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Solvent-free anhydrous Li⁺, Na⁺ and K⁺ salts of [B(3,5-(CF₃)₂C₆H₃)₄]⁻, [BAr^F₄]⁻. Improved synthesis and solid-state structures†

Antonio J. Martínez-Martínez * and Andrew S. Weller *

A modified, convenient, preparation of solvent-free, anhydrous, Li⁺, Na⁺ and K⁺ salts of the ubiquitous [BAr^F₄]⁻ anion is reported, that involves a simple additional recrystallisation step. Anhydrous Na[BAr^F₄], K[BAr^F₄], and [Li(H₂O)][BAr^F₄], were characterised by single-crystal X-ray diffraction.

The use of weakly coordinating anions¹ for the stabilisation of reactive low, or latent-low, coordinate cationic metal and main-group complexes now plays a central role in synthesis and catalysis,² both in solution and in the solid-state.³ The anion [BAr^F₄]⁻ (Ar^F = 3,5-(CF₃)₂C₆H₃),⁴ Fig. 1, enjoys particular utility amongst the small suite of common anions used, e.g. [B(C₆F₅)₄]⁻,⁵ [Al(OR^F)₄]⁻ (R^F = fluoroalkyl),⁶ [B(3,5-Cl₂C₆H₃)₄]⁻,⁷ and [CB₁₁X₁₂]⁻ (X = halogen)⁸ derivatives. A combination of synthetic accessibility, desirable properties of the resulting salts, *i.e.* solubility and crystallinity, and simple NMR-reporter groups, *i.e.* solubility and crystallinity, and simple NMR-reporter groups, make [BAr^F₄]⁻ the go-to choice for many organometallic, main-group and catalytic applications. Very often such reactive species are generated by metathesis with the group 1 salts M[BAr^F₄] (M = Li, Na, K), although alternative activating cations are also known, e.g. [(Et₂O)₂H][BAr^F₄] (Taubé and Brookhart)⁹ and [Ph₃C][BAr^F₄] (Boudjouk).¹⁰ The alkali salts have also been used as polymerisation initiators,¹¹ in electrochemistry,¹² as an additive in lithium ion batteries,¹³ in ionic liquids,¹⁴ and for the extraction of aqueous lanthanide ions.¹⁵ While considered to be non-interacting, under appropriate conditions [BAr^F₄]⁻ can coordinate to metal centres through its arene ring,^{16,3a} or *via* metal...F-CF₂ interactions.¹⁷ It can also undergo B-C bond cleavage.¹⁸

The synthesis and use, as a phase transfer catalyst,⁴ of the [BAr^F₄]⁻ anion was first reported by Kobayashi in 1981, fol-

lowed by the preparation of hydrated [Na(H₂O)₃][BAr^F₄].¹⁹ Brookhart subsequently reported the synthesis of Na[BAr^F₄], by drying under vacuum and a cold CH₂Cl₂ wash.^{9a} Both these preparations used the Grignard reagent 1,3,5-XMg(CF₃)₂C₆H₃ (X = Br, I). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture²⁰ for the preparation of anhydrous Na[BAr^F₄],²¹ but required prolonged drying under vacuum over P₂O₅. Synthetic protocols have been reported for hydrated Li⁺ and K⁺ salts;²² or where the water content has not been reported.²³ To date, the synthesis (Li⁺, K⁺) and structures²⁴ (Li⁺, Na⁺, K⁺) of anhydrous M[BAr^F₄] have not been reported in the open literature. Such anhydrous salts are of importance when using the [BAr^F₄]⁻

A Generation of a vacant site using M[BAr^F₄]



B Publications reporting the use of [BAr^F₄]⁻ (period 1981–2018)

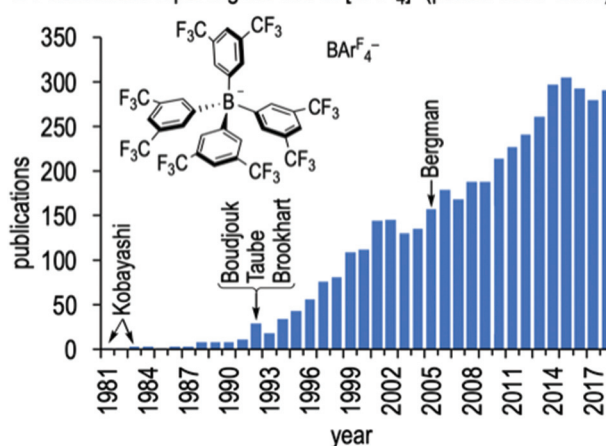


Fig. 1 (A) Generalised use of the [BAr^F₄]⁻ anion for the generation of low-coordinate metal centres. (B) Number of publications per year reporting use of the [BAr^F₄]⁻ anion. Scifinder CAS (<https://scifinder.cas.org>) accessed 18/12/2018.

