**RESEARCH ARTICLE**

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# Gram-Scale Synthesis, Isolation and Characterisation of Sodium Organometallics: *n*BuNa and NaTMP

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To the memory of *Jack Dunitz*

Organolithium compounds represent one of the most widely utilised commodity reagents in synthetic chemistry. However, their analogues with the heavier alkali-metal sodium are much less utilised and their reactivity is less understood. Recent studies have shown the excellent potential of organosodium reagents in synthesis, finding widespread applications in cornerstone organic transformations such as deprotonative metalation, metal-halogen exchange or Pd catalysed C−C bond formation. However, detailed procedures for the preparation of these compounds are scarce. Therefore, we report a step-by-step synthesis of two organosodium reagents: *n*BuNa and NaTMP (TMP = 2,2,6,6-tetramethylpiperidide) as key building blocks in sodium organometallics, which allows the easy access to other sodiated compounds and enables chemical reactivity that is not feasible with organolithium compounds. Both can be prepared in high yields (up to 92%), and isolated as pure solids that can be stored under argon for long periods of time (up to six months) without observed degradation. Here we further illustrate the synthetic utility of NaTMP as an efficient metalating reagent for 1-methoxynaphthalene which can be subsequently employed in *Suzuki–Miyaura* couplings, as well as a precursor for sodium zincate [(TMEDA)NaZn(TMP)Et$_2$], which has been obtained by co-complexation of NaTMP, ZnEt$_2$ and TMEDA in hexane, for which a structure has been established by X-ray crystallography.

**Keywords:** amide base, gram-scale, organometallics, sodium, synthetic methods.

## Introduction

Pioneered more than a hundred years ago, organolithium reagents are amongst the most widely used polar organometallic reagents in synthesis, finding widespread applications in industry and academic research.[1] Contrastingly, while organosodium compounds were reported 50 years earlier,[2] their use has lagged behind their lighter lithium congeners.[3] This can be partly attributed to the notorious insolubility of organosodium compounds in hydrocarbon solvents combined with their incompatibility with ethereal solvents in which they can rapidly undergo degradation.[4] With a growing emphasis on sustainability in organometallic chemistry and the superior reactivity expected for this type of reagents, the interest in the synthesis and reactivity of organosodium compounds has significantly increased in the recent years.[5] Within the area of deprotonative metalation, several studies have disclosed the enormous potential of sodium amides,[6] as well as bimetallic systems which combine Na with a another divalent metal such sodium zincates,[7−9] magnesiates,[10−12] and ferrates.[13−15] Sodium alkyls can also engage in other cornerstone reactions such as Na-halogen exchange,[16] or palladium-catalysed cross-couplings.[17,18] These recent innovations have highlighted the importance of stablishing straightforward synthetic routes to access suitable organosodium precursors. Recently employed methods involve the

use of elemental sodium which include the *in situ* generation of an alkyl sodium base in flow,[16,19] as well as employing a fine sodium dispersion.[17,20] While synthetically useful, these methods also have some drawbacks: the sodiated intermediates are often difficult to isolate or characterise, excess sodium metal is usually needed, and the sodium packed-bed reactors or the finely divided sodium dispersions employed in these studies are still not widely commercially available. The classical approach to the synthesis of organosodium reagents in a laboratory scale has been the reaction of a sodium alkoxide with a commercially available organolithium reagent,[21,22] with the insoluble organosodium product simply separated from the soluble lithium alkoxide by-product to afford the pure organosodium.[23,24] The bases *n*BuNa and NaTMP are known precursors to a plethora of well-established sodiated compounds including sodium containing bimetallic bases, as well as homometallic sodium reagents.[25–30] They can be prepared through the alkali-metal exchange technique,[21–24] however, a detailed literature protocol describing their synthesis is currently lacking. Herein, we seek to report a detailed synthesis of both *n*BuNa and NaTMP on a multigram scale, from easily available commercial reagents, affording the sodiated precursors without the need for further purification. We also demonstrate the synthetic utility of NaTMP to promote the regioselective borylation of 1-methoxynaphthalene and to access heterobimetallic sodium zincate [(TMEDA)NaZn(TMP)Et$_2$] (**1**).

