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# Multigram Syntheses of Magnesium(I) Compounds Using Alkali Metal Halide Supported Alkali Metals as Dispersible Reducing Agents

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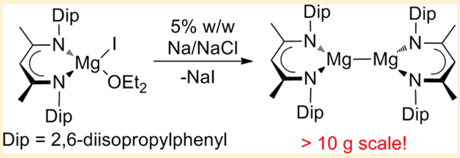
*Supporting Information*

**ABSTRACT:** The alkali metal halide supported alkali metal materials, ca. 5% w/w Na/NaCl and 5% w/w K/KI, are prepared without specialist equipment by rapidly stirring molten alkali metal with finely ground alkali metal halide powder. Scanning electron microscopy reveals the particles of 5% w/w Na/NaCl to lie largely in the 10−100 $\mu$M size range. The freely flowing powders are easily dispersible in organic solvents and are used as reducing agents for the facile syntheses of three magnesium(I) compounds, $[\{HC(MeCNAr)_2\}Mg]_2$, Ar = mesityl (Mes), 2,6-diethylphenyl (Dep), or 2,6-diisopropylphenyl (Dip), which can be obtained in yields of up to 12 g. The potential advantages Na/NaCl and K/KI powders offer to synthetic inorganic/organometallic chemists, relative to currently available alkali metal reducing agents, are discussed.



## INTRODUCTION

Developments in the chemistry of the main group elements over the last several decades have largely centered on complexes containing those elements in very low oxidation states. While such complexes have always been of considerable fundamental interest, due to the unusual structural types and bonding they exhibit,[1] the past decade has seen these reactive species finding widespread applications in stoichiometric and catalytic synthetic protocols. Particular interest has focused on developing cheap, essentially nontoxic main group complexes for use in processes which normally require expensive and toxic late transition metal complexes to proceed.[2] As low oxidation state main group complexes are typically prepared by reduction of common oxidation state precursor complexes, the development of new classes of reducing agent can only aid the expansion of this field.

In 2007, our group reported on the first isolable magnesium(I) compounds, LMg−MgL, which are kinetically stabilized by bulky guanidinate or $\beta$-diketiminate ligands (L).[3] Since that time, $\beta$-diketiminate coordinated magnesium(I) compounds have emerged as soluble, stable, selective, and safe reducing agents that have been widely utilized by many research groups around the world.[4] These efforts have allowed entry to numerous low oxidation state p-block complexes (and related d-block systems) that cannot be accessed, or are difficult to access, when using more traditional reducing agents such as insoluble s-block metals, $KC_8$, or alkali metal naphthalenide solutions.[5] The success of magnesium(I) compounds in this respect is a result of their moderately reducing nature, their ease of preparation and handling, and the fact that reduction reactions involving them are carried out in a controlled fashion with all reactants in the solution phase. Despite their increasing importance as reducing agents, all currently available synthetic routes to $\beta$-diketiminato magnesium(I) compounds involve reduction of magnesium(II) iodide precursor complexes with alkali metal mirrors. The relatively low surface areas of such mirrors typically limits the scale of these reduction reactions to yield less than 2 g of the magnesium(I) product, though higher weight yields (but lower percentage yields) can be obtained inconsistently when large reaction flasks (e.g., 1 L round-bottomed Schlenk flask) are employed.[6] Here we show that alkali metals supported on finely ground alkali metal halide salts can be easily prepared without specialist equipment, and can be utilized as dispersible reducing agents for the facile, high yield synthesis of up to 12 g of magnesium(I) compounds in a single batch.

## RESULTS AND DISCUSSION

Considering the limitations of the synthesis of magnesium(I) compounds on multigram scales by reduction of $\beta$-diketiminato magnesium(II) precursor complexes using alkali metal mirrors as reducing agents, we have explored a number of reduction methodologies that involve greater alkali metal surface areas.[7] These include liquid Na/K alloys, Na/Hg amalgam, $KC_8$, lithium powder, sodium dispersions generated by rapidly stirring molten sodium in toluene, and graphite, silica gel, or diatomaceous earth supported sodium powders.[5,8] However, in all cases the yields of magnesium(I) compounds obtained were low, and the products were typically contaminated with large amounts of homoleptic bis($\beta$-diketiminato) magnesium(II) compounds, $\beta$-diketimine, and/or other byproducts.

