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Divergent Syntheses of Copper−Indium Bimetallic Single-Source Precursors via Thiolate Ligand Exchange

Chivin Sun,[†] Richard D. Westover,[†] Kelsey R. Margulieux,[†] Lev N. Zakharov,[‡] Andrew W. Holland,*[,†] and Joshua J. Pak*[,†]

[†]*Department of Chemistry, Idaho State University, Pocatello, Idaho 83209, and*
[‡]*Department of Chemistry, University of Oregon, Eugene, Oregon 97403*

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Several copper−indium bimetallic single-source precursors (SSPs **2**−**9**) have been prepared efficiently by exchange reactions of $(Ph_3P)_2CuIn(SEt)_4$ (**1**) with protic ligands. This divergent approach has been successfully applied on multigram scales to produce nearly quantitative yields of known and newly reported SSPs. The former group features the previously difficult target $(Ph_3P)_2CuIn(SePh)_4$ (**2**), and the latter includes $(Ph_3P)_2CuIn(SEt)_2(SePh)_2$ (**3**), the first SSP to incorporate both sulfur and selenium within a single copper−indium bimetallic complex.

Many binuclear inorganic systems have attracted interest for their unique magnetic,[1−3] optical,[4] and semiconducting properties.[5−8] In recent years, there have been several reports of the preparation of chalcopyrite $CuInS_2$ materials through the decomposition of molecular copper−indium complexes, often referred to as single-source precursors (SSPs), by conventional thermolysis,[9−14] photolysis,[15] and microwave irradiation.[16,17] Each SSP molecule contains the requisite elements to form $CuInS_2$ semiconductor materials, offering a unique level of control over product stoichiometry during the decomposition process. Species of the form $(Ph_3P)_2Cu(\mu\text{-}ER)_2M(ER)_2$ (where E = S or Se, M = In or Ga, and R = alkyl or aryl) have shown particularly great promise for the controlled formation of corresponding nanoparticles.[9−22]

Hirpo et al. first reported I−III bimetallic SSPs in 1993,[18] and in 2003, Banger et al. synthesized a series of such SSPs, each prepared on a 30-g scale, by parallel synthetic pathways.[11] Our own efforts to prepare large quantities of related SSPs by reported procedures have been hampered by irreproducibility, a lack of generality, and long reaction times. In order to overcome these obstacles, we recently developed an effective alternative approach that affords $(Ph_3P)_2Cu(\mu\text{-}SEt)_2In(SEt)_2$ (**1**) in 94% yield on a 500-g scale.[20] The amount of $CuInS_2$ required for device research and development[23−30]

*To whom correspondence should be addressed. E-mail: hollandr@isu.edu (A.W.H.), pakjosh@isu.edu (J.J.P.).

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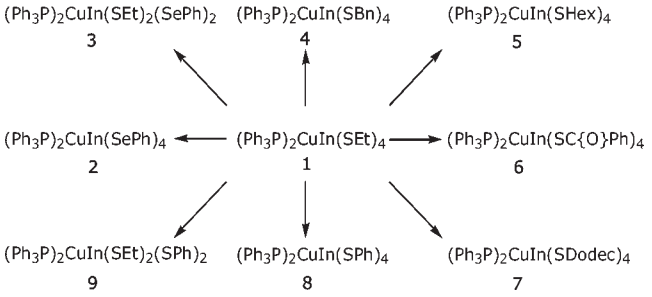
Scheme 1. SSP Syntheses from **1**



demands a readily scalable synthetic method for the production of SSPs, particularly given that 1 g of **1** yields a maximum of 0.25 g of $CuInS_2$.

The flexibility to prepare *diverse* SSPs on large scales is also important because subtly varied SSPs differ in important qualities such as decomposition temperature, air sensitivity, and solubility. However, access to a wide variety of SSPs has been limited by time-consuming or inefficient synthetic procedures, particularly for more elusive targets such as I−III selenium complexes.[21] Given the relative cost-effectiveness and convenience of preparing **1**, we sought to synthesize the selenium analogue and other similar SSPs by a divergent approach, exploiting simple exchange of the ethanethiolate ligands in **1** with protic reagents. Herein, we report the application of this method to prepare several Cu−In bimetallic SSPs of the form $(Ph_3P)_2Cu(\mu\text{-}ER)_2In(ER)_2$ in nearly quantitative yields.

Complex **1** was synthesized by employing our reported method[20] and used to prepare SSPs **2**−**9** in the single-step transformations shown in Scheme 1.

