

Cite this: *RSC Mechanochem.*, 2025, 2, 503Received 19th March 2025
Accepted 9th May 2025

DOI: 10.1039/d5mr00039d

rsc.li/RSCMechanochem

Mechanochemically micronised Na/NaCl; a superfine reductant†

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A free-flowing, homogeneous and non-pyrophoric powder of Na/NaCl is prepared *via* planetary ball-milling. The mechanochemically micronised Na/NaCl serves as a highly activated source of sodium and was used to prepare $[(^{\text{Ar}}\text{BDI})\text{Mg}]_2$ (BDI = HC{(Me)CNAr}₂; Ar = Dipp, 2,6-*i*-Pr₂C₆H₃; Mes, 2,4,6-CH₃C₆H₂) *via* ball milling in 75 and 45 minutes, respectively.

Group 1 (alkali metal) reagents are ubiquitous throughout chemistry, utilised as powerful reductants and nucleophilic bases (*e.g.* ⁿbutyl lithium) within the remit of synthetic chemistry.^{1,2} Of the alkali metals, sodium is by far the most abundant in the Earth's crust,³ and readily available from electrolysis of sodium chloride.⁴ Yet, in the context of applied organometallic chemistry, lithium and potassium reagents remain dominant. The applications of organosodium chemistry are currently limited due to the pyrophoric nature, poor-solubility and difficulty in handling of these reagents. Nevertheless, organosodium reagents such as NaTMP (sodium 2,2,6,6-tetramethylpiperidide) and NaDA (sodium di-*iso*-propylamide) have begun to be investigated as sustainable alternatives to classical organolithium reagents,^{5,6} demonstrating superior reactivity in many cases.^{7,8} Moreover, to overcome the insoluble nature of organosodium reagents and to enhance accessibility, new approaches to synthesise organosodium species have begun to be developed. For example, Asako and Takai reported the preparation of aryl sodiums using a Br/Na exchange reaction of aryl bromides with neopentyl sodium, which was derived from neopentyl chloride and sodium dispersion. However, the presence of residual sodium in the aryl sodium reagents results in side reactions, limiting the scope of electrophilic substrates with which they can be reacted.⁹ To circumvent this problem, Knochel recently reported the on-demand generation of (2-

ethylhexyl)sodium, a hexane soluble organosodium reagent, through a continuous-flow method using a sodium-packed bed reactor (sodium dispersion, particle size <0.1 mm), allowing for the preparation of benzylic sodium organometallics as well as the functionalisation of aryl sodiums with a wide range of electrophiles, including ketones, aldehydes, Weinreb-amides, imines, allyl bromides, disulfides and alkyl iodides.¹⁰

Alkali metals are commonly employed within the field of low oxidation state metal chemistry, specifically as one electron reductants, facilitating access to elements in unusual oxidation states.¹¹ For example, in 2007 Jones and co-workers reported the reduction of a β -diketaminato magnesium(II) iodide precursor, $[(^{\text{Dipp}}\text{BDI})\text{MgI}(\text{OEt}_2)]$ (BDI = HC{(Me)CNDipp}₂; Dipp = 2,6-*i*-Pr₂C₆H₃) with an alkali metal mirror, affording the first stable magnesium(I) dimer, $[(^{\text{Dipp}}\text{BDI})\text{Mg}]_2$.¹² More recently, Jones and co-workers developed an alternative to alkali metal mirrors; stirring molten alkali metal with its corresponding finely ground alkali metal halide powder to afford alkali metal halide supported alkali metals (*i.e.* 5% w/w Na/NaCl, 5% w/w K/KI) as readily weighable dispersible reducing agents. These have been used for the preparation of magnesium(I) compounds on the

