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Aluminum Hydride: A Reversible Material for Hydrogen Storage

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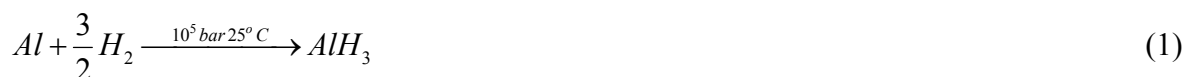
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Hydrogen storage is one of the greatest challenges for implementing the ever sought hydrogen economy. Here we report a novel cycle to reversibly form high density hydrogen storage materials such as aluminium hydride. Aluminium hydride (AlH₃, alane) has a hydrogen storage capacity of 10.1 wt% H₂, 149 kg H₂/m³ volumetric density and can be discharged at low temperatures (< 100 °C).^{1,2} However, alane has been precluded from use in hydrogen storage systems because of the lack of practical regeneration methods; the direct hydrogenation of aluminium to form AlH₃ requires over 10⁵ bars of hydrogen pressure at room temperature and there are no cost effective synthetic means. Here we show an unprecedented reversible cycle to form alane electrochemically, using alkali alanates (e.g. NaAlH₄, LiAlH₄) in aprotic solvents. To complete the cycle, the starting alanates can be regenerated by direct hydrogenation of the dehydrided alane and the alkali hydride being the other compound formed in the electrochemical cell. The process of forming NaAlH₄ from NaH and Al is well established in both solid state and solution reactions.³⁻⁷ The use of adducting Lewis bases is an essential part of this cycle, in the isolation of alane from

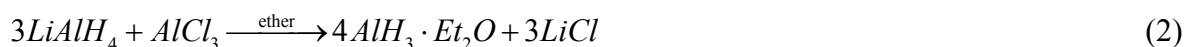
the mixtures of the electrochemical cell. Alane is isolated as the triethylamine (TEA) adduct and converted to pure, unsolvated alane by heating under vacuum.

Discovering efficient and economic methods for storing hydrogen is critical to realizing the hydrogen economy. The US Department of Energy (DOE) is supporting research to demonstrate viable materials for on-board hydrogen storage. The DOE goals are focused on achieving a storage system of 6 mass% H₂ and 45 kg H₂/m³ by 2010 and developing a system reaching 9 mass% H₂ and 81 kg H₂/m³ by 2015.⁸

Researchers worldwide have identified a large number of compounds with high hydrogen capacity that can fulfill these gravimetric and volumetric requirements. Unfortunately, the majority of these compounds fail to fulfill the thermodynamic and kinetic requirements for on-board storage systems. Alane has the gravimetric (10.1 mass% H₂) and the volumetric (149 kg H₂/m³) density needed to meet the 2010 DOE goals. In addition, rapid hydrogen release from alane can be achieved using only the waste heat from a fuel cell or a hydrogen internal combustion engine.⁹ The main drawback to using alane in hydrogen storage applications is unfavorable hydriding thermodynamics. The direct hydrogenation of aluminium to alane requires over 10⁵ bars of hydrogen pressure at room temperature as shown in equation(1). This impracticality of using high hydriding pressure has precluded alane from being considered as a reversible hydrogen storage material.



The typical formation route for alane is through the chemical reaction of an alanate compound (e.g. - LiAlH₄) with aluminium chloride in diethyl ether:



This reaction yields dissolved alane etherate, $\text{AlH}_3 \cdot \text{Et}_2\text{O}$, and precipitates lithium chloride. Alane can then be separated from the ether by heating *en vacuo*.^{2, 10-12} The synthesis of AlH_3 by this methods also results in the formation of alkali halide salts such as LiCl . The formation of these salts becomes a thermodynamic sink because of their immense stability. For a cyclic process, lithium metal must be recovered from lithium chloride by electrolysis of a LiCl/KCl melt at $600\text{ }^\circ\text{C}$ and costing at least -429 kJ/mol of energy equivalent to the heat of formation and heat of fusion of LiCl .¹³ In addition, -117 kJ/mol is required to regenerate LiAlH_4 . The tremendous amount of energy required to regenerating AlH_3 from spent aluminium and the alkali halide makes this chemical synthesis route impractical for a reversible AlH_3 storage system.