Our attention then turned to the possibility of supporting sodium or potassium metal on finely divided sodium chloride or potassium iodide powders, respectively. The former has been previously prepared as a ca. 10% w/w powder by ball-

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milling sodium metal and sodium chloride in a glovebox and has proved effective as a reducing agent.[9] As far as we are aware, the latter system has not been previously explored. In order to circumvent the need to use a ball-milling apparatus and a glovebox, we have developed a related procedure that can be simply performed in any organometallic research laboratory. NaCl or KI are ground to fine powders in a domestic kitchen blender for approximately 30 min. The powders are then placed in a large round-bottomed Schlenk flask and heated under a dynamic vacuum at ca. 300 °C using a heat gun for several hours. Approximately 5% w/w of Na or K metal is then added to the cooled flask, and the mixture is heated under a nitrogen atmosphere, or a static vacuum, at just above the melting point of the alkali metal, while stirring rapidly with a large magnetic stir bar. After about 30 min, no bulk alkali metal remains, and the resultant mixture is a freely flowing, fine blue/gray powder that can be stored indefinitely in a Schlenk flask or a glovebox and is easily weighed out in stoichiometric amounts for further reactions. The powder rapidly decomposes on exposure to the atmosphere, and should be treated as a fire hazard when manipulated.

During one preparation of Na/NaCl powder, samples were taken before and after addition of sodium metal and analyzed by scanning electron microscopy. This revealed a wide particle size range, with the majority of irregularly shaped fractured crystals lying between 10 and 100 $\mu$m across (see Figure 1a).

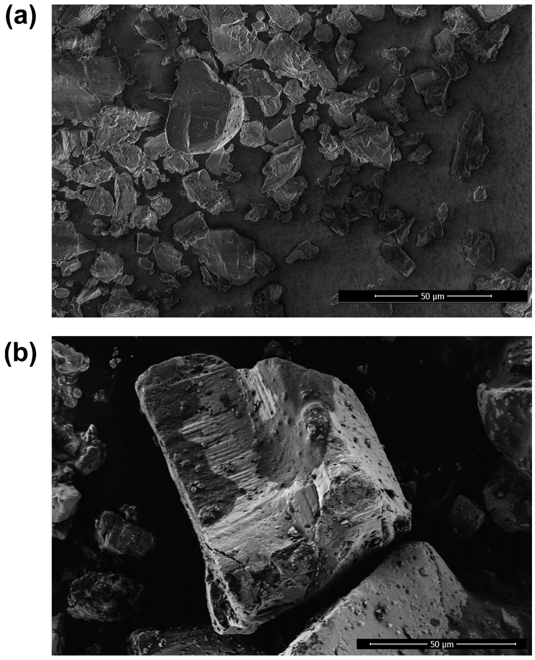
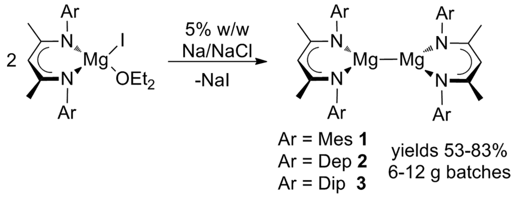


**Figure 1.** Scanning electron microscope images of (a) finely ground NaCl powder, and (b) large fractured NaCl crystals partially coated with Na metal (dark gray patches).

After the addition of sodium metal, the particles are partially coated with sodium metal, but this coating is typically not uniform, as can be seen in Figure 1b. It is clear, however, that the surface area of sodium has markedly increased relative to that which would be expected of a mirror of sodium coating the inside of a Schlenk flask.