For example, complex **1** was treated with 4 equiv of PhSeH in dried benzene for less than 1 h at room temperature under anaerobic conditions, and solvent and ethanethiol were removed under vacuum to afford $(Ph_3P)_2Cu(\mu\text{-}SePh)_2Cu(SePh)_2$ (**2**) in 97% isolated yield. This marks a considerable improvement over the most successful published approach, by which a 5-day multistep procedure reportedly affords **2** in only 59% yield.[21] The use of **1** as a synthetic intermediate in the preparation of **2** allows relatively benign and inexpensive sulfur ligands to be utilized until the last step of the synthesis, minimizing the use of toxic and expensive selenium compounds and generating little or no selenium waste.[31,32] Furthermore, it is worth noting that the benzene solvent and ethanethiol may be easily recycled for future use. Under analogous reaction conditions, SSPs **3**−**9**, including previously unreported complexes **3**, **4**, and **9**, were prepared in 98−99% isolated yields. To test the scalability of this method, complex **8** was produced on a 500-g scale in 98% yield, in a reaction time of less than 1 h.

This exchange pathway provides facile access to a diverse array of SSPs boasting a variety of advantageous properties. For example, while **1** is slightly moisture-sensitive and thus must be stored under an inert atmosphere or used quickly, derivatives **4** and **8** are very robust and exhibit little or no decomposition even after months of normal storage. Solid SSP **1** can easily be converted to liquid SSPs **5** and **7**, which exhibit improved solubility in common nonaromatic hydrocarbon solvents.

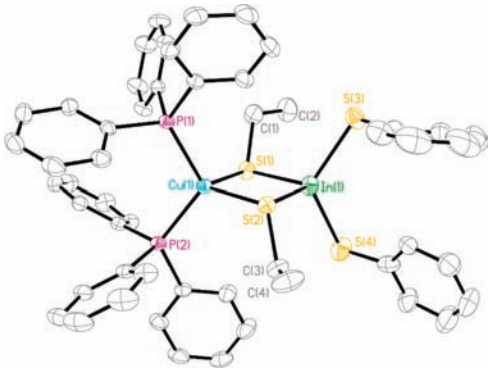


Figure 1. X-ray crystal structure of **9** with 30% probability thermal ellipsoids depicted. Hydrogen atoms are omitted for clarity. Complex **9** has a four-membered $Cu(\mu\text{-}S)_2In$ cycle that is planar within 0.017 Å. Selected bond lengths (Å) and angles (deg): Cu(1)−P(1) 2.2739(9), Cu(1)−S(1) 2.4554(10), Cu(1)−S(2) 2.4244(10), In(1)−S(1) 2.4739(10), In(1)−S(2) 2.4961(9), In(1)−S(3) 2.4423(12), In(1)−S(4) 2.4216(12), S(1)−C(1) 1.852(5); P(1)−Cu(1)−P(2) 114.00(3), S(1)−Cu(1)−S(2) 99.16(3), Cu(1)−S(1)−In(1) 81.94(3), S(3)−In(1)−S(4) 119.39(5).

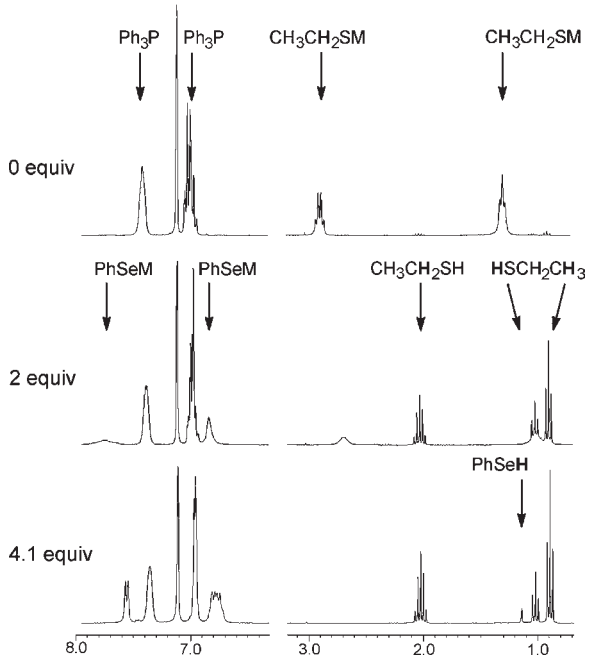


Figure 2. ^1H NMR (C_6D_6) spectra showing the titration of **1** with PhSeH.

This approach has also allowed for the formation of unsymetrically substituted SSPs from complex **1**. The treatment of **1** with alkyl- and arylthiols in less than 4 equiv affords mixed-thiolate complexes, and the product of exchange of **1** with 2 equiv of PhSH, $(Ph_3P)_2Cu(\mu\text{-}SEt)_2In(SPh)_2$ (**9**), was characterized by X-ray crystallography (Figure 1). In addition to the steric factors driving the larger phenyl substituents to the terminal positions, the electronic preference of this system appears to direct more electron-rich ligands to bridging positions,[20] leading to regioselective exchange processes.