For these reasons, our research focused on developing a novel cycle to cost effectively regenerate AlH_3 under practical conditions. The cycle uses electrolysis and catalytic hydrogenation of products to avoid both the high hydriding pressure for aluminium and the formation of stable by-products such as LiCl . The cycle, shown in Figure 1, utilizes electrochemical potential to drive the formation of alane and alkali hydride from an ionic alanate salt (e.g. sodium alanate, NaAlH_4). The starting alanate is regenerated by reacting spent aluminium with the byproduct alkaline hydride in the presence of titanium catalyst under moderate hydrogen pressure. In comparison to chemical methods, using the electrochemical cycle should in principle cost the heat of formation of NaAlH_4 , which is -115 kJ/mol .

The electrolysis reaction is carried out in an electrochemically stable aprotic polar solvent (e.g. THF). NaAlH_4 dissolved in polar solvent THF forming an ionic solution ($\text{Na}^+/\text{AlH}_4^-/\text{THF}$) was used as an electrolyte. Though not directed at the regeneration of alane, elaborate research and extensive studies on the electrochemical properties of this

type of electrolyte ($\text{Na}^+/\text{AlH}_4^-/\text{THF}$) has been reported.^{14, 15} Although attempts in the past were made to make alane electrochemically,^{16, 17} none of these attempts has shown isolated and characterized alane product. Using the reversible cycle described here alane was electrochemically produced, isolated, and characterized.

Thermodynamic calculations were made to determine the reduction potentials for possible electrochemical reactions with NaAlH_4 in an aprotic solution (THF) with an aluminium electrode. From the half reaction potentials of all possible reactions in solution (shown in the supplementary information), the cell voltage for alane formation was calculated and a theoretical cyclic voltammogram was constructed (see Figure 2). AlH_3 formation is confirmed by observing the rapid formation and precipitation of the insoluble $\text{AlH}_3 \cdot \text{TEDA}$ complex when triethylenediamine (TEDA) is added to the electrochemical cell. $\text{AlH}_3 \cdot \text{TEDA}$ was identified using Powder XRD. Two separate reaction mechanisms can produce alane at the aluminium electrode. One mechanism is the oxidation of the alanate ion to produce alane, an electron, and hydrogen as shown in equation (4):



The other possible electrochemical reaction is having AlH_4^- ion react with the aluminium anode to form alane. In this reaction route, the evolution of hydrogen is suppressed and the reaction is expected to consume the Al electrode as in equation(5).



Experimental observations confirm that the anode is indeed consumed as shown in Figure 3.

Once the correct operating voltage for the formation of alane was calculated, constant voltage experiments were performed. During these experiments, the current was steady and increased slightly with time. The electrochemical production of alane is not slowed by the formation of AlH_3 . In contrast to previous reports, no perception of alane is observed and the alane produced by our method is completely dissolved in solution as a THF adduct.¹⁷ During electrolysis, dendritic material was deposited on the platinum counter electrode. This material was collected and determined to be Na_3AlH_6 from XRD data.

Experiments were conducted to determine the feasibility of plating sodium at the platinum cathode as an alternative to NaH formation in the fueling cycle. The platinum cathode and aluminium anode potentials were -2.89 V and -1.31 V respectively. Plating of Na metal was observed at the cathode while alane was produced at the aluminium anode. Reacting sodium with aluminium from used alane under pressurized hydrogen will regenerate the starting material NaAlH_4 leading to a reversible cycle.

In addition to determining the electrochemical processes for producing AlH_3 , recovering AlH_3 from the solution is a major step of this cycle. The separation of alane from $\text{AlH}_3\cdot\text{Et}_2\text{O}$ is well established and affords pure AlH_3 .¹⁰⁻¹² However, separation of the $\text{AlH}_3\cdot\text{THF}$ adduct is more complicated because it decomposes when heated under vacuum. Therefore, adducts such as triethylamine (TEA) were added to the reaction product to stabilize the alane during purification. Adduct free alane is recovered by heating the neat liquid $\text{AlH}_3\cdot\text{TEA}$ *en vacuo*.