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†Electronic supplementary information (ESI) available: Full experimental details, characterisation, NMR and selected crystallographic X-ray data. CCDC 1886445–1886447. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt00235a



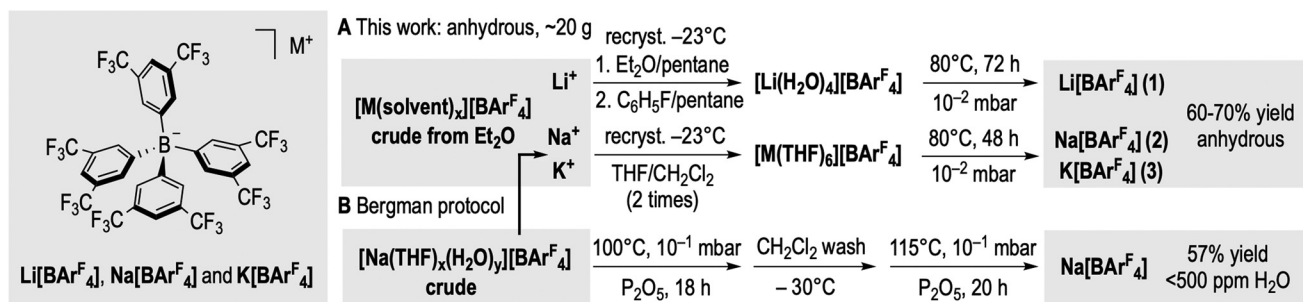


Fig. 2 Preparation and isolation of solvent-free anhydrous Li^+ , Na^+ and K^+ salts of $[\text{BARF}_4]^-$ and comparison with the Bergman synthesis.

anion to access highly Lewis-acidic, and low-coordinate, complexes.²⁵

We now detail here a robust multigram protocol to prepare solvent-free anhydrous Li^+ , Na^+ and K^+ salts of the $[\text{BARF}_4]^-$ anion on ~20 g scale in 60–70% yields, by adding a simple recrystallisation step of the crude product prior to drying under vacuum. As well as being synthetically expedient, this allows for the structures of solvent-free anhydrous Na^+ and K^+ , and mono aquo Li^+ salts of $[\text{BARF}_4]^-$ to be determined.

Following a modified Kobayashi synthesis, Li^+ , Na^+ and K^+ salts of $[\text{BARF}_4]^-$ (Fig. 2) were prepared from 1,3,5- $\text{BrMg}(\text{CF}_3)_2\text{C}_6\text{H}_3/\text{BF}_3$ followed by treatment with the aqueous alkali metal carbonate of choice (M_2CO_3 , $\text{M} = \text{Li}^+$, Na^+ and K^+). Extraction into diethyl ether gave the corresponding crude $[\text{M}(\text{solvent})_x][\text{BARF}_4]$ (solvent = H_2O and/or Et_2O). Our key improvement is a subsequent double recrystallisation step to yield the corresponding pure solvent-complexes in high yield. $[\text{Li}(\text{solvent})_x][\text{BARF}_4]$ was successively recrystallised from undried diethyl ether/*n*-pentane and then undried fluorobenzene/*n*-pentane at -23°C to give $[\text{Li}(\text{H}_2\text{O})_4][\text{BARF}_4]$ ^{22a} as determined by NMR spectroscopy and single-crystal X-ray diffraction (ESI). Anhydrous $\text{Li}[\text{BARF}_4]$ **1** was then conveniently obtained as a highly hygroscopic off-white solid (64% yield) after drying under dynamic vacuum (10^{-2} mbar) at 80°C for 72 h. Shorter drying times (24 h) gave $[\text{Li}(\text{H}_2\text{O})][\text{BARF}_4]$ **4**. Using $[\text{Li}(\text{H}_2\text{O})_4]^+$ is crucial, as any bound ether results in decomposition on drying. Anhydrous $\text{Na}[\text{BARF}_4]$, **2** (68%, white solid), and $\text{K}[\text{BARF}_4]$, **3** (58%, off-white solid), were obtained from drying the pure THF solvates $[\text{M}(\text{THF})_6][\text{BARF}_4]$ under vacuum (80°C , 48 h).^{22c} $[\text{M}(\text{THF})_6][\text{BARF}_4]$ were themselves isolated by two consecutive recrystallisations of crude $[\text{M}(\text{solvent})_x][\text{BARF}_4]$ from THF/ CH_2Cl_2 . These two recrystallisation steps ensure high purity of the final anhydrous salts. These procedures routinely yield ~20 g of anhydrous hygroscopic Li^+ , Na^+ and K^+ salts of $[\text{BARF}_4]^-$. This method also works for the Bergman synthesis, by recrystallising crude $[\text{Na}(\text{solvent})_x][\text{BARF}_4]$ prior to drying, to give anhydrous $\text{Na}[\text{BARF}_4]$ (12.3 g isolated yield, 58%).

