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Room-Temperature Synthesis of $(LiMo_3Se_3)_n$ and the Determination of the Relative Reduction Potential of *tert*-Butyllithium

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A room-temperature synthesis of the inorganic polymer $(LiMo_3Se_3)_n$ by reductive intercalation is described. Instead of the traditional preparation by ion exchange at approximately 460 °C, $(LiMo_3Se_3)_n$ was prepared by treating $(InMo_3Se_3)_n$ with a 10-fold excess of *tert*-butyllithium in pentane/toluene at 23 °C for 1 week. While there is some reductive attack of the $(Mo_3Se_3^-)_n$ chain core, reductive intercalation of lithium competed successfully to form $(LiMo_3Se_3)_n$, as confirmed by X-ray powder diffraction, TEM, SEM microprobe, and product solubility in polar solvents. Proton NMR spectroscopy was used to confirm that *tert*-butyllithium reacts by a radical disproportionation process, providing lithium atoms that diffuse into the interstitial spaces of the inorganic polymer matrix. The nonreversible reduction potential of *tert*-butyllithium was estimated at 0.83 V above Li/Li^+ by preparation of the reference solid $Li_{0.37}WO_2$. Knowledge of this potential has allowed us to assign *tert*-butyllithium a relative position within the relative hierarchy of organolithium reagents commonly used in the reductive intercalation of solids.

Introduction

Interest in organic and inorganic low-dimensional solids has increased steadily over the past decade, as part of a search for new materials displaying novel physical properties including anisotropic conductivity, superconductivity, nonlinear optical phenomena, or piezoelectric behavior.[1] Parallel to this search for new materials is the impetus to develop low-temperature synthetic methods, popularly known as "chimie douce" or "soft chemistry", methods. Soft chemical strategies typically encompass a range of low-temperature solution techniques, including coprecipitation, decomposition or reaction of organometallic precursors,[2a] reactions in critical fluids,[2b,c] and the intercalation or deintercalation of solids that permit rapid diffusion of one species.[2d] These techniques bypass traditional high-temperature (>400 °C) synthetic strategies and can yield metastable compounds with elements in unusual oxidation states. To this end, we have examined soft chemical synthetic routes to the metastable linear chain compound, $(LiMo_3Se_3)_n$.

In 1980, Potel et al.[3] described a series of metallic linear chain compounds, $(MMo_3X_3)_n$ (M = a monovalent main group metal, X = Se, S). The structure of $(MMo_3X_3)_n$ is based on the condensation of octahedral clusters of molybdenum face capped by chalcogen atoms, to form linear $(Mo_3X_3^-)_n$ chains with interstitial M monovalent cations, as shown in Figure 1. The structure may also be viewed as antiprismatically stacked triangles of Mo, with edge-bridging chalcogen atoms. These compounds are one member of the family of materials generally known as the Chevrel phases,[4] with the general chemical composition of $M_xMo_{3n}Se_{3n+2}$, for $n \geq 2$.

These linear chain compounds display a unique variety of physical properties including highly anisotropic conductivity, superconductivity, and semiconducting behavior at low temperatures, depending on the identity of the interstitial cation sitting between the chains.[5-8] Perhaps the most interesting physical property arises when lithium is the interstitial cation. When $(LiMo_3Se_3)_n$ is treated with highly polar solvents including propylene carbonate, NMF, DMSO, or water, the compound dissolves to form burgundy/red solutions that are highly absorbing ($\epsilon = 10^5$ M^{-1} cm^{-1}).[9] Indefinitely stable if kept oxygen free, these solutions have been shown to consist of solvated Li^+ cations and individual $(Mo_3Se_3^-)_n$ anionic polymer chains that align under shear and flow.[9] Strong Mo–Mo bonding in $(Mo_3Se_3^-)_n$ is thought to impart considerable stiffness to the chains, producing solutions of rigid rod polyanions and solvated lithium cations. Recently it has been shown that 10^{-2} M solutions of $(LiMo_3Se_3)_n$ in NMF display lyotropic liquid-crystalline behavior.[10]