Alane recovered from the electrochemical cells was characterized by powder X-ray diffraction, Raman spectroscopy, and thermal gravimetric analyzer (TGA). Powder X-ray diffraction patterns data for two different separation methods are shown in Figure 4.

Heating the $\text{AlH}_3 \cdot \text{THF}$ product after removing left over starting materials (Figure 4a) showed the presence of a large amount of aluminum as well as α -alane. Separation using the TEA (Figure 4b) yields only α -alane. The unrefined unit cell parameters from indexing of this pattern were $a = 4.446 \text{ \AA}$ and $c = 11.809 \text{ \AA}$. Based on the systematic absences, the space group was assigned as R-3c and is consistent with α -alane.¹⁸

Raman spectra and TGA data collected for AlH_3 isolated from the electrochemical cell are available in the supplementary information. Raman modes present at 510, 715, 1050, and 1515 cm^{-1} are consistent with the literature for α -alane.¹⁹ The TGA weight loss onset temperature was identical to that of a standard sample obtained from Dow analyzed on the same equipment.

In conclusion, we have demonstrated the feasibility of a recyclable and reversible hydrogen storage material. We have used the nature of the alane molecule and its tendency to form complexes to our advantage helping in the isolation of a pure, highly crystalline compound. This generation cycle of alane provides a clean facile route to a high capacity H_2 storage material while avoiding unrecoverable thermodynamic costs.

Methods

Electrochemical Preparation of AlH_3 . Cell preparation and electrochemical experiments were performed in an argon environment using traditional air sensitive techniques. Electrochemical alane generation experiments were performed using an air-tight three electrode electrochemical cell. The working electrode was an aluminum sheet. Prior to experiments, the aluminum electrode was sanded and rinsed with acetone in an inert environment to remove any oxide layer on the electrode. A “leak-free” 3M KCl Ag/AgCl

reference electrode (Warner Instruments) was used to measure the potential of the working electrode. A platinum foil counter electrode was used. The electrolyte was 1.0M NaAlH₄.

Electrochemical experiments were performed with a CH Instruments 660C potentiostat. After assembly of the cell and before cell characterization or bulk electrolysis, the working electrode was held at a constant potential of +1.3 V vs. SHE. Cyclic voltammograms were performed between -3.0 V and -1.0 V vs. SHE. Bulk electrolysis experiments were carried out at -1.5 V vs. SHE.

Chemical Separation and Isolation of Alane. The product solution was decanted from the cell apparatus and filtered. An equal volume of pentane was added to this solution and stirred overnight. The resulting precipitate was filtered on a frit over celite. To the filtrate, 100 mL of a 4:1 mixture of triethylamine and pentane was added, stirred overnight and filtered over celite. The solvent was removed *en vacuo* leaving a viscous clear liquid. This liquid was heated at 65°C in a sand bath for 2 hours to remove the remaining triethylamine. Approximately 15 mL of benzene was added to the flask and stirred. The solution was placed under vacuum and heated again at 65°C. After another 2 hours the product rendered was a fine blue grey powder. This powder was rinsed with 3 times with 20 mL portions of THF and dried under vacuum.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Contribution of Authors R.Z. was responsible for the idea of the reversible cycle of the regeneration of alane using organic solvent and complex hydride salt and directing the project.

B.L.G-D. was responsible for the design of electrochemical cells and experiments as well as the analysis of experimental results. She was also responsible for the coordination of laboratory operations and interpretation of analytical experiments.

C.S.F. was responsible for chemical isolation and wet chemistry treatment of the electrochemical cells. He has also assisted in conducting and interpreting powder x-ray diffraction data.

R.Z., B.L.G-D and C.S.F. were responsible for writing the manuscript.

A.S. helped in designing several parts of the apparatus, conducted experiments, and characterized resultant products of the electrochemical experiments.

J.R.G. contributed to experimental design and execution, as well as data analysis and interpretation.