## Experimental Section

All chemicals used in these procedures are potentially hazardous and reactions must only be carried out by experimentally trained persons wearing full and appropriate PPE. Prior to performing each reaction, a thorough hazard analysis and risk assessment should be carried out regarding each chemical substance, the experimental operation on the scale planned and in the context of the laboratory where the procedures will be carried out. In the case of this procedure, the risk assessment should include (but not necessarily be limited to) an evaluation of the potential hazards associated with the manipulation of *n*BuLi, as well as the proper procedures for carrying out a filtration under inert atmosphere. The substances prepared here are pyrophoric in contact with air (especially in the absence of solvent) and therefore preventive measures must be taken to minimize the risk of fire. We would like to highlight that it is imperative that all

glassware be properly dried prior its use and that all materials that have been in contact with organometallic compounds must be properly quenched (small quantities of organosodium or organolithium reagents can be safely quenched by adding a few millilitres of an 80:20 toluene/$^i$PrOH solution at room temperature, followed by a few millilitres of EtOH and H$_2$O). Waste disposal should be performed safely and in accordance with local regulations.

*Synthesis of* n*BuNa (Scheme 1)*

An oven-dried and argon-filled *Schlenk* flask containing a *Teflon*-coated magnetic stirrer was charged with sodium *tert*-butoxide (3.84 g, 40 mmol, CAS: 865-48-5, 99%, *Thermo Fisher Scientific*) and connected to a *Schlenk* line. The glass stopper on the *Schlenk* flask was then replaced with a rubber septum, and dry hexane (75 mL, purified with an *SPS* system and further dried by storage under activated molecular sieves for at least 24 h) was added to form a fine, white suspension under stirring which was then cooled to 0 °C with an ice bath. *n*BuLi (25 mL, 40 mmol, CAS: 109-72-8, 1.6 M in hexanes, *Sigma – Aldrich*) was added dropwise with a disposable syringe to form a thick, white suspension (*Scheme 1*). The mixture was allowed to reach room temperature, the rubber septum replaced with a glass stopper, and the mixture was stirred overnight. The next day (*Figure 1,A*), the glass stopper was replaced with a rubber septum, and the suspension was then transferred under argon to an oven-dried glass *Schlenk*-frit using a PTFE canula (inner diameter of 1.0 mm and an outer diameter of 2.5 mm) and applying positive argon pressure (*Figure 1,B*).[1] The white solid was then filtered through the frit, and the filter cake washed with dry hexane (2×10 mL, *Figure 1,C*). Under argon flow, the *Schlenk* flask containing the lithium *tert*-butoxide in hexane was removed and

NaO$^t$Bu + *n*BuLi → *n*BuNa + LiO$^t$Bu
(Hexane, 0 °C to r.t., 16 h)
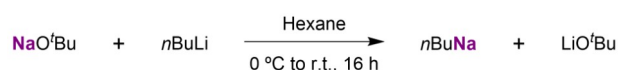
**Scheme 1.** Preparation of *n*BuNa.

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[1] Further details of how to perform a canula transfer can be found at the *Schlenk* Line Survival Guide: https://schlenklinesurvivalguide.com/. Alternatively, the filtration can be performed by directly connecting the flask containing the reaction mixture to the glass frit and carefully turning the set-up 180°. However, in this case, additional washings cannot be performed.
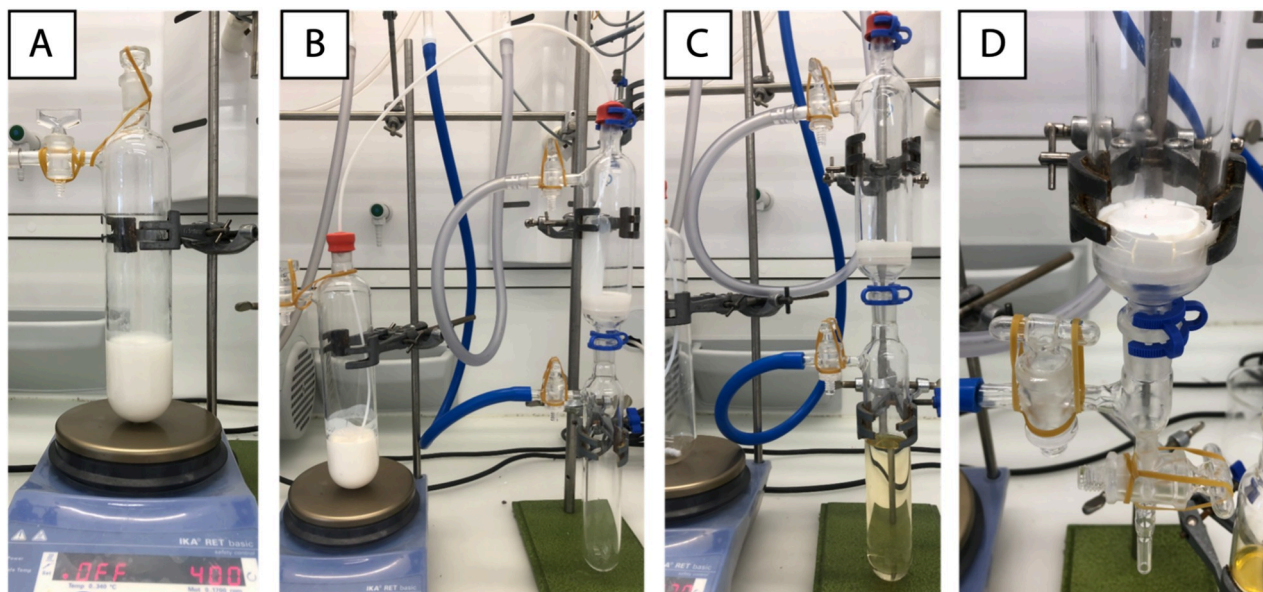
**Figure 1.** Experimental set-up for the synthesis of *n*BuNa. A: reaction mixture after overnight stirring; B: canula transfer of the reaction mixture to a glass *Schlenk*-frit ; C: reaction set-up after filtration and washings with fresh solvent; D: *Schlenk*-frit under vacuum to obtain dry *n*BuNa.