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

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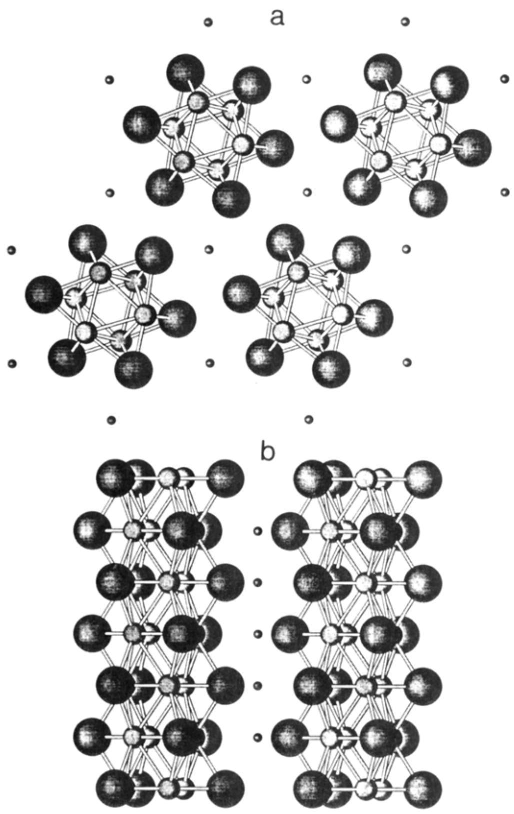

Figure 1. (a) Projection of the $(\mathrm{MMo_3Se_3})_n$ structure (M = Li) onto the hexagonal (001) plane and (b) the $(11\bar{2}0)$ plane (side view, $n = 7$). Atoms in order of increasing size are Li, Mo, Se. Intra- and intertriangle Mo–Mo bond lengths approach those found in Mo metal (2.723 Å).

As shown in eq 1, $(\mathrm{LiMo_3Se_3})_n$ is traditionally produced by ion exchange,[11] since the compound is not stable at typical preparation temperatures (1000 °C).

$$(\mathrm{InMo_3Se_3})_n + \mathrm{LiI} \xrightarrow[3\text{–}8\ \text{weeks}]{460\ ^\circ\mathrm{C}} (\mathrm{LiMo_3Se_3})_n + \mathrm{InI(sublimes)} \quad (1)$$

In an attempt to develop a direct low-temperature soft chemical route to $(\mathrm{LiMo_3Se_3})_n$, we investigated the heterogeneous solution reaction of $(\mathrm{InMo_3Se_3})_n$ with several commonly available or easily prepared organolithium reagents. Specifically, three lithium radical anion reagents and two alkyllithium reagents were investigated. Both types of reagents have previously been used successfully in a variety of intercalation reactions involving layered and interstitial solids.[12,13] However, the relative reducing power of the different reagents was not an issue, since all will react with typical layered compounds. Here we show considerable differences in the reactivity of the reagents with respect to $(\mathrm{InMo_3Se_3})_n$.

The reaction of the lithium radical anion and alkyllithium reagents is easily monitored. Specifically, the radical anions become colorless as they undergo oxidation, while the alkyl lithium reagents undergo irreversible radical disproportionation to yield products that are easily monitored by GC/MS or ^{1}H NMR spectroscopy.[12c,e,13,14]

Some possible reaction pathways of organolithium reagents with $\mathrm{InMo_3Se_3}$ are illustrated in eq 2–4. Equation

$$\mathrm{InMo_3Se_3} + \mathrm{LiR} \rightarrow \mathrm{LiMo_3Se_3} + \mathrm{InR} \quad (2)$$

$$\mathrm{InMo_3Se_3} + x\mathrm{LiR} \rightarrow \mathrm{Li}_x\mathrm{InMo_3Se_3} + x\mathrm{R} \quad (3)$$

$$\mathrm{InMo_3Se_3} + 6\mathrm{LiR} \rightarrow \mathrm{In} + 3\mathrm{Mo} + 3\mathrm{Li_2Se} + 6\mathrm{R} \quad (4)$$

2 is a direct metathesis reaction requiring both in diffusion of lithium and out diffusion of indium at the reaction temperature (InR may be alkylindium or In + R, depending on the nature of R). Equation 3 is a direct reductive intercalation reaction, wherein the rate of lithium in diffusion is much faster than indium out diffusion, while eq 4 illustrates only one of several possible decomposition reactions that may compete with or even dominate eqs 2 and 3. In eqs 3 or 4, if R is a radical, dimeric and/or disproportionation products are formed.

Experimental Section

Preparation of Inorganic Solids. Unless otherwise noted, all manipulations and reactions were carried out under argon in dried Schlenkware and/or in an argon-filled dry inert-atmosphere box. $(\mathrm{InMo_3Se_3})_n$ and $\mathrm{WO_2}$ were prepared according to previously published methods.[3,15] In the case of $\mathrm{WO_2}$, the literature procedure[15] calls for firing an intimate mixture of the reactants at 950 °C for 40 h in an evacuated quartz tube. We found it necessary to fire the reaction mixture at 1100 °C to obtain pure $\mathrm{WO_2}$ free of unreacted $\mathrm{WO_3}$, as monitored by X-ray powder diffraction.[16]