**Scheme 1. Multigram Syntheses of Magnesium(I) Compounds 1−3 Using ca. 5% w/w Na/NaCl Powders As Reducing Agents**



Three $\beta$-diketiminato magnesium(II) iodide complexes with varying steric bulk of their N-substituents were chosen for reduction reactions, [{HC(MeCNAr)$_2$}MgI(OEt$_2$)] (Ar = mesityl (Mes), 2,6-diethylphenyl (Dep), and 2,6-diisopropylphenyl (Dip); Scheme 1).[6] These were dissolved in toluene/diethyl ether solvent mixtures in large round-bottomed Schlenk flasks, to which large excesses of Na/NaCl (ca. 5 equiv of Na) had been added. The resultant suspensions were stirred for 2−3 days, and the reactions were monitored by $^1$H NMR spectroscopy to determine when all magnesium(II) iodide precursor had been consumed. At this stage the suspensions were filtered, which yielded yellow solutions of the target magnesium(I) compounds, **1**−**3**. In the cases of [{HC(MeCNAr)$_2$}Mg]$_2$ (Ar = Mes **1** or Dip **3**),[6a,c] volatiles could simply be removed and the residues washed with hexane to give good yields (60 and 83%, respectively) of the magnesium(I) compounds as yellow powders. $^1$H NMR spectroscopic analyses (see Supporting Information) revealed the powders to be >97% pure, and they could be used in subsequent reactions without further purification. The purification of the other magnesium(I) compound, [{HC(MeCNDep)$_2$}Mg]$_2$ (**2**),[6b] required recrystallization to obtain it in a moderate isolated yield (53%). The excess Na/NaCl from the reactions can be safely decomposed by slow addition of isopropanol, with stirring, to the Schlenk flask containing this residue. The reactions do give similar yields when only 2 equiv of Na/NaCl are used, but they take considerably longer (7−8 days) to reach completion.

The main advantage of this synthetic technique over those previously published is that the magnesium(I) compounds can be obtained on multigram scales (6−12 g) with minimal workup and in two cases without recrystallization. The obtained yields are significantly greater than when a sodium mirror is used as the reducing agent, and the reaction times (2−3 days) are considerably shorter than when using sodium mirrors (4−5 days).[6] Moreover, the Na/NaCl powder can be easily prepared and stored for indefinite periods prior to use. Given the facility of preparations of [{HC(MeCNAr)$_2$}Mg]$_2$, it seems likely that Na/NaCl powders could find use as an alternative to sodium mirrors or sodium dispersions in synthetic procedures where those reagents are utilized.

For the sake of comparison, the preparation of the bulkiest magnesium(I) compound, [{HC(MeCNDip)$_2$}Mg]$_2$ (**3**), was attempted using K/KI powder in place of Na/NaCl. Although the isolated yield (57%) was not as high as when Na/NaCl was used, the reaction was quicker (1 day), and only a slight excess of K/KI powder (ca. 1.1 equiv of K) was required. In addition, after decomposing the small amount of residual potassium in the K/KI powder with isopropanol, the remaining KI can be washed, dried and used again for the preparation of K/KI powders.

With K/KI in hand, it was seen of interest to explore its use as a reducing agent in the preparation of other low oxidation state main group systems that are difficult to prepare using potassium metal. As an example, we chose the neutral β-diketiminato aluminum(I) heterocycle, [{HC(MeCNDip)$_2$}Al:] (**4**), the literature preparation of which by reduction of [{HC(MeCNDip)$_2$}AlI$_2$] with potassium is low yielding (21%).[10] At least in our hands, we have found from numerous attempts to repeat this procedure that the outcome is difficult to regularly reproduce, and only rarely can the literature yield be obtained. In contrast, reductions of [{HC(MeCNDip)$_2$}AlI$_2$] with a slight excess of K/KI in toluene were reproducible, though typically afforded [{HC(MeCNDip)$_2$}Al:] in lower yields (ca. 14%) than the literature procedure. With that said, the greater certainty associated with this procedure may well benefit the increasing number of chemists who utilize [{HC(MeCNDip)$_2$}Al:] as a reactant in their research.[2b,11] Reduction of [{HC(MeCNDip)$_2$}AlI$_2$] with a 5-fold excess of Na/NaCl led to an intractable mixture of many products after 1 day, while reaction with a 20% excess of Na/NaCl led to only partial consumption of [{HC(MeCNDip)$_2$}AlI$_2$] and a complicated product mixture, not including **4**, after 2 days.