quenched with isopropanol, the glass *Schlenk*-frit containing the white solid was connected to the *Schlenk* line and placed under vacuum for 2 h (*Figure 1,D*). The dry solid could then be entered into an argon filled glovebox (under vacuum, using the glass frit) and transferred into a scintillation vial for storage in the glovebox. Analytically pure *n*BuNa (typically 2.60 g, 80% yield) was obtained as a white solid (see below, *Figure 3*, *left*), which can be kept in the glovebox for up to two weeks at room temperature or up to six months in a freezer at −30 °C without apparent decomposition. *n*BuNa is not soluble in $C_6D_6$, but good NMR spectra can be obtained when two drops of THF are added to a suspension of *n*BuNa in $C_6D_6$: $^1$H-NMR (300 MHz, $C_6D_6$): 2.14–1.95 (*m*, 2 H); 1.86–1.67 (*m*, 2 H); 1.28 (*t*, *J*=7.3, 3 H); −0.54 (*t*, *J*= 8.6, 2 H). $^{13}$C-NMR (75 MHz, $C_6D_6$): 36.5; 34.5; 14.2; 9.2. Satisfactory elemental analysis could be obtained: Anal. calc. for $C_4H_9Na$: C 59.98, H 11.33; found: C 59.90, H 11.42.

### Synthesis of NaTMP (Scheme 2)

In an argon-filled glovebox, *n*BuNa (2.60 g, 32.5 mmol) was transferred into an oven-dried *Schlenk* flask equipped with a *Teflon* coated magnetic stirrer and connected to a *Schlenk* line. The glass stopper on the *Schlenk* flask was then changed to a rubber septum, and dry hexane (60 mL, purified with an *SPS* system

and further dried by storage under activated molecular sieves for at least 24 h) was added through a canula to form a fine, white suspension under stirring which was then cooled to 0 °C with an ice bath. With continuous, vigorous stirring TMP(H) (5.5 mL, 32.5 mmol, CAS: 768-66-1, *Fluorochem*, 99%, dried over $CaH_2$, distilled and stored over molecular sieves prior to use) was added dropwise, affording a pale-yellow suspension, which was warmed up to room temperature (*Scheme 2*). The rubber septum was replaced with a glass stopper and the mixture was stirred overnight (*Figure 2,A*). The next day, using the same procedure that has been described for the filtration of *n*BuNa (see above), the suspension was transferred under argon to an oven-dried glass *Schlenk*-frit, with a PTFE canula. The solid was then filtered, the filter cake washed with dry hexane (3×5 mL) and dried under vacuum on the *Schlenk* line for 2 h (*Figure 2,B*). The resultant off-white solid was then transferred and stored in an argon-filled glovebox (*Figure 3*, right). The obtained NaTMP (4.85 g, 92% yield) can be stored at room temperature for up to three months or up to six months in a freezer at −30 °C without apparent decomposition. NaTMP is
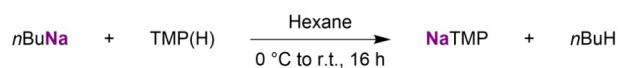
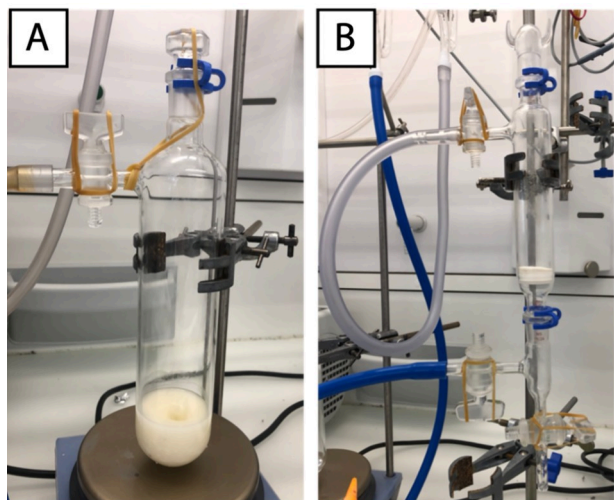