Preparation and Reaction of the Lithium Radical Anion Reagents. All manipulations were carried out in an argon-filled inert box unless otherwise noted. The radical anion reagents were prepared using 99% 325 mesh (45 μm) lithium powder (Aldrich), sublimed 4,4′-di-*tert*-butylbiphenyl (Aldrich), sublimed naphthalene (Aldrich), and sublimed benzophenone (Fisher). Tetrahydrofuran, distilled from sodium–benzophenone, was degassed via several freeze–thaw cycles (to 10^{-3} Torr) using standard Schlenk techniques on a double-manifold inert-vacuum line. The solvent was then transferred into an argon-filled inert box, in which it was kept tightly stoppered. The standard radical anion solutions were typically prepared by magnetically stirring, with a glass-encased stir bar, 1 equiv of the sublimed aromatic compound in a known amount of dry THF. Once dissolution was deemed complete, a 2-fold excess of 325-mesh lithium powder was slowly added using a powder funnel. The solution immediately became deeply colored (blue-green for the biphenylide, forest green for the naphthalide, and burgundy-purple for the dianion of benzophenone). The solution(s) were then magnetically stirred with a glass encased stir bar, with exclusion of light, until it appeared that the bulk of the lithium was dissolved (2–7 h).

An aliquot of the standard radical anion solution was then withdrawn using a dry glass syringe with Teflon plunger and then quickly delivered to 1.0 mmol (0.64g) of 325 mesh (45 μm)

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(13) Hung, P. L. K.; Sundararajan, G.; San Filippo, J., Jr. *Organometallics* **1982**, *1*, 957.

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$(InMo_3Se_3)_n$ in a tightly stoppered 50-mL round-bottom flask. With exclusion of light, the closely monitored mixture was allowed to stir at 23 °C until the reaction appeared appeared complete by color change or loss thereof. After reaction, the solutions were filtered using a dry glass frit, and the solid was washed with dry pentane and toluene until free of color. The black air-sensitive powder product was then stored in a tightly stoppered vial under argon until further analysis.

Preparation and Reaction of the Alkyllithium Reagents. Both *n*-butyllithium (1.6 M in hexane, Aldrich) and *tert*-butyllithium (1.7 M in pentane, Aldrich) were titrated using a standard solution of 2,5-dimethoxybenzyl alcohol (Aldrich), as described by Winkle et al.[17] Titration of *tert*-butyllithium was achieved using anhydrous *sec*-butyl alcohol (Aldrich) and 1,10-phenanthroline indicator (Aldrich) in toluene and pentane, as described by Watson and Eastman.[18] All titrations were carried out in an argon-filled inert-atmosphere box using dry glassware.

In a typical reaction, 6.0 mL (10 mmol) of 1.7 M *tert*-butyllithium in pentane was quickly added via dry glass of syringe with Teflon plunger to 1.0 mmol (0.64 g) of $(InMo_3Se_3)_n$ in a dry 10-mL glass vial. The solution was then diluted with a few milliliters of dry toluene, tightly stoppered, and magnetically stirred with exclusion of light for 7–10 days. After stirring, the solution was vacuum filtered using a dry glass frit in the argon atmosphere of the box. After washing with dry pentane and toluene, the solvent-free black solid was transferred to a tightly stoppered vial for later analysis.

Preparation of $Li_{0.37}WO_2$. Unless otherwise noted, all manipulations and reactions were carried out under argon in dried Schlenkware and/or in an argon-filled dry inert atmosphere box. In a typical reaction, 0.60 mL (1.0 mmol) of standardized 1.7 M *tert*-butyllithium[18] in pentane was quickly added via dry glass syringe with Teflon plunger to 1.0 mmol (0.22g) of WO_2 in a 10-mL glass vial. The solution was diluted to 0.33 M by addition of 2.4 mL of dry toluene, tightly stoppered, and then magnetically stirred for 7–10 days with exclusion of light. After stirring, the solution was vacuum filtered using a dry glass frit in the argon atmosphere of the box. After washing with pentane, the solvent-free dark brown Li_xWO_2 solid was transferred to a tightly stoppered vial for later analysis.

The separated pale yellow filtrate containing unreacted *tert*-butyllithium in pentane and toluene was immediately titrated using 1,10-phenanthroline indicator.[18] Three separate runs using 1.00 M *sec*-butyl alcohol in toluene discharged the red color to give pale yellow end points corresponding to 0.37 ± 0.086 mmol of lithium consumed by WO_2.