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Non-Aqueous Solution Regeneration Cycle

(LiAlH_4 , KAlH_4 or NaAlH_4) in (THF or Ether)

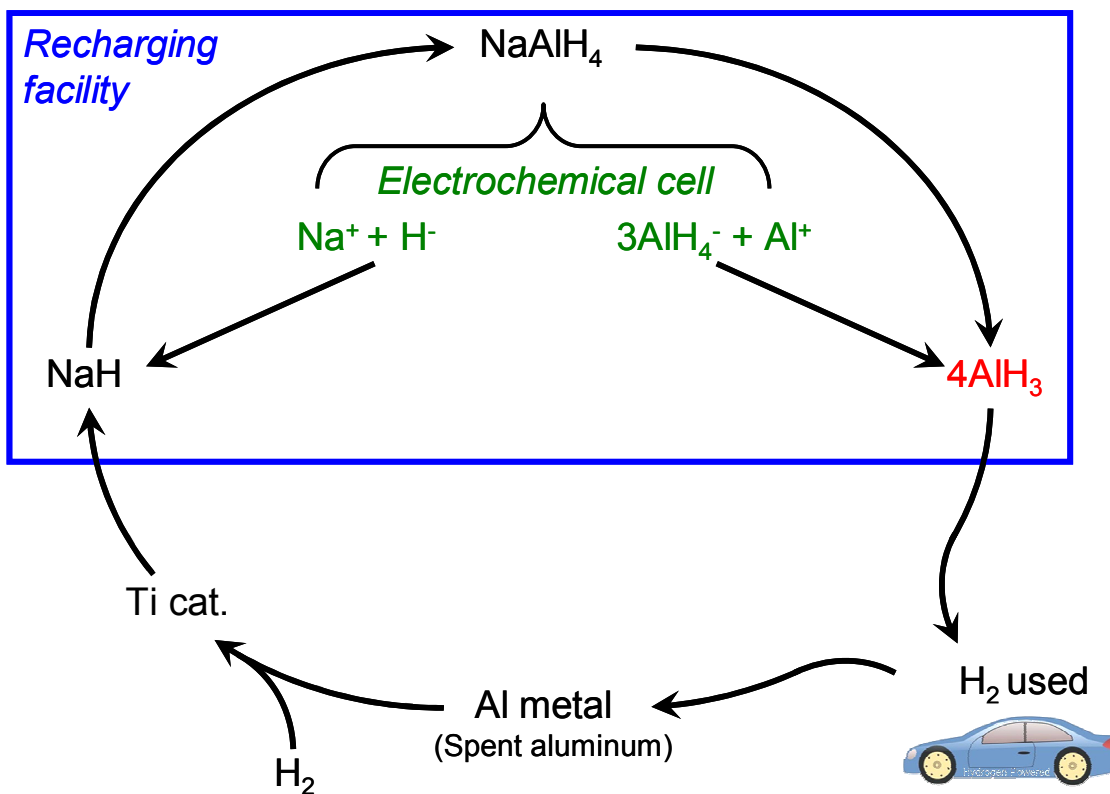


Figure 1. Proposed reversible fuel cycle for alane. All components of the electrochemical process can be recycled to continually afford a viable solid state storage material for the hydrogen economy.