## ■ CONCLUSIONS

In summary, a straightforward method for the preparation of alkali metal halide supported alkali metals has been developed. These freely flowing powders are readily dispersible in organic solvents, and have been used as reducing agents in facile, multigram (up to 12 g) syntheses of three synthetically applicable magnesium(I) compounds. It has also been demonstrated that one of the reagents, K/KI, can be employed as a reducing agent in reproducible, but low yielding, syntheses of a known neutral aluminum(I) heterocycle. We continue to explore applications of Na/NaCl and K/KI in the synthesis of low oxidation main group compounds, and believe these materials will find use in the broader inorganic/organometallic community.

## ■ EXPERIMENTAL SECTION

**General Methods.** All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity dinitrogen. Hexane and toluene were distilled over potassium, while diethyl ether and pentane were distilled over Na/K alloy (50:50). $^1$H NMR spectra were recorded on a Bruker AvanceIII 400 spectrometer and were referenced to the resonances of the solvent used. Scanning electron microscope images were acquired from uncoated NaCl or Na/NaCl samples using the Magellan FEGSEM at the Monash Centre for Electron Microscopy. The microscope was operated using a 2 kV landing energy utilizing beam deceleration to minimize sample charging. The compounds [{HC(MeCNAr)$_2$}MgI(OEt$_2$)] (Ar = Mes, Dep, or Dip)[6] and [{HC(MeCNAr)$_2$}AlI$_2$][10] were prepared by literature procedures. All other reagents were used as received.

**Preparation of 5% w/w Na/NaCl Powder.** Sodium chloride (80 g) was dried overnight in an oven at 110 °C. It was then ground to a fine powder, using a 1.2 L, 1500 W, domestic kitchen blender over ca.30 min. The resultant powder was subsequently transferred to a 1 L Schlenk flask containing a large magnetic stirrer bar and dried under vacuum, with stirring, for 3 h at ca. 300 °C (using a heat gun; approximate temperature determined using a hand-held infrared thermometer). After cooling, sodium metal (4.00 g, 174 mmol) was added, and the flask was gently heated to ca. 110 °C under an N$_2$ atmosphere with constant agitation and/or stirring. Once the sodium melted, rapid stirring and agitation continued until no bulk metal was visible (ca. 30 min), leaving a freely flowing blue/gray powder which could be stored in a Schlenk flask or in a glovebox until needed (yield 84.0 g).

**Preparation of 5% w/w K/KI Powder.** Potassium iodide (55 g) was ground to a fine powder over 30 min using a 1.2 L, 1500 W, domestic kitchen blender. The powder was dried in an oven for 3 days at 125 °C. It was then further ground with a mortar and pestle before being placed in a 500 mL Schlenk flask where it was flame-dried three times under reduced pressure. After cooling, freshly cut pieces of potassium (2.57 g, 66 mmol) were introduced. The flask was then placed under a static reduced pressure (ca. $10^{-2}$ mm Hg) and heated with a heat gun to ca. 100 °C (using a heat gun; approximate temperature determined using a laboratory thermometer). Once the potassium had melted, rapid stirring and agitation continued until no bulk metal was visible (ca. 30 min), leaving a freely flowing blue/gray powder which could be stored in a Schlenk flask or in a glovebox until needed (yield 57.5 g).