**Scheme 2.** Preparation of NaTMP.

**Figure 2.** Synthesis of NaTMP. A: reaction mixture after overnight stirring; B: NaTMP under vacuum after filtration and washing.



**Figure 3.** Isolated samples in glovebox. Left: *n*BuNa; Right: NaTMP.

poorly soluble in $C_6D_6$, which can be solved by the addition of two drops of THF. However, it decomposes quickly in presence of THF and therefore TMP(H) is present in the $^1$H-NMR spectrum. $^1$H-NMR (300 MHz, $C_6D_6$): 2.15–2.01 (*m*, 2 H); 1.71–1.57 (*m*, 4 H); 1.41 (*s*, 12 H). $^{13}$C-NMR (75 MHz, $C_6D_6$): 52.7; 42.8; 38.1; 21.4. Anal. calc. for $C_9H_{18}NNa$: C 66.22, H 11.11, N 8.58; found: C 65.60, H 11.18, N 8.05.
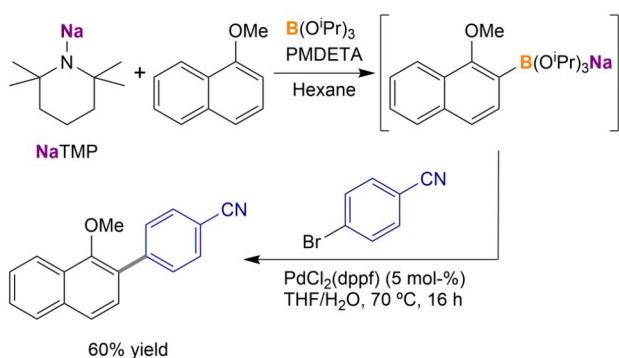
## Discussion

