



Li deposited on LiCl: an efficient reducing agent†

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Lithium was deposited onto lithium chloride powder in a ~5% weight/weight ratio. This material serves as a source of elemental lithium with benefits over bulk lithium alternatives including increased mass to facilitate measurement for small scale reactions and increased surface area. The Li/LiCl material is applied in the synthesis of a dilithiobutadienide that is transformed into a stannole with a drastic decrease in reaction time and notable increase in yield over commercial lithium granules.

Metallic lithium (Li) is a highly reactive alkali metal with a low ionization energy ($520.2 \text{ kJ mol}^{-1}$) readily forming Li^+ via the loss of the 2 s valence electron. Accordingly, lithium is a powerful reductant in organic synthesis. Applications include the reduction of alkyl halides to alkyllithium reagents that are ubiquitous nucleophiles in lithium–halogen exchange and transmetallation reactions to prepare fine chemicals.^{1,2} Birch reductions take advantage of the reducing ability of lithium as a single electron transfer reagent in the conversion of arenes to cyclohexadienes.^{3,4} Dilithium complexes, like lithiophenylalkyllithiums, 3,4-dilithio-2,4-hexadienes and substituted 1,4-dilithio-1,3-butadienes can be prepared by direct lithiation and utilized as reagents to access organic compounds and main group metalloids.^{5–9} For example, 1,4-dilithio-1,3-butadienes are efficient building blocks for the synthesis of cyclic compounds by reaction with main group dihalides.^{9–16}

Despite the necessity of organolithium compounds, accessing them via the direct lithiation with organic halides or alkynes with metallic lithium presents challenges. Lithium is not soluble in common solvents and reactions occur on the surface. Bulk solids have low surface area that limits the reaction efficiency in heterogeneous reactions. The low molecular weight of elemental lithium (6.94 g mol^{-1}) is problematic for precise measurements required in small scale reactions for exploratory research. Among commercially available lithium sources, lithium pellets/granules

Table 1 Statistical weight of 714 lithium granules

Samples	Mean	Standard deviation	Standard error of mean
714	5.3	1.4	0.05

have been widely used for synthesis due to the rather small average grain sizes. Weighing 714 granules of lithium at random from a commercial bottle indicates that the weight obeys a Gaussian distribution with a mean value of 5.3 mg and standard deviation of 1.4 mg (Table 1, Fig. 1 and Table S1, ESI†). This corresponds to greater than 95% of the granules being within 2.5–8.2 mg in weight.¹⁷ Although small in weight, this translates to a considerable amount for a stoichiometric reaction on typical research scale (1 mmol lithium = 6.9 mg). Moreover, it is tedious if one were to do a reaction of 20 mg or less of lithium, in which one would have to select a specific combination of granules that add up to the required amount. Lithium ribbon presents a slight advantage in the fact that the surface area is potentially greater, but the ribbon is larger in size.

Sandification of alkali metals is a useful method to increase the surface area in reducing agents, however, the complicated and dangerous manipulations limit their practical application.¹⁸

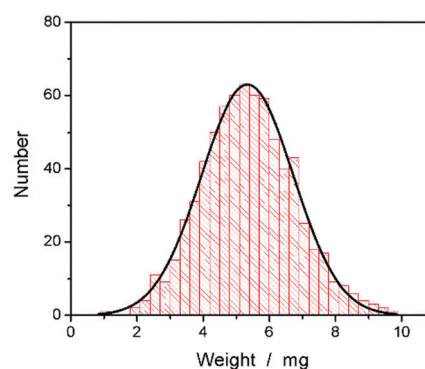


Fig. 1 Distribution of the weight of 714 lithium granules at random from a commercial bottle.