**Preparation of [{HC(MeCNMes)$_2$}Mg]$_2$ (1).** A solution of [{HC(MeCNMes)$_2$}MgI(OEt$_2$)] (20.0 g, 35.8 mmol) in a mixture of toluene (600 mL) and diethyl ether (50 mL) was added to a 1 L Schlenk flask containing 84 g of ca. 5% w/w Na/NaCl powder (174 mmol Na). The resultant suspension was stirred vigorously for 2 days at room temperature. After this time, the mixture was filtered, and volatiles were removed from the yellow/orange filtrate *in vacuo* to give a yellow solid. This was washed with pentane (2 × 50 mL) and hexane (2 × 50 mL), then dried *in vacuo* to give **1** as a pale yellow powder with a purity of >97% as determined by $^1$ H NMR spectroscopy (7.70 g, 60%). The characterizing data for the compound were identical to those reported.[6a]

**Preparation of [{HC(MeCNDep)$_2$}Mg]$_2$ (2).** A solution of [{HC(MeCNDep)$_2$}MgI(OEt$_2$)] (20.0 g, 34.0 mmol) in a mixture of toluene (300 mL) and diethyl ether (40 mL) was added to a 500 mL Schlenk flask containing 84 g of ca. 5% w/w Na/NaCl powder (174 mmol Na). The resultant suspension was stirred vigorously for 3 days at room temperature. After this time, the mixture was filtered and volatiles were removed from the yellow/orange filtrate *in vacuo* to give a yellow/brown oil. This was taken up in ca. 15 mL of hexane, and the solution was held at −30 °C overnight to give **2** as a dark yellow crystalline solid (6.95 g, 53%). The characterization data for the compound were identical to those reported.[6b]

**Preparation of [{HC(MeCNDip)$_2$}Mg]$_2$ (3).** *Method A.* A solution of [{HC(MeCNDip)$_2$}MgI(OEt$_2$)] (20.0 g, 31.2 mmol) in a mixture of toluene (500 mL) and diethyl ether (50 mL) was added to a 1 L Schlenk flask containing 84 g of ca. 5% w/w Na/NaCl powder (174 mmol Na). The resultant suspension was stirred vigorously for 2 days at room temperature. After this time, the mixture was filtered, and volatiles were removed from the yellow/orange filtrate *in vacuo* to give a yellow solid. This was washed with hexane (2 × 100 mL), then dried *in vacuo* to give **3** as a bright yellow powder with a purity of >97% as determined by $^1$ H NMR spectroscopy (12.3 g, 83%). The characterization data for the compound were identical to those reported.[6a]

*Method B.* [{HC(MeCNDip)$_2$}MgI(OEt$_2$)] (10.0 g, 15.6 mmol) and ca. 5% w/w K/KI powder (15.0 g, 17.3 mmol K, 1.11 equiv) were combined in a 250 mL Schlenk flask and toluene (80 mL) then added at room temperature. The suspension was stirred for 23 h, whereupon filtration and concentration under reduced pressure and storage at −30 °C overnight led to incipient crystallization of yellow crystalline **3** from the filtrate solution. All volatiles were removed from the mother liquor *in vacuo* and the residue washed with hexane (3 × 20 mL). The resultant yellow residue was dried *in vacuo* and added to the first crystalline crop (3.90 g, 57%). The characterization data for the compound were identical to those reported.[6a]

**Preparation of [{HC(MeCNDip)$_2$}Al:] (4).** Toluene (100 mL) was added to a mixture of [{HC(MeCNDip)$_2$}AlI$_2$] (6.51 g, 9.32 mmol) and ca. 5% w/w K/KI powder (17 g, 19.6 mmol K, 2.1 equiv) in a 250 mL Schlenk flask. The reaction mixture quickly became darker, then was stirred for 88 h. The suspension was then filtered, and the dark red filtrate concentrated under reduced pressure to incipient crystallization. Placement of the filtrate at −30 °C for 5 days led to the deposition of red-orange crystalline **4**, which was isolated and dried *in vacuo* (561 mg, 14%). The characterizing data for the compound were identical to those reported.[10] The mother liquor

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obtained after crystalline **4** was isolated was evaporated to dryness to leave an orange-brown solid (3.30 g). An $^1$H NMR analysis of this showed it to contain **4** among other products. Attempts to recrystallize **4** from this mixture were not successful.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00803.

$^1$H NMR spectra of compounds **1**–**4** (PDF)

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### Notes

The authors declare no competing financial interest.

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