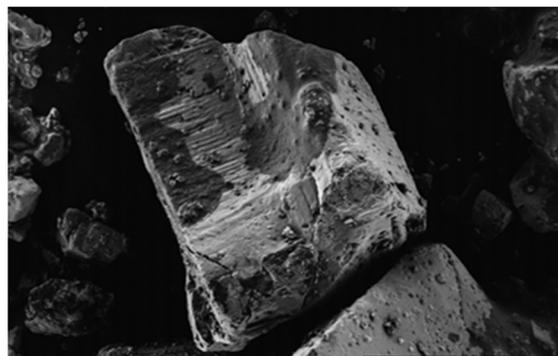


Fig. 1 Scanning electron microscope image of large fractured NaCl crystals partially coated with Na metal. This material was made in a Schlenk flask.¹²

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† Electronic supplementary information (ESI) available: Experimental details, NMR spectra, SEM/EDX images and Powder X-ray diffraction patterns can be found in electronic format. See DOI: <https://doi.org/10.1039/d5mr00039d>



multigram scale.¹³ The Na/NaCl powder prepared by Jones and co-workers was analysed by scanning electron microscopy (SEM; Fig. 1), revealing a wide particle size range, comprised of irregularly shaped crystals lying between 10 and 100 μm . This material must still be treated as a fire hazard when manipulated due to its vigorous decomposition upon exposure to air.

Inspired by the preparation of Na/NaCl in a Schlenk flask, we sought to explore the mechanochemical preparation of Na/NaCl in different loadings (5, 10, 20% w/w), with the intent to develop a highly activated source of sodium that is homogeneous and non-pyrophoric. Therefore, we combined finely divided sodium with sodium chloride in the appropriate ratio, in a stainless-steel 50 ml milling jar containing 7 mm diameter stainless-steel balls (4.1 g each) under argon and milled them together using a planetary ball mill (Retsch PM100). In our hands, we found that a black free-flowing powder of 5% w/w Na/NaCl, which was non-pyrophoric upon exposure to air, could consistently be obtained after 16 hours at 500 rpm. Chen and co-workers report a similar mechanochemical approach,¹⁴ though they describe the formation of a material which was pyrophoric upon exposure to air. We found that if the sodium and sodium chloride were milled together for <4 hours, the sodium was not fully dispersed, which could explain the pyrophoric nature noted by Chen. To prepare 10% w/w Na/NaCl a second portion of sodium was added to the reaction mixture and milled for an additional two hours. Two further portions could subsequently be added to the 10% w/w Na/NaCl material and milled for two hours a time to access 20% w/w Na/NaCl as a free-flowing black powder (Fig. 2).

Intrigued by the free-flowing nature of Na/NaCl, we were curious to survey the homogeneity. Therefore, we analysed the mechanochemically prepared Na/NaCl as well as the equivalent material made *via* Jones' procedure in a Schlenk flask by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). Jones reports a wide particle size range, comprised of irregularly shaped crystals lying between 10 and 100 μm ,¹³ similarly, when analysing the 5% w/w Na/NaCl we prepared in a Schlenk flask, we observed large crystals of up to 200 μm in diameter. In comparison, the mechanochemically prepared material comprises of particulates of <10 μm and

clearly bears a different morphology, where the larger particulates are aggregates of smaller powder-like components and no longer possess a microcrystalline structure (Fig. 3). In addition, the Na is much more dispersed and a greater degree of homogeneity is present within the material. This is supported by EDX imaging, which shows that in the case of the mechanochemically prepared Na/NaCl, both Na and Cl are present homogeneously throughout the material, whilst in the Schlenk made material there are regions where the free sodium and sodium chloride are not completely integrated (see ESI page S8†).