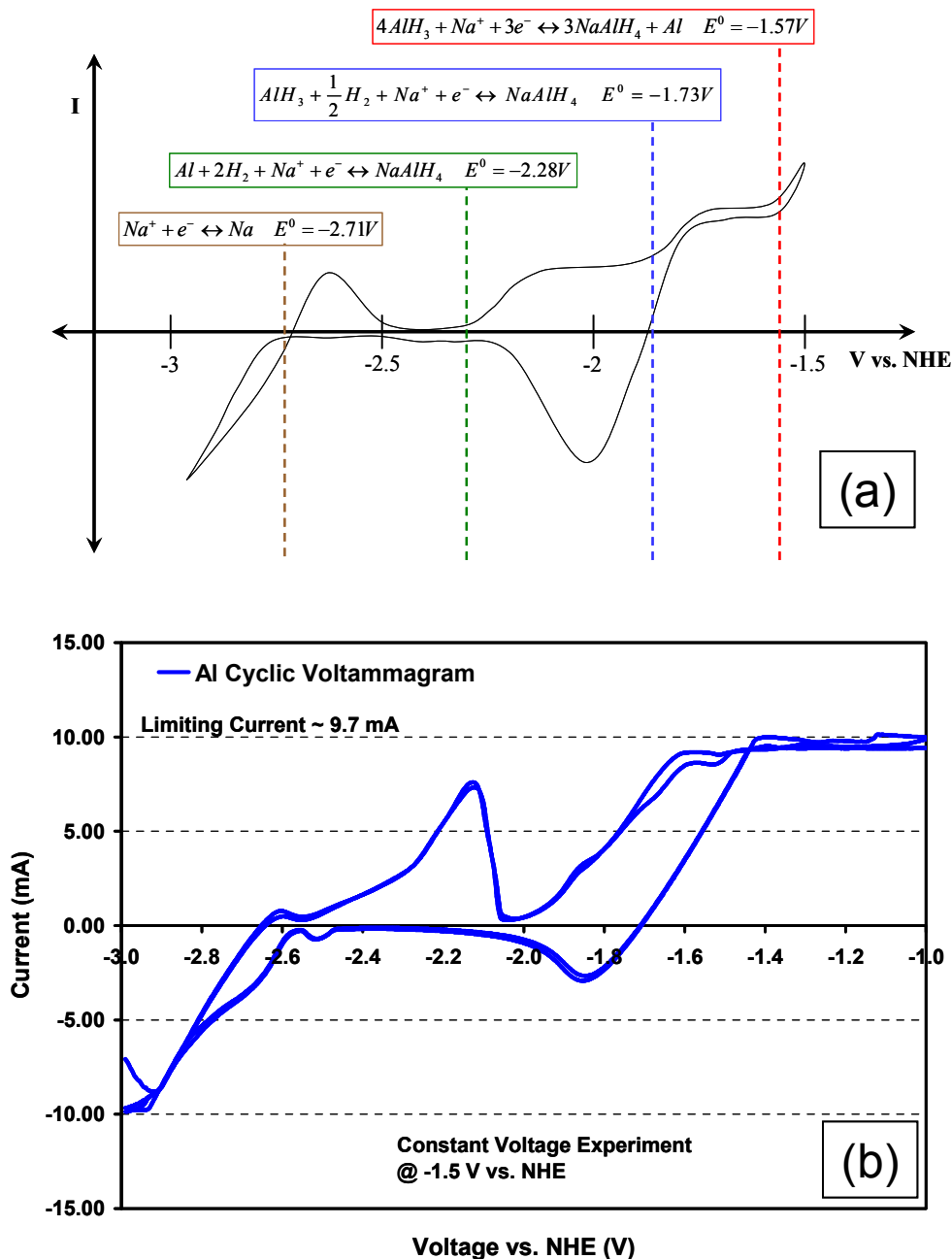


Figure 2. Experimental and hypothetical cyclic voltammograms for the electrochemical formation of alane. (a) A hypothetical cyclic voltammogram was formulated from the equilibrium potential data for possible reactions and the anticipated state of each species generated. (b) Bulk electrolysis experiment at an aluminum wire electrode for a cell containing a 1.0 M solution of NaAlH₄ in THF at

25°C. The CV shows an unexpected reduction current above the -2.71 V equilibrium potential for the Na/Na⁺ reaction. This current can be explained by the generation of Na₃AlH₆. The onset potential of the NaAlH₄ decomposition reaction to Al is shifted to approximately -2.05 V vs. SHE. The over 250 mV shift in potential indicates a high overpotential for the decomposition reaction. A limiting current of 9.7 mA was reached near -1.5 V.



Figure 3. The aluminum electrode is consumed during the reaction as predicted from experimental modeling. When the appropriate voltage is applied, alane is produced at the anode. Two separate reaction mechanisms can produce alane at an aluminium electrode. The desired half-reaction at the anode for alane production is: $AlH_4^- \rightarrow AlH_3 + \frac{1}{2}H_2 + e^-$. This reaction mechanism has the lower reduction potential and thus requires less energy input to drive the oxidation in an electrolytic cell. The second mechanism for alane production is by the equation: $3AlH_4^- + Al^+ \rightarrow 4AlH_3$ (in THF). In this mechanism the aluminium electrode is consumed, which is consistent with experimental observations.