Analytical. ^1H NMR spectra were recorded at 200 MHz using a Varian instrument with a variable-temperature probe. Five-millimeter NMR tubes were charged with sublimed *tert*-butyllithium and 325-mesh $(InMo_3Se_3)_n$, followed by vacuum transfer of dry and degassed C_6D_6. After freezing, the tube(s) were sealed with a torch, and spectra were then recorded at different times over a 1-week period. The samples were stored in the dark between measurements and subjected to daily agitation.

All samples prepared for X-ray diffraction were kept air and moisture free by placement in holders sealed with Mylar in an Ar-filled inert box. X-ray powder diffraction data was collected using a Scintag XDS 2000 diffractometer using Cu Kα radiation. TEM and SEM samples were loaded outside the inert box, with a minimum of air exposure (approximately 60 s). TEM and SEM analysis were conducted using JEOL 200 CX and 733 instruments, respectively.

Results and Discussion

Reactions with Lithium Naphthalide and Lithium Di-*tert*-butylbiphenylide. Following the treatment of 1 mmol of $(InMo_3Se_3)_n$ with 1 equiv of lithium naphthalide, or lithium di-*tert*-butylbiphenylide in THF, a color change was observed in ca. 1–2 h and 1 min, respectively. However, while color change is indicative of chemical reaction, it does not necessarily mean intercalation is successful. For intercalation to occur, lithium must diffuse into the solid, while the indium may or may not diffuse out, as illustrated in eqs 2 and 3. For example, if a fast in-diffusion rate of 10^{-10} cm^2/s for Li^+ is assumed, as in the layered compound TiS_2,[12d] one would expect a diffusion time of approximately 5 h based on the $(InMo_3Se_3)_n$ particle size of 45 μm.[19] The reaction times of 1–2 h and 1 min for lithium naphthalide and lithium di-*tert*-butylbiphenylide, correspond to a diffusion coefficients of 10^{-9} and 10^{-7} cm^2/s,[19] 1 and 3 orders of magnitude faster, respectively. If one assumes diffusion to be the rate-determining step, all lithiating reactions should be this rapid, assuming a negative free energy of reaction. The fact that they are not suggests that some unwanted side reaction is taking place, such as over-reduction of the particle surface and subsequent attack of the chain structure, as illustrated in eq 4.

The X-ray powder diffraction pattern of the lithium naphthalide product was identical to that of the starting material[20a,b] except for some slight line broadening. Careful examination of the X-ray patterns showed no new peaks or peak shfts, as would be expected for lithium intercalation. These observations suggest some amorphous reaction product is formed. In contrast to $(Li_xIn_{1-x}Mo_3Se_3)_n$ $(0.5 \leq x \leq 1.0)$,[9] the product was insoluble in DMSO/water. However, the formation of gas and bubbling observed upon solvent addition indicated that lithium was still chemically active.

Lithium di-*tert*-butylbiphenylide appeared to be a more active reducing agent, affording a black powder product with an X-ray powder diffraction pattern displaying three new unindexed reflections at the large *d* spacings of 9.87, 9.15, and 8.42 Å. The remaining peaks, indexible to unreacted $(InMo_3Se_3)_n$,[20a,b] displayed a 75% decrease in intensity. This suggests that both intercalation and decomposition have occurred concurrently. Once again, this material was insoluble in DMSO/water, with substantial gas formation and bubbling observed upon DMSO/water addition.

Treatment of $(InMo_3Se_3)_n$ with a 10-fold excess of lithium naphthalide or lithium di-*tert*-butylbiphenylide in THF typically resulted in further decomposition as evidenced by new unindexed lines at large *d* spacings. Addition of DMSO/water resulted in considerable gas formation, with no apparent dissolution.

Reaction with the Lithium Dianion of Benzophenone. The reaction of 1, 2, or 12.5 equiv of the lithium dianion of benzophenone in THF with $(InMo_3Se_3)_n$ is accompanied by a change in the color of the solution (visually) from dark purple to blue, over a period of 4 days. Since the benzophenone monoanion is blue, this color change suggests that the dianions are oxidized by one electron. The X-ray diffraction pattern(s) of the black powder products were identical to $(InMo_3Se_3)_n$,[20a,b] except for reduced line intensities and some slight line broadening.

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[17] Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.

[18] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

[19] For TiS_2, a particle size of 45 μm (325 mesh) is assumed. From the diffusion equation: $x = (D_t t)^{1/2}$, where x is distance (cm), D_t is the diffusion coefficient (cm^2 s^{-1}), and t = time (s). See: *CRC Handbook of Chemistry and Physics*, 64th ed.; pp F47–F54.