To confirm the change in morphology was not a result of sodide formation (Na^-), for which there is mechanochemical precedent,¹⁵ we turned to solid-state (SS) NMR spectroscopy (Fig. S20–S22†). The ^{23}Na SS-NMR spectrum exhibits two distinct resonances at δ_{Na} 1131.6 and 6.8 ppm, consistent with the presence of Na and NaCl respectively,^{16,17} with a corresponding single resonance observed in the ^{35}Cl SS-NMR spectrum, identified as NaCl (δ_{Cl} -39.2). Similarly, powder X-ray diffraction (PXRD) analyses were performed on the mechanochemically micronised 5% w/w Na/NaCl as well as NaCl as a reference. Upon overlaying the two diffraction patterns, the major component of our material can clearly be identified as NaCl, exhibiting an identical diffraction pattern as to that of the NaCl reference (Fig. S27†). In addition, a secondary minor component was observed, exhibiting 2θ values of 29.41, 38.15 and 62.50°, consistent with the presence of Na metal.¹⁸ Overall, these analyses support our supposition that the mechanochemically prepared Na/NaCl is a homogeneous physical mixture of only Na and NaCl, which has been mechanochemically micronized to significantly reduce the particle size.

To investigate the effects of the morphology of the Na/NaCl powder produced by ball-milling, we set out to explore its use as a reducing agent. Jones and co-workers have previously reported the use of the Schlenk prepared Na/NaCl as a reductant towards β -diketaminato magnesium(II) iodide complexes, $[(^{\text{Ar}}\text{BDI})\text{MgI}(\text{OEt}_2)]$ ($\text{BDI} = \text{HC}\{(\text{Me})\text{CNAr}\}_2$; Ar = Dipp, 2,6-*i*-Pr₂C₆H₃; Mes, 2,4,6-CH₃C₆H₂), affording the Dipp and Mes Mg(I) reagents over the course of 2 days in 83 and 60% yield, respectively in toluene/ether. Similarly, Harder and co-workers report the reduction of $[(^{\text{Dipp}}\text{BDI})\text{MgI}(\text{OEt}_2)]$ within a mixer

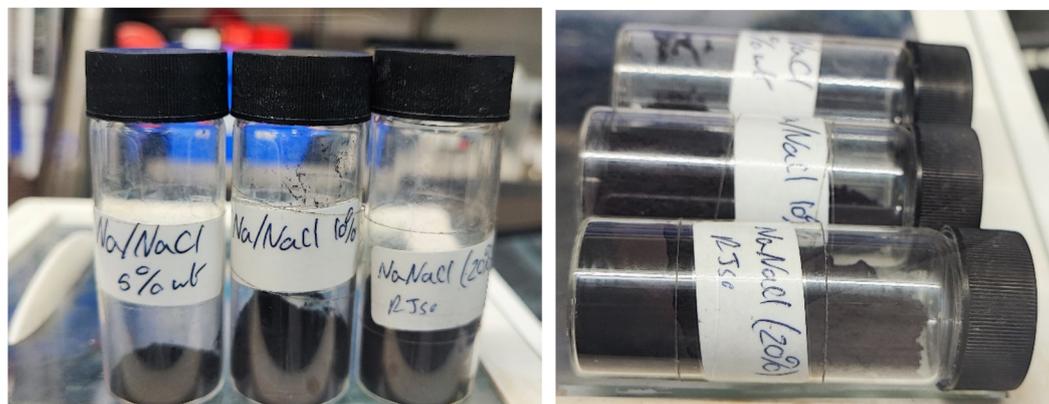


Fig. 2 Free-flowing black powders of 5, 10, 20% w/w Na/NaCl, respectively, made *via* planetary ball-milling.