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An effective strategy to make alkali metals easier to measure and increase the surface area is to disperse the alkali metals onto salts in which the cation is the ionized form of the metal.¹⁹ For example, Jones and coworkers recently reported that elemental sodium and potassium supported on sodium chloride and potassium iodide, respectively, can be used as dispersible reducing agents for the multigram synthesis of magnesium(i) and aluminum(i) compounds.²⁰ Inspired by this and our need for a practical lithium source, we prepared LiCl supported Li powder and investigated its ability in the preparation of tetraphenyl substituted 1,4-dilithio-1,3-butadiene. This dilithium compound can be readily converted to 1,1-dimethyl-2,3,4,5-tetraphenylstannole, an intermediate in the synthesis of boroles.⁹

Lithium chloride was dried in an oven for 3 d at 135 °C and ground to a fine powder in a household blender for 30 min. 40.00 g of the powder was transferred to a 1 L Schlenk flask and dried under dynamic vacuum for 4 h at 200 °C. After cooling, 2.00 g of Li granules were added into the Schlenk flask under an argon atmosphere and the mixed solids were heated to 200 °C gradually using an aluminum heating block with rigorous stirring. Elemental lithium melts at 180.5 °C²¹ and exceeding the melting temperature enables the dispersion. The temperature was kept at 200 °C for an hour until no bulk lithium granules were observed. A gray powder with visual consistency comparable to lithium chloride was obtained and was stored in an argon filled glovebox.

Scanning electron microscopy (SEM) was used to examine the uniformity of the LiCl and *ca.* 5% w/w Li/LiCl powders (Fig. 2 and Fig. S1–S5, ESI†). The images obtained revealed that both LiCl and Li/LiCl powders have a wide particle size range and most of the irregularly shaped grains lie between 5 and 50 µm. Images with 50 or 20 µm scale show that there are some visual fissures or defects on the surface of bare LiCl powder (Fig. S1–S3, ESI†), while, the images of Li/LiCl powders reveal that the LiCl is coated with the Li metal with the disappearance of the fissures (Fig. S4 and S5, ESI†).

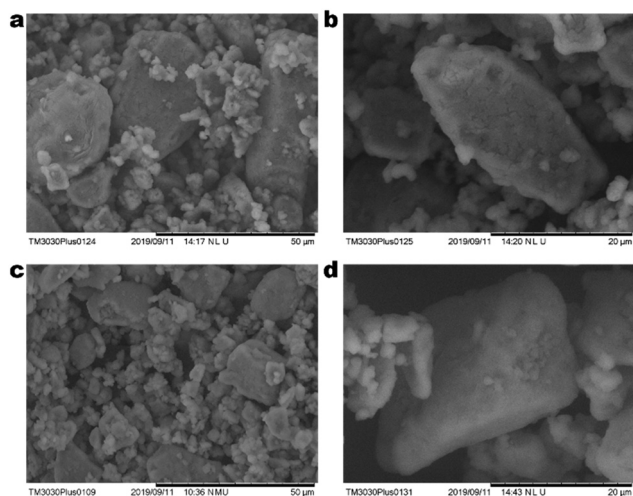
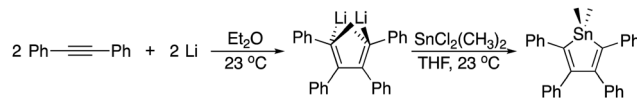


Fig. 2 Scanning electron microscope images of fine ground LiCl powder with 50 µm scale (a) and 20 µm scale (b), *ca.* 5% w/w Li/LiCl powder with 50 µm scale (c) and 20 µm scale (d). Enlarged images are in the ESI.†



Scheme 1 Synthesis of 1,1-dimethyl-2,3,4,5-tetraphenylstannole by using Li metal as the reducing agent.

Tetraphenyl substituted 1,4-dilithio-1,3-butadiene can be prepared by the 2:2 stoichiometric reaction of diphenylacetylene and lithium in diethyl ether (Scheme 1).⁹ To prepare 1,1-dimethyl-2,3,4,5-tetraphenylstannole, the solution is transferred into a solution of dimethyltin dichloride in THF resulting in a bright yellow solution that is immediately dried under vacuum to give the crude product of 1,1-dimethyl-2,3,4,5-tetraphenylstannole. Since tetraphenyl substituted 1,4-dilithio-1,3-butadiene can be readily converted to 1,1-dimethyl-2,3,4,5-tetraphenylstannole, the yield of stannole was determined by quantitative ¹H NMR spectroscopy using tetramethylsilane (TMS) as an internal standard at incremental times using the Li/LiCl powder. Examining the reactivity of the ~5% Li/LiCl powder revealed the reaction reached 80% yield after 2 h (Fig. 3).