The $[\text{BARF}_4]^-$ salts **1–4** were fully characterised in solution using multinuclear ^1H , ^{11}B , ^{13}C and ^{19}F NMR spectroscopy in THF-*d*₈ (298 K) and ESI-MS, and these data are consistent with previously reported examples (ESI†).^{21,22a,23} Additionally, in the ^7Li NMR spectrum of **1** a single resonance is observed at δ

-0.54 , which shifts to $\delta -0.38$ in **4**. The H_2O ligand in complex **4** is observed at $\delta 4.02$ as a sharp singlet (2 H) in the ^1H NMR spectrum. While elemental analysis did not suggest the presence of water in **1–3**, following Bergman's procedure, ($\eta^5\text{-C}_5\text{H}_5$)₂ZrMe₂ was used to determine H_2O content, using ^1H NMR spectroscopy to measure the thus formed oxo-bridged complex (and CH_4).²¹ No evidence of residual H_2O was observed in any of the dried salts. Importantly, this ^1H NMR titration method confirmed the presence of one molecule of H_2O in **4**.

Single-crystals of solvent-free anhydrous $\text{Na}[\text{BARF}_4]$ **2** and $\text{K}[\text{BARF}_4]$ **3** suitable for X-ray diffraction studies were obtained by slow diffusion of dry *n*-pentane into a solution of the corresponding anhydrous salt in a 1 : 1 mixture of dry $\text{C}_6\text{H}_5\text{F}/\text{CH}_2\text{Cl}_2$ (Fig. 3). For $\text{Li}[\text{BARF}_4]$ **1**, although isolated in bulk in its anhydrous form, its highly hygroscopic nature meant that adventitious moisture present during the recrystallisation process routinely resulted in single crystals of $[\text{Li}(\text{H}_2\text{O})][\text{BARF}_4]$ **4** being isolated (Fig. 3A). Complexes **2**, **3**, and **4** crystallise in the tetragonal space group *P4/n* as contact ion-pairs (Fig. 3A–C). The contents of asymmetric units include 1/4 of the alkali metal and $[\text{BARF}_4]^-$ anion (*S*₄ symmetry), with an additional quarter of one molecule of water for **4**. The $[\text{BARF}_4]^-$ anions dictate the microenvironment around the $[\text{Li}(\text{H}_2\text{O})]^+$, Na^+ and K^+ cations, and eight $[\text{BARF}_4]^-$ anions encapsulate each alkali metal cation through $\text{CF}_3\cdots$ alkali metal interactions forming an essentially cubic environment (Fig. 3D–F). The alkali metal sits in a pseudo body centred position, displaced towards one face of the cube. The Li^+ ion in **4** has a square pyramidal geometry, interacting with CF_3 groups from four distinct $[\text{BARF}_4]^-$ anions [$\text{Li}\cdots\text{F}$, 1.995(7)–2.045(4) Å] with the water molecule [$\text{Li}\cdots\text{O}$, 1.842(8) Å] in the apical position (Fig. 3D). Additional $\text{CF}_3\cdots\text{H}_2\text{O}$ interactions are also present in **4** ($\text{F}\cdots\text{H}$, 1.854(5)–2.09(1) Å). In **2** and **3** the Na^+ and K^+ centres, respectively, interact with a total of eight CF_3 groups from the $[\text{BARF}_4]^-$ anions that surround each cation (Fig. 3E and F) through $\text{M}\cdots\text{F}$ interactions. The increase in the ionic radius,²⁶ in the series $\text{Li} < \text{Na} < \text{K}$, translates into correspondingly longer $\text{M}\cdots\text{F}$ distances [Li : 1.995(7)–2.045(4); Na : 2.473(2)–2.631(3); and K : 2.72(3)–2.74(2) Å].