[20] Depending on the sample, X-ray peaks were referenced and corrected by: (a) the (111) reflection of the aluminum X-ray holder, JCPDS 4,787. (b) The (002) reflection (intratriangular spacing) of $(InMo_3Se_3)_n$, which is independent of interstitial cation identity, JCPDS 35,1142. (c) The Mo (110), JCPDS 4,809. (d) Indium, JCPDS 5,642. (e) Li_2Se, JCPDS 23,72.

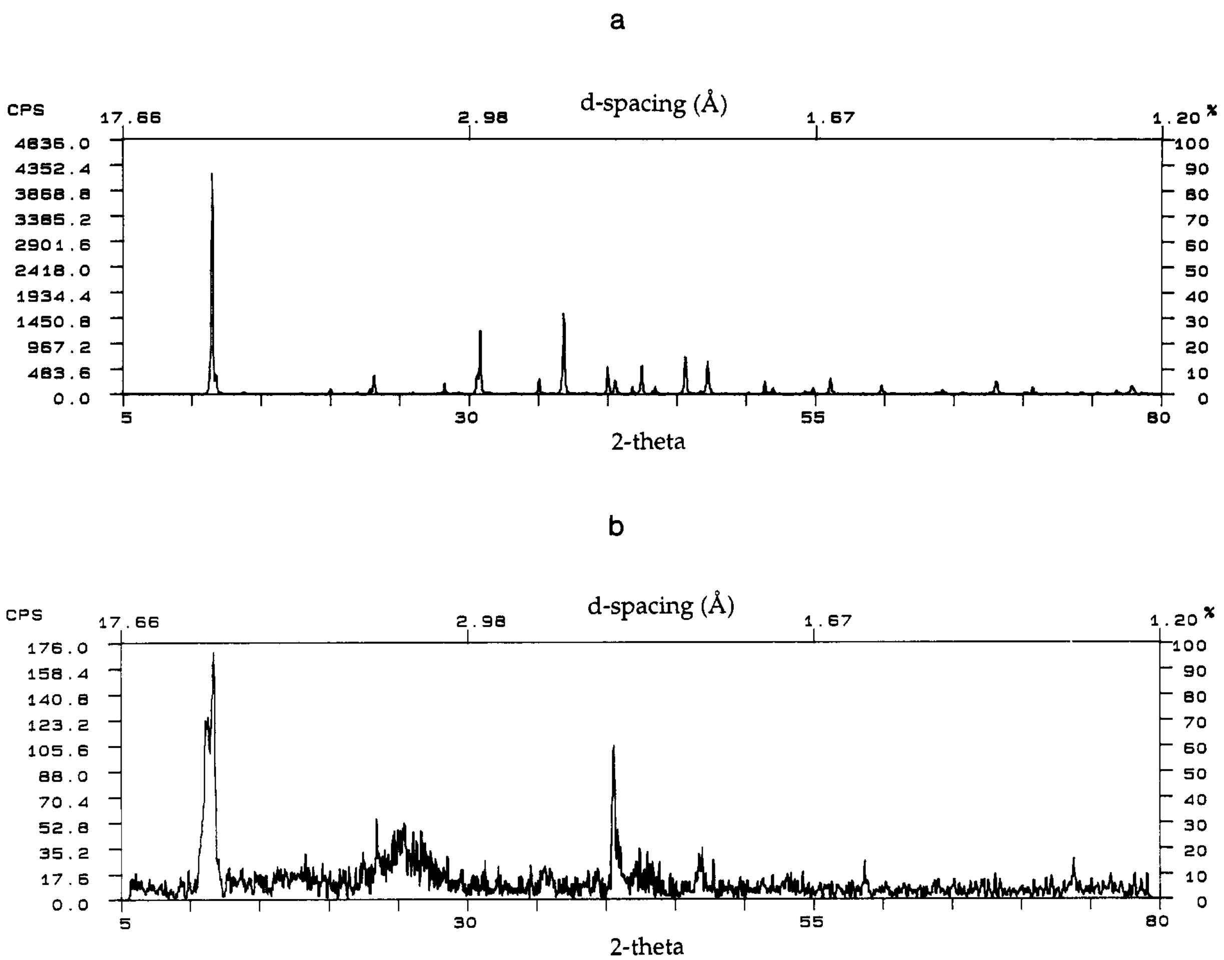

Figure 2. (a) X-ray powder diffraction pattern of $(InMo_3Se_3)_n$. The peak at $2\theta = 11.54°$, corresponds to an interchain d spacing of 7.67 Å. (b) The powder diffraction pattern of $(Li_xInMo_3Se_3)_n$ isolated from reaction of 10 equiv of *tert*-butyllithium with 1 equiv of $(InMo_3Se_3)_n$. The broad doublet ranging from $d = 7.67$ to 8.03 Å corresponds to a maximum interchain expansion of 0.36 Å. The Mo (110) peak, resulting from a competing decomposition reaction (eq 4), is seen at $2\theta = 40.510°$, $d = 2.225$ Å.