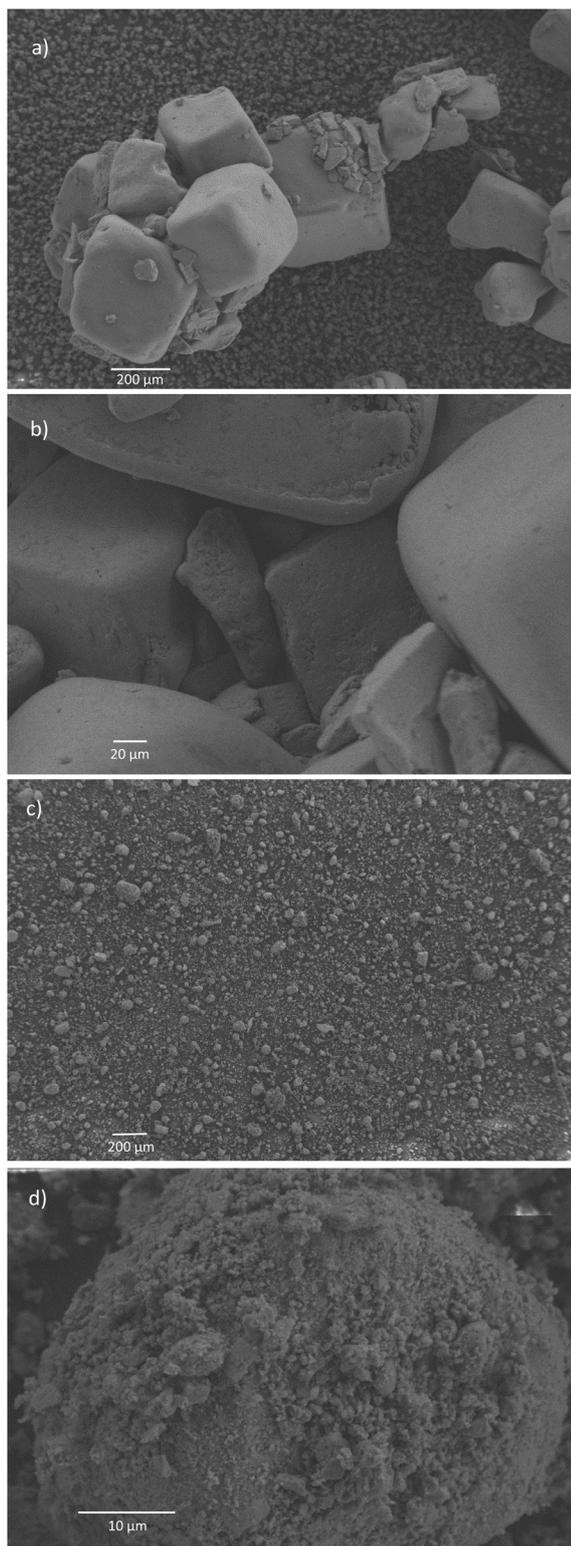


Fig. 3 SEM images of (a) Na/NaCl prepared in a Schlenk flask, 200 μm scale bar. (b) Na/NaCl prepared in a Schlenk flask, 20 μm scale bar. (c) Na/NaCl prepared in a ball mill, 200 μm scale bar (d) Na/NaCl prepared in a ball mill, 10 μm scale bar.

mill (ULTRA-TURRAX[®]), using Na/NaCl prepared in a Schlenk flask.¹⁹ They describe the *in situ* generation of $[(\text{BDI})\text{Mg}^{\bullet}]$ radicals in the solid state, which readily react with aromatic solvents

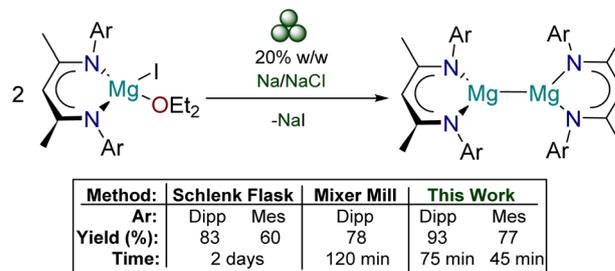


Fig. 4 Mechanochemical preparation of $[\text{ArBDIMg}]_2$, Ar = Dipp, Mes. Alongside a table comparing the reaction outcomes when using Na/NaCl prepared in a Schlenk flask and when the reaction is performed in a mixer or planetary ball mill.

upon extraction, to afford $[(\text{DippBDI})\text{Mg}]_2$ and $[(\text{DippBDI})\text{Mg}(\text{C}_6\text{H}_6)\text{Mg}(\text{DippBDI})]$. Alternatively, if the extraction is performed in pentane, they were able to isolate $[(\text{DippBDI})\text{Mg}]_2$ in 78% yield after milling for 2 hours.