In conclusion, solvent-free anhydrous $\text{Li}[\text{BARF}_4]$, $\text{Na}[\text{BARF}_4]$ and $\text{K}[\text{BARF}_4]$ has been prepared in multigram scale following a revised protocol, that rests upon a simple recrystallisation



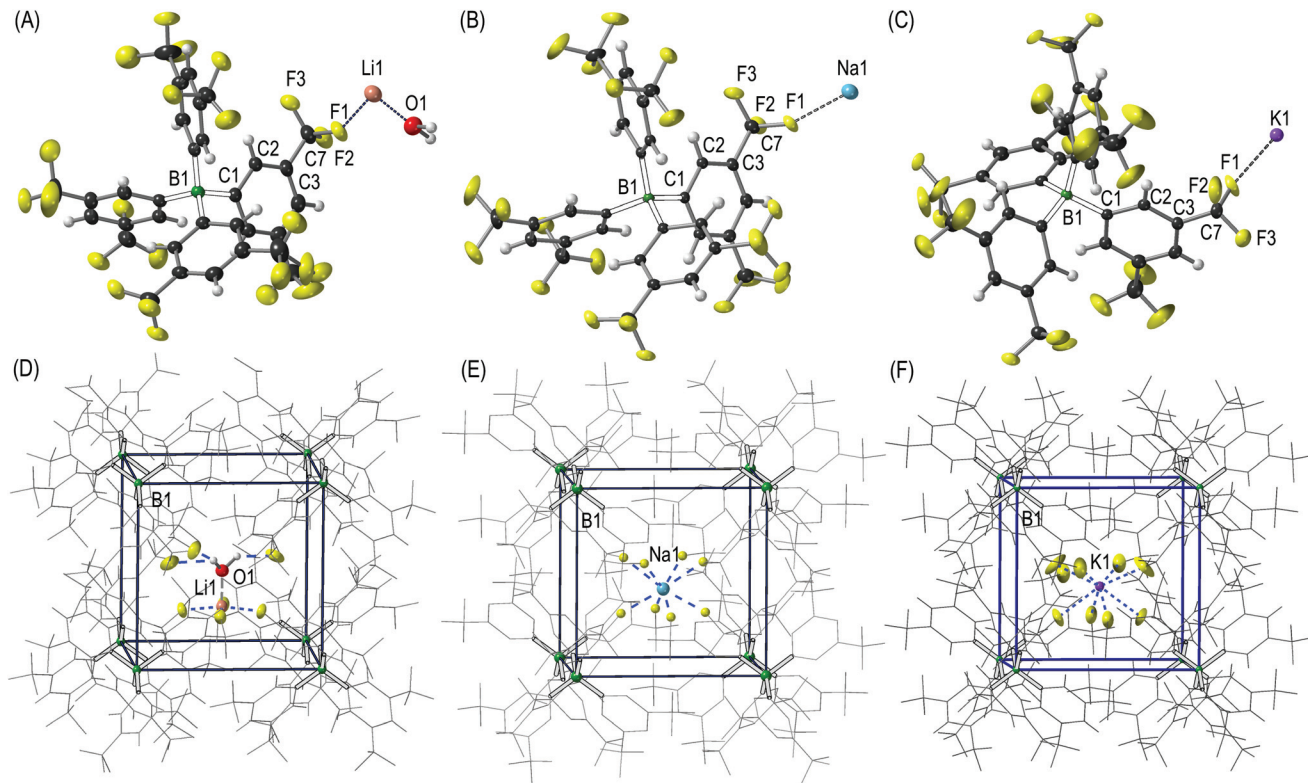


Fig. 3 Molecular structures of (A) $[\text{Li}(\text{H}_2\text{O})][\text{BARF}_4]$ **4**, (B) anhydrous $\text{Na}[\text{BARF}_4]$ **2** and (C) $\text{K}[\text{BARF}_4]$ **3**. Crystal packing diagrams showing the cubic arrangement of $[\text{BARF}_4]^-$ anions around (D) $[\text{Li}(\text{H}_2\text{O})]^+$, (E) Na^+ and (F) K^+ cations. Minor disordered components for the CF_3 groups have been omitted for clarity. Displacement ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles ($^\circ$): **4**, C1–B1 1.641(2), Li1–O1 1.842(8), Li1...F1 2.045(4), Li1...F1a 1.995(7), H1a...F5a' 1.854(5), H1b...F5'' 2.096(10), H1b...F5a'' 1.894(5), C1–B1–C1' 110.41(6), C1–B1–C1''' 107.6(1); **2**, C1–B1 1.639(2), Na1...F1 2.473(2), Na1...F5' 2.631(3), C1–B1–C1'' 110.68(7), C1–B1–C1''' 107.1(2); **3**, C1–B1 1.641(2), K1...F1 2.72(3), K1...F1a 2.74(2), C1–B1–C1' 110.59(7), C1–B1–C1'' 107.3(1). Intermolecular B...B distances (Å): **4**, 9.51755(7) and 9.66072(13); **2**, 9.44044(10) and 9.3899(2); and **3**, 9.53420(15) and 9.4747(5).

step. Our method stands by its simplicity to obtain the Li^+ , Na^+ and K^+ salts of the $[\text{BARF}_4]^-$ anion and high purity. This allows for the characterisation of these salts by single-crystal X-ray diffraction. Given the importance of these salts in synthesis and catalysis we hope the community finds these improvements useful.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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