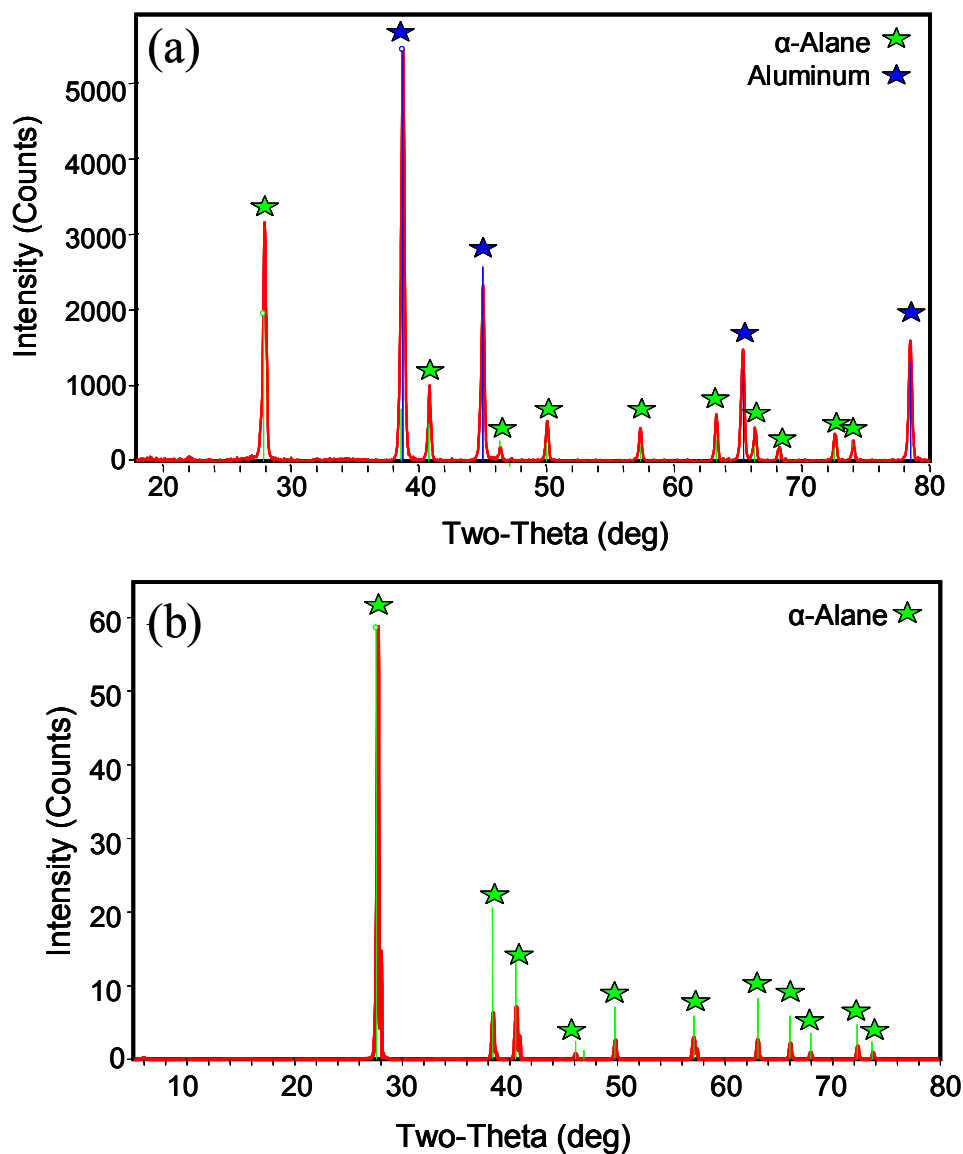


Figure 4. XRD patterns for products recovered from an electrochemical cell. (a) Alane separated from reaction mixture as the THF adduct. When heated under vacuum to remove THF, the solid partially decomposes, losing hydrogen and affording aluminum. (b) Alane separated using triethylamine to stabilize the adduct, prevent polymerization, and increase yield.