With this in mind, the reduction of $[(\text{ArBDI})\text{MgI}(\text{OEt}_2)]$ (Ar = Dipp, Mes) using our mechanochemically micronised Na/NaCl, serves as an ideal reaction for comparison against Na/NaCl prepared in a Schlenk flask as well as between mixer and planetary ball milling approaches. Therefore, in this instance we milled $[(\text{ArBDI})\text{MgI}(\text{OEt}_2)]^{20}$ and 20% w/w Na/NaCl inside a 50 ml milling jar (Fig. 4), fitted with 7 stainless-steel milling balls (7 mm diameter; 4.1 g each) under argon at 500 rpm in a Retsch PM100 planetary ball mill, observing quantitative conversion after just 75 and 45 minutes, *via* ^1H NMR spectroscopy (Fig. S23–S25[†]). $[(\text{DippBDI})\text{Mg}]_2$ and $[(\text{MesBDI})\text{Mg}]_2$ were extracted into toluene and ether respectively, without any evidence of solvent activation and were isolated in 93 and 77% yield. Comparison with traditional solvated reactions reported by Jones and co-workers ($[(\text{DippBDI})\text{Mg}]_2$ in 83% yield, 2 days, 10 : 1 toluene/ether; $[(\text{MesBDI})\text{Mg}]_2$ in 60% yield, 2 days, 12 : 1 toluene/ether) demonstrates a decrease in reaction time, and minimisation of deleterious side-reactions resulting in improved yield. Direct comparison with the mixer mill route of Harder and co-workers ($[(\text{DippBDI})\text{Mg}]_2$ in 78% yield, 2 hours mixing, ULTRA-TURRAX[®]) demonstrates not only a significant reduction in reaction time but an increase in isolated yield, without the concern of solvent activation upon extraction. This study highlights the difference between Schlenk and mechanochemically prepared materials as well as the distinction between mixer and planetary ball milling approaches, which have a significant impact upon the reaction outcome.

Conclusions

In summary, we have mechanochemically micronised Na and NaCl together to afford a homogeneous mixture of Na/NaCl at three different loadings (5, 10, 20% w/w), affording in each case a free-flowing powder, which upon exposure to air or water does not catch fire as a consequence of the uniform distribution of reactive sodium dispersed within inert salt. This material has been characterised by SEM/EDX, demonstrating small particle sizes ($<10 \mu\text{m}$) and high homogeneity, whilst SS-NMR and PXRD



confirm the presence of only Na and NaCl. This material serves as a highly activated source of sodium to reduce $[(^{\text{Ar}}\text{BDI})\text{MgI}(\text{OEt}_2)]$ to $[(^{\text{Ar}}\text{BDI})\text{Mg}]_2$ (Ar = Dipp, Mes), *via* ball milling with a Retsch PM100 in 75 and 45 minutes, respectively. The highly dispersed sodium on sodium chloride shows rapid, selective reactivity but is readily handled, and in this case we propose the salt acts in a fashion analogous to solvent, increasing the number of reactive sites whilst modulating reactivity and acting as a sink for energy released in the reaction. We are now extending our investigation, using micronised Na/NaCl in a broader swathe of reduction reactions as well as in organic transformations.

The authors acknowledge EPSRC (EP/X01181X/1, 'Molecular s-block Assemblies for Redox-active Bond Activation and Catalysis: Repurposing the s-block as 3d-elements'). DJL thanks the Royal Society for the support of a University Research Fellowship. We thank the UK high-field solid-state NMR facility at the University of Warwick (Dr Dinu Luga) and Henry Royce Institute (Dr Phani Karamched) at the University of Oxford for use of their facilities.

Data availability

Experimental details, NMR spectra, SEM/EDX images and Powder X-ray diffraction patterns can be found in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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