Dissolution of the products in DMSO/water failed, and substantial gas evolution was observed.

Reaction with *n*-Butyllithium. Even when used in 10-fold excess, *n*-butyllithium proved to be inert toward $(InMo_3Se_3)_n$ after 1 week of stirring in toluene and hexanes. The X-ray powder diffraction patterns of the recovered samples showed no change when compared to $(InMo_3Se_3)_n$.[20a,b]

Synthesis of $(InMo_3Se_3)_n$ with *tert*-Butyllithium. In contrast to the previous reactions, the heterogeneous reaction of $(InMo_3Se_3)_n$ with a 10-fold excess of *tert*-butyllithium in pentane and toluene generated some $(Li_xInMo_3Se_3)_n$ intercalation product after 1 week of stirring at 23 °C. Figure 2a shows the powder diffraction pattern of hexagonal $(InMo_3Se_3)_n$. The d spacing of the lowest angle peak is proportional to the interchain spacing a, where $d = \sqrt{3}/2a = 7.67$ Å. Figure 2b shows an X-ray powder pattern of the $(Li_xInMo_3Se_3)_n$ intercalation product that is dominated by a broad doublet, ranging from $d =$ 7.67 Å to $d = 8.03$ Å. Other than this doublet peak, the absence of other peaks characteristic of $(InMo_3Se_3)_n$ or $(LiMo_3Se_3)_n$ is indicative of a disordered product. The peaks seen at approximately $2\theta = 41°$, 58°, and 74° are due to Mo metal, an obvious decomposition product (eq 4).

We interpret the broad peak centered near 8 Å as due to an interchain expansion of 0.36 Å, suggesting that reductive intercalation of Li into the interstitial sites of $(InMo_3Se_3)_n$ has occurred. This expansion is consistent with with the respective (100) d spacings of 7.67 and 7.37 Å for $(InMo_3Se_3)_n$ and $(LiMo_3Se_3)_n$.[8,20a,b] If indium were somehow removed, a decrease in the (100) spacing from 7.67 to 7.37 Å would be expected.[8] The fact that an expansion occurs has led us to surmise that lithium atoms have taken positions within the interstitial spaces of $(InMo_3Se_3)_n$.

In an effort to identify any competing decomposition pathways in which elemental indium or Li_2Se is also produced (eq 4), a pressed pellet of $(Li_xInMo_3Se_3)_n$ was heated to 350 °C in an evacuated quartz tube for 3 days (In mp = 157 °C). After slow cooling to 23 °C, the pellet was removed and inspected visually. A shiny thin metallic film was observed on the pellet surface, later confirmed to be elemental indium via X-ray diffraction.[20d] Additional peaks indexed to Li_2Se were also observed.[20e] SEM microprobe analysis of $(Li_xInMo_3Se_3)_n$ lent further support to our supposition that decomposition (eq 4) had also occurred.[21] A 20 wt % enrichment of molybdenum found in some areas of the sample correlates with the Mo peaks observed in the X-ray diffraction pattern of $(Li_xInMo_3Se_3)_n$ (Figure 2b).

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[21] Standardless microprobe analyses of $(InMo_3Se_3)_n$ typically yield the following atomic percents: In = 15.0–15.5, Se, Mo = 42.0–42.5. $(LiMo_3Se_3)_n$ is the same, for Li fixed at 1.00. The atomic ratios of Mo to Se may vary due to sample nonuniformity in thickness or density.

Isolation of $(\mathrm{LiMo_3Se_3})_n$ free of decomposition products and unreacted starting material was achieved by stirring $(\mathrm{Li}_x\mathrm{InMo_3Se_3})_n$ for 1 week in DMSO/water. This yielded the dark viscous burgundy solution that is characteristic of $(\mathrm{Li}_x\mathrm{In}_{1-x}\mathrm{Mo_3Se_3})_n$ $(0.5 \le x \le 1)$.[9] Initial dissolution was also accompanied by evolution of both heat and gas. After 2 h of ultrasound followed by overnight stirring, the solution was centrifuged at 3000 rpm for 2 h in an attempt to remove any decomposition products and unreacted starting material. After centrifugation, the viscous dark burgundy supernatant was decanted and set aside. The remaining precipitated solid was filtered and washed with dry DMSO until free of color. The solid, which turned gray upon air exposure, was shown to contain unreacted $(\mathrm{InMo_3Se_3})_n$, as well as decomposition products, by X-ray diffraction and SEM microprobe analysis.[20a–e,21]

