The synthesis is based on the preparation of $LnCl_3$ reported by Meyer, et al.,[8] eqs 2 and 3, which is a refinement of the synthesis of rare-earth trichlorides originally described by Reed, Hopkins, and Audrieth in 1935[40] and later in the inaugural volume of *Inorganic Syntheses* in 1939.[41]

$$\mathrm{Ln(metal)} + \mathrm{xsNH_4I} \xrightarrow[\text{(2) } 10^{-4}\text{ torr, 430 °C, 3 h}]{\text{(1) argon, 350 °C, 18 h}} \mathrm{LnI_3} \quad (1)$$

We have found that an 8-fold excess of ammonium iodide (8 equiv of $NH_4I$ to 1 equiv of Ln metal) gives the best yields of $LnI_3$ which ranged from 72% for $ScI_3$ to 98% for $LaI_3$. Complexometric titration of the isolated material found the metal content to be generally within 0.2−1% of the expected values, indicating the purity of the $LnI_3$ material. The purity of the $LnI_3$ batches was further demonstrated by numerous subsequent syntheses that provided inorganic and organometallic products in the expected yields.



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$$\mathrm{Ln(metal) + 6NH_4Cl} \xrightarrow[270-300\ ^\circ\mathrm{C},\ 10-12\ \mathrm{h}]{} \mathrm{(NH_4)_3LnCl_6 + 3NH_3 + 3/2H_2} \quad (2)$$

$$\mathrm{(NH_4)_3LnCl_6} \xrightarrow[350-400\ ^\circ\mathrm{C},\ 10^{-4}\ \mathrm{torr},\ 2\ \mathrm{h}]{} \mathrm{LnCl_3 + 3NH_4Cl} \quad (3)$$

The exact sequence of reactions in the $LnI_3$ preparation may differ from those in the $LnCl_3$ synthesis because the decomposition of $(NH_4)_3LnI_6$ could form $LnI_3$, gaseous ammonia, and hydrogen iodide, eq 4, rather than $LnI_3$ and $NH_4I$ in analogy to eq 3.[35] The reactants and products in eq 4 have been previously observed for yttrium to be in equilibrium at the temperatures involved in these reactions.[35] $NH_4I$ also has a different thermal profile than $NH_4Cl$[42] and decomposes into ammonia and hydrogen iodide between 175 and 430 °C.[35] However, as noted by Meyer, the synthesis of rare-earth triiodides from the metal can benefit from the presence of hydrogen iodide.[9] Formation of a small amount of iodine vapor was frequently observed inside the reaction vessel during the course of the reaction. This could be indicative of the presence of HI, which is in equilibrium with $H_2$ and $I_2$ at the temperatures used in these reactions.[43,44]

$$\mathrm{(NH_4)_3LnI_6} \xrightarrow[>230\ ^\circ\mathrm{C}]{} \mathrm{LnI_3 + 3NH_3(g) + 3HI(g)} \quad (4)$$

The small-scale reactions can be accomplished in a regular borosilicate tube of appropriate dimensions that is equipped with a 24/40 (or other) ground glass joint, Figure 1. The sublimation tube must be of sufficient length that the excess ammonium iodide neither clogs the gas adapter nor deposits in such a thick layer in the upper part of the tube that the $LnI_3$ becomes contaminated upon removal from the vessel. Images of the small-scale preparation of yttrium triiodide are shown in Figure 2.

The large-scale reaction uses bespoke apparatus assembled in the UCI Glass Shop as shown in Figure 1 and described in the Experimental Section. Figure 3 shows both incomplete and complete large-scale reactions for $NdI_3$. These images demonstrate the large pieces of $LnI_3$ material that are formed when using Ln metal pieces. This is a benefit of using larger metal pieces as starting material, as these can be easily separated by hand from any residual ammonium iodide that may inadvertently become mixed with the desired product.

While the basic experimental procedure is straightforward, there are several practices which lead to a high yield of highly pure product. First, we have achieved the highest yields using rare-earth metal chunks or pieces rather than filings or powder. The lower surface area of rare-earth metal pieces serves to reduce the potential for surface oxidation of the metal and the subsequent formation of oxide byproducts during the reaction. Next, the first stage of the reaction must be carried out under an atmosphere of inert gas. Here, argon has been used. Attempts to prepare $LnI_3$ from several rare-earth metals and ammonium iodide under vacuum were unsuccessful in our hands. In addition, the filling of any void space between the apparatus and the furnace with glass wool is necessary to assist in maintaining a uniform temperature in the glassware. In cases where there was not sufficient insulation, $NH_4I$ was observed to deposit on colder areas of the glass and the desired $LnI_3$ product was not obtained. It should also be noted that while an oil diffusion pump is typically used in this laboratory during the final stage of the large-scale synthesis of $LnI_3$, comparable yields and purities have been achieved using more typical and widely available mechanical pumps when performing these reactions at small scale.

## CONCLUSION

Although the synthesis of donor-free rare-earth triiodides $LnI_3$ by the reaction between ammonium iodide and the corresponding metal at 700 °C has been described for yttrium since 1959[34] and lower temperature routes were proposed in 1991,[9] a preparative route using commercially available equipment has not been reported until now. Given the unusual complexes that have been accessed through the use of these triiodides as starting materials,[25−29] we hope that the preparative methods described here will lead to the development of future groundbreaking exploratory chemistry.

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### Notes

The authors declare no competing financial interest.

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