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Solvent-free anhydrous Li^+ , Na^+ and K^+ salts of $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$, $[\text{BAr}^{\text{F}}_4]^-$. Improved synthesis and solid-state structures†

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A modified, convenient, preparation of solvent-free, anhydrous, Li^+ , Na^+ and K^+ salts of the ubiquitous $[\text{BAr}^{\text{F}}_4]^-$ anion is reported, that involves a simple additional recrystallisation step. Anhydrous $\text{Na}[\text{BAr}^{\text{F}}_4]$, $\text{K}[\text{BAr}^{\text{F}}_4]$, and $[\text{Li}(\text{H}_2\text{O})][\text{BAr}^{\text{F}}_4]$, 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 $[\text{BAr}^{\text{F}}_4]^-$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$),⁴ Fig. 1, enjoys particular utility amongst the small suite of common anions used, *e.g.* $[\text{B}(\text{C}_6\text{F}_5)_4]^-$,⁵ $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ ($\text{R}^{\text{F}} = \text{fluoroalkyl}$),⁶ $[\text{B}(