The decanted dark burgundy solution was cast into a thin film by placing a few milliliters of solution in a petri dish, followed by heating to 200 °C at 10^{-4} Torr for 48 h. The silver film that remained was then scrapped off for TEM and SEM microprobe analysis. TEM images of the bulk film material showed the fibrous morphology typical of cast films of $(\mathrm{LiMo_3Se_3})_n$ originally obtained from the reaction of $(\mathrm{InMo_3Se_3})_n$ with LiI (eq 1).[9] Electron diffraction and spot elemental analysis confirmed the existence of pure bulk $(\mathrm{LiMo_3Se_3})_n$ and some $(\mathrm{Li}_x\mathrm{In}_{1-x}\mathrm{Mo_3Se_3})_n$ $(0.5 \le x \le 1)$ in a small area of the film. SEM microprobe analysis of the bulk film was consistent with this data.[21] However, the small areas of the film assigned the stoichiometry $(\mathrm{Li}_x\mathrm{In}_{1-x}\mathrm{Mo_3Se_3})_n$ $(0.5 \le x \le 1)$ may be portions in which very fine particles of indium, not separated by centrifugation, remained dispersed in solution. By gravimetric measurement, the yields of $(\mathrm{LiMo_3Se_3})_n$ typically range from 40 to 60%.

The reaction of 1 and 5 equiv of *tert*-butyllithium with $(\mathrm{InMo_3Se_3})_n$ was ineffective. Little change was observed in either X-ray powder diffraction pattern, but treatment with DMSO/water produced pale burgundy solutions, suggesting that lithium intercalation had occurred to some small extent in these reactions. The bulk of the material remained undissolved.

Proton NMR spectroscopy confirms that *tert*-butyllithium reacts with $(\mathrm{InMo_3Se_3})_n$ via a radical pathway.[22,23] Using 1 equiv of *tert*-butyllithium and $(\mathrm{InMo_3Se_3})_n$ in $\mathrm{C_6D_6}$, a series of spectra for $t = 0$, $t = 30$ h, $t = 4$ days, and $t - 7$ days were collected at 23 °C. These spectra showed the disappearance of *tert*-butyllithium and the simultaneous evolution of the radical disproportionation products isobutane, isobutylene, and 2,2,3,3-tetramethylbutane.[23] The formation of these products is consistent with the findings of San Filippo et al.,[13] in which various layered transition metal dichalcogenides were treated with *tert*-butyllithium. At higher temperatures (35–180 °C) unidentified resonances dominate the spectra, with almost total loss of the aforementioned radical disproportionation product signals. The product obtained from the high-temperature reaction was not soluble in DMSO/water. This suggests that at room temperature, the rate of intercalation and decomposition are comparable, while at higher temperatures, decomposition dominates.

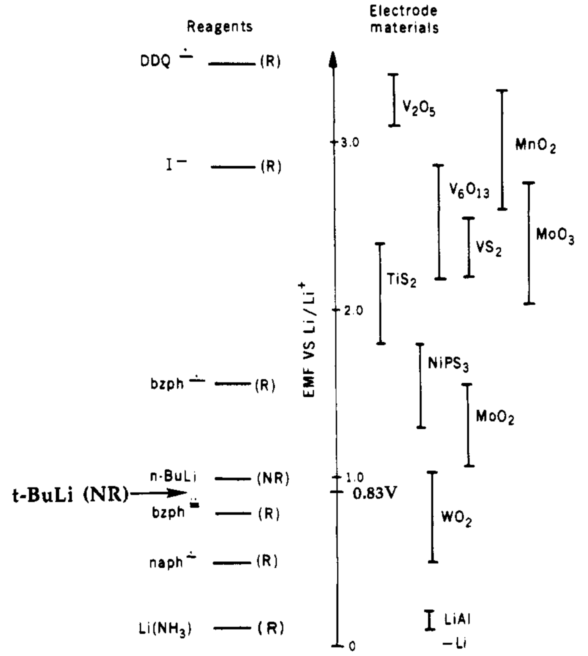

Figure 3. Adapted from ref 12 d. Potentials of a variety of electrode materials and reagents for modeling cell reactions are given relative to $\mathrm{Li/Li^+}$. The reduced form of the reagent is shown; (R) denotes reversible and (NR) denotes irreversible reagents. Other abbreviations: DDQ, 2,3-dichloro-4,5-dicyclobenzoquinone; bzph, benzophenone; naph, naphthalene. The potentials of the reagents may vary slightly with solvent, concentration, and supporting electrolyte.