Under the same conditions using Li granules as the reducing agent a maximum stannole yield of 63% was achieved after 20 h (Fig. 4). Notably only 6% yield was obtained after 2 h, the time required with the Li/LiCl powder. The decreased reaction time and higher product yield indicate Li/LiCl powder is a better reagent than Li granules in the stannole synthesis.

It has been demonstrated that LiCl can be an effective additive to organometallic reactions (*e.g.* Turbo-Grignards and Turbo-Hauser bases).^{22–24} To investigate if LiCl played a role in the increased yield and decreased reaction times in the preparation of 1,1-dimethyl-2,3,4,5-tetraphenylstannole, a control reaction was conducted with Li granules and 20 fold LiCl powder by weight. No statistical difference in yield or reaction time was observed (5% yield after 2 h and the maximum stannole yield of 65% after 20 h) in comparison to the reaction with only lithium granules. Moreover, a control reaction with only LiCl showed no conversion. The experiments indicate that the high reactivity of *ca.* 5% w/w Li/LiCl

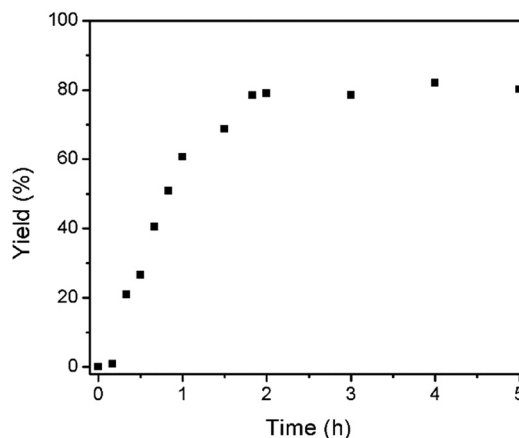


Fig. 3 Plot of yields of 1,1-dimethyl-2,3,4,5-tetraphenylstannole by using *ca.* 5% w/w Li/LiCl versus time.

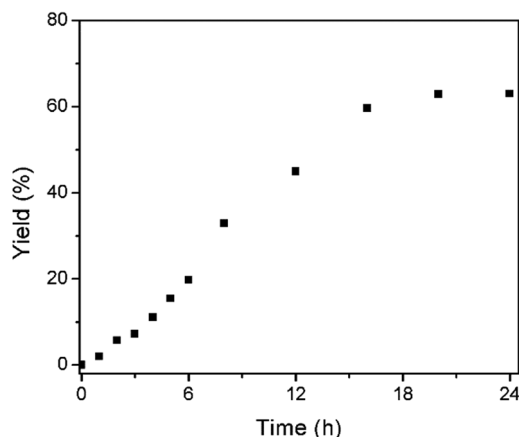


Fig. 4 Plot of yields of 1,1-dimethyl-2,3,4,5-tetraphenylstannole by using Li granules versus time.

powder is from the deposition of granular lithium onto LiCl, rather than the LiCl additive.

In summary, we report a facile method to disperse lithium onto lithium chloride in ~5% w/w ratio. A case study comparing bulk Li granules to the Li/LiCl powder revealed a decrease in reaction time from 20 h to 2 h as well as an increase in yield from 63% to 80%.²⁵ An additional benefit to this powder is the increased mass that enables measurements of small molar quantities for research scale reactions. Li/LiCl is an appealing reducing agent for the synthetic chemist and can conceivably be applied to a wide variety of reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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- Lithium salts with heavier halide counterions (X = Br or I) might also be effective in the transformation. Lithium chloride was selected for this reaction as LiCl is the reaction byproduct facilitating isolation of the desired product.