This method also produced the first reported I−III−VI SSPs to contain both sulfur and selenium in a single complex; the reaction of **1** with 2 equiv of PhSeH produced $(Ph_3P)_2CuIn(SEt)_2(SePh)_2$ (**3**) in nearly quantitative yield. This complex may allow for the production of $CuInSe_2$ without

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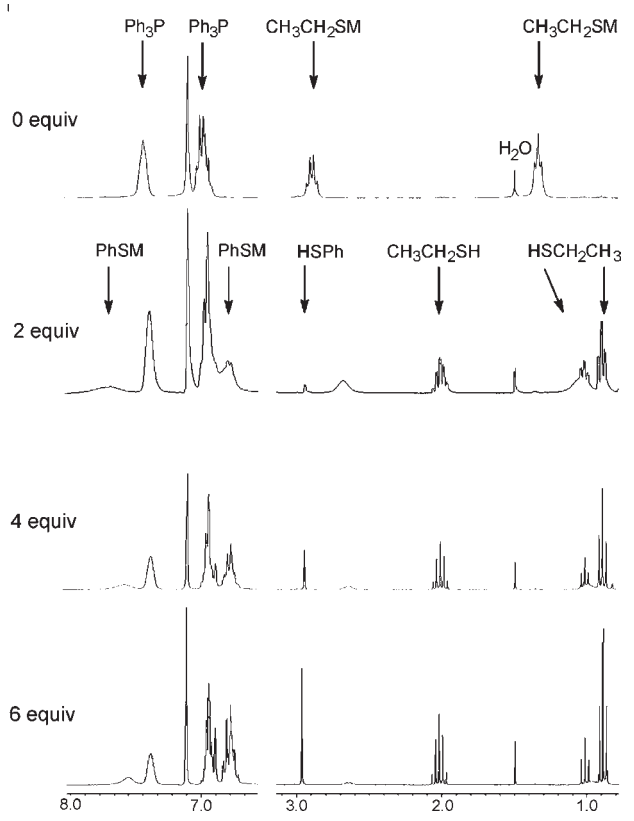

Figure 3. ^{1}H NMR (C_6D_6) spectra showing the titration of **1** with PhSH.

generation of selenium byproducts, and mixed substitution, in general, may modify the controlled decomposition process. The use of all of these SSPs to prepare CuIn(S/Se)$_2$ nanomaterials is currently under investigation.

To better understand the ligand-exchange process, titration studies were conducted by the addition of 2−4.1 equiv of PhSeH (Figure 2) or 2−6 equiv of PhSH (Figure 3) to complex **1**. The ^{1}H NMR resonances of the ethanethiolate groups in **1** appear at δ 1.39 and 2.98 ppm in benzene-d_6. As increasing amounts of PhSeH were added, new resonances corresponding to free $HSCH_2CH_3$ and to bound phenyl selenide (**2**; MSePh, δ 6.8 and 7.6 ppm) appeared immediately upon mixing. In addition, the disappearance of the starting material and the appearance of ethanethiol resonances confirmed the loss of bound ethanethiolate. The exchange of ethanethiolate groups with PhSeH appears to proceed to completion at room temperature; after the addition of just over 4 equiv of PhSeH, all bound ethanethiolate resonances had been quantitatively replaced by free ethanethiol peaks and the signals of **2**.

The titration of **1** with PhSH was conducted in an analogous manner (Figure 3). As increasing amounts of PhSH were added, free $HSCH_2CH_3$ and MSPh gradually appeared, and the resonances corresponding to $MSCH_2CH_3$ diminished correspondingly. Even upon the addition of 4 equiv or more of PhSH, however, small amounts of $MSCH_2CH_3$ and PhSH remained, indicating that the exchange is limited by equilibrium. Nonetheless, the equilibrium can be driven to complete formation of **8** without the addition of excess PhSH by simple removal of free ethanethiol (bp 35 °C) under vacuum, allowing the quantitative incorporation of PhSH (bp 169 °C).

These two examples illustrate that the exchange can be driven to completion either by the thermodynamics of the system or by the selective removal of the product thiol under vacuum. While the relative binding affinities of different ligands are currently under investigation, exploitation of boiling point differences alone enables the incorporation of a wide variety of groups. By this technique, quantitative exchange with $PhCH_2SH$, $CH_3(CH_2)_5SH$, Ph{O}CSH, and $CH_3(CH_2)_{11}SH$ has been achieved.

In summary, simple protic exchange processes offer facile access to a large variety of exotic SSPs in one-step, high-yield reactions from one readily accessible synthon complex. This approach both offers a route to novel SSPs and replaces much more demanding direct procedures for the synthesis of selenium complexes. Previously, we have reported the synthesis of **1** in a large scale with 94% yield; consequently, overall yields for the synthesis of selenium complexes **2** and **3** are well over 90%. Even more dramatically, this approach decreases the quantities of selenium reagents required and minimizes the quantity of selenium waste produced. In addition, the exchange of fewer than 4 equiv of thiol or selenol affords the first unsymmetrical SSPs in this series. These exchange reactions have been shown to be easily adapted to large scales, and further investigations of the details of these reactions and their novel products are underway.

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Supporting Information Available: Experimental procedures, crystallographic data of **9** in CIF format, and characterization of **2**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.