Estimation of the Reduction Potential of *tert*-Butyllithium. Our observation that *tert*-butyllithium can form $(\mathrm{Li}_x\mathrm{InMo_3Se_3})_n$, while successfully competing with reductive decomposition, raised the question of the relative reducing strength of *tert*-butyllithium in comparison to other organolithium reagents typically used in the reductive intercalation of layered or interstitial solids. Using the data compiled by Murphy and Christian,[24] it was reasoned that the reducing potential of *tert*-butyllithium should lie somewhere between *n*-butyllithium and the dianion of benzophenone, since *n*-butyllithium proved to be inert toward $(\mathrm{InMo_3Se_3})_n$, while the dianion of benzophenone formed both partially intercalated and decomposed material.

Figure 3 shows the placement *tert*-butyllithium in this hierarchy of organolithium reagents vs intercalable solids. This relative reactivity is confirmed in an experiment involving the treatment of the reference interstitial solid $\mathrm{WO_2}$ with one equivalent of *tert*-butyllithium in pentane. After 10 days of stirring, with exclusion of light, the dark rust colored powder was filtered and washed with dry toluene and pentane. The X-ray powder diffraction pattern for this material was indexed and found to be consistent with patterns previously reported for the intercalated rutile $\mathrm{Li}_x\mathrm{WO_2}$.[25]

The filtrate, containing unreacted *tert*-butyllithium, was then titrated to a colorless endpoint with a standared solution of anhydrous 2-butanol and 1,10-phenanthroline

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(22) (a) Nonhebel, D. C.; Walton, J. C. *Free Radical Chemistry*; Cambridge: New York, 1974. (b) See refs 12a and 13. (c) Hellwege, K. H., Ed. *Landolt Börnstein*; Springer-Verlag: Berlin, 1984; Subvolume 13a, pp 29–34. (d) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098. (e) Ashby, E. C.; Tung, N. P. *Tetrahedron Lett.* **1985**, *26*, 4691. (e) Ashby, E. C.; Tung, N. P. *J. Org. Chem.* **1987**, *52*, 1291.

(23) ^{1}H NMR ($\mathrm{C_6D_6}$): *tert*-butyllithium, δ 0.975 (s, 9H, $-\mathrm{CH_3}$). Isobutane, δ 0.832 (d, 9H, $-\mathrm{CH_3}$, $J = 6.51$ Hz), δ 0.864 (d, 9H, $-\mathrm{CH_3}$, $J = 6.51$ Hz), δ 1.59 (m, 1H, $-\mathrm{CH}$). Isobutylene, δ 4.74, (m, 2H, vinyl), δ 1.58 (t, 6H, $-\mathrm{CH_3}$). 2,2,3,3-Tetramethylbutane, δ 0.843 (s, 18H, $\mathrm{CH_3}$).

(24) Adapted from ref 12d with permission.

(25) Murphy, D. W.; DiSalvo, F. J.; Carides, J. N.; Waszczak, J. V. *Mater. Res. Bull.* **1978**, *13*, 1395.

indicator.[18] Three runs gave an average of 0.37 ± 0.086 mmol of lithium consumed per WO_2 octahedral vacancy. Using this value and previously reported charge–discharge curves for Li_xWO_2,[25] where $0 \leq x \leq 1$, a reduction potential of 0.83 V was determined by extrapolation. As expected, this value lies between *n*-butyllithium and the dianion of benzophenone on the linear voltage scale in Figure 3 and is consistent with our observations of the relative reactivity of *n*-butyllithium, *tert*-butyllithium, and the dianion of benzophenone towards $(InMo_3Se_3)_n$. The observed reactivity for the alkyllithium reagents also correlates well with empirically determined metalating strengths of lithium alkyls (and carbon radical stability), where *t*-BuLi > *s*-BuLi > *n*-BuLi.[12a,b]

Conclusion

Proton NMR spectroscopy confirms that in the presence of $(InMo_3Se_3)_n$, *tert*-butyllithium disproportionates to form isobutane, isobutylene, and 2,2,3,3-tetramethylbutane. Lithium intercalation appears to compete successfully with reductive decomposition, to afford yields of $(LiMo_3Se_3)_n$ that reach 60%. This result is in contrast to the comparable reactions with *n*-butyllithium, or the radical anion reagents, which proved unreactive or caused only decomposition of the starting material.

Knowledge of the relative reduction potential of *tert*-butyllithium, and thus its relative reactivity toward intercalable solids such as WO_2, now gives the synthetic chemist greater flexibility in the choice of reagents for the reductive intercalation of layered and interstitial solids, especially in cases where over reduction leads to unwanted products.

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Registry numbers: $(Mo_3Se_3^-)$, [82638-61-7]; *tert*-butyllithium, 1.7 M in pentane, [594-19-4].