The higher reactivity and lower solubility of organosodium compounds have traditionally precluded their use and study, favouring the development of lithium organometallics for synthetic purposes. However, sodium bases, such as NaTMP, hold a great potential for accessing new synthetic landscape. Recently, our
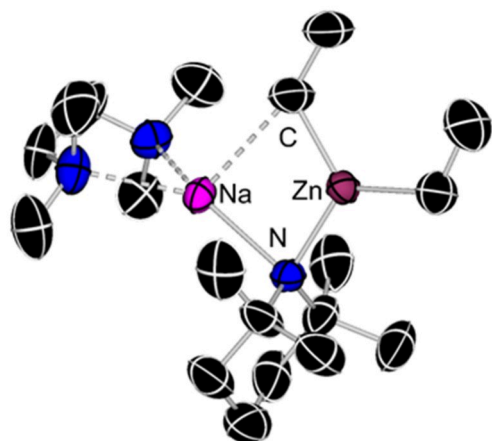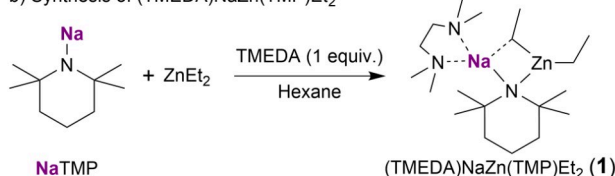
laboratory has reported the combination of this base with the tridentate donor PMDETA (*N,N,N',N'',N''*-pentamethyldiethylenetriamine) and B(O$^i$Pr)$_3$ for the selective deprotonative borylation of inactivated arenes,[31] which could be cross-coupled to give a new versatile route to the synthesis of biaryl motifs. Here, we illustrate this approach with 1-methoxynaphthalene, which can be easily borylated and directly coupled with an aryl bromide to obtain the corresponding biaryl product in a 60% isolated yield (*Scheme 3,a*). While NaTMP alone fails to deprotonate 1-methoxynaphthalene in satisfactory yields, in the presence of PMDETA and B(O$^i$Pr)$_3$ it forms the corresponding sodium borate, which is active in the transmetallation to palladium and allows the *Suzuki–Miyaura* coupling without the need of an added base. Moreover, alkali-metal amides can form ate-complexes with organozinc reagents, exhibiting higher degrees of reactivity and selectivity than their monometallic components in metallation reactions.[32–35] In this case, we could obtain an unreported sodium zincate [(TMEDA)NaZn(TMP)Et$_2$] (*Scheme 3,b*; **1**) by co-complexing the prepared NaTMP with commercially available ZnEt$_2$ in the presence of the bidentate *Lewis* donor TMEDA in a 62% yield. The bimetallic constitution of **1** was confirmed by X-ray crystallographic studies (*Scheme 3,b*).[36] Displaying a contacted ion-pair structure, the Zn and Na atoms are connected by the amide TMP and one of the ethyl groups, closing a four-membered {NaNZnC} ring. The remaining ethyl binds terminally to Zn whereas Na completes its coordination sphere by bonding to a chelating TMEDA ligand. The Na–N$_{TMP}$ distance of 2.379(3) Å is, as expected, slightly shorter than the Na–N$_{TMEDA}$ bond distances (2.482(4) and 2.471(4) Å). This structural motif is similar to those reported for related bis(alkyl) sodium TMP-zincates.[8] If we compare the Na–N$_{TMP}$ distance with other related complexes, (TMEDA)NaZn(TMP)$^t$Bu$_2$ (Na–N$_{TMP}$: 2.432(2) Å),[36] or (TMEDA·NaTMP)$_2$ (Na–N$_{TMP}$: 2.4273(18) and 2.5420(17) Å),[37] a slightly shorter Na–N$_{TMP}$ distance is observed in **1**, likely due to the presence of less bulky ethyl groups at the zinc centre. Compound **1** was also characterised in $C_6D_6$ solution by $^1$H- and $^{13}$C-NMR. These spectra showed a single set of signals for the ethyl groups (at 0.38 and 1.97 ppm) which is consistent with a fast fluxional process which interconverts both ethyl groups, probably by cleavage of Na–C bond and rotation across the Zn–N bond.

Overall, organosodium chemistry not only has the potential to replace the synthetic space now governed by lithium, but it could feasibly surpass it to achieve

**Scheme 3.** Examples of synthetic utility of NaTMP. a) NaTMP Mediated borylation and cross coupling of 1-methoxynaphthalene. b) Synthesis and molecular structure of (TMEDA)Na(TMP)ZnEt$_2$ (**1**) with 50% probability displacement ellipsoids. All H-atoms have been omitted. The unit cell contains two identical structures, but just one is shown for clarity. PMDETA: *N,N,N′,N″,N″*-pentamethyldiethylenetriamine. TMEDA: *N,N,N′,N′*-tetramethylethylenediamine.

transformations that are unconceivable using the classic and widely utilised organolithium methods. For this reason, a safe and practical synthesis of organosodium compounds in a laboratory scale is necessary to aid with its continuous growth and expansion. Even though this synthetic procedure makes use of *n*BuLi, we believe that the synthesis reported for *n*BuNa and NaTMP can be achieved safely with easily available commercial reagents, in a multigram scale and with

high purity, which will allow a rapid expansion of the use of organosodium in research laboratories for synthetic purposes.

## Conclusions

A detailed procedure for the synthesis of *n*BuNa and NaTMP is described, making use of commercially available reagents and obtaining the pure compounds as solids in a multigram scale. We make use of the solubility of LiO*t*Bu in hexanes to favour the formation of the insoluble alkyl sodium, which can be easily isolated by filtration under argon. *n*BuNa is then used to access NaTMP by the deprotonation of the parent amine, in a straightforward manner and in high yields. We expect that this report will expand the access to and the use of organosodium reagents in synthetic transformations, allowing the growth of this emerging field.

## Supplementary Material

Supporting information for this article is available on the WWW under https://doi.org/10.1002/hlca. 202200060. The cif file of (TMEDA)Na(TMP)ZnEt$_2$ (**1**) has been deposited at the CCDC (Deposition number CCDC-2173670). These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe.

## Acknowledgements

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

## Author Contribution Statement

*A. T.* and *D. E. A.* performed the experiments. *E. H.* conceived and supervised the work. All authors collaborated in the writing of the article and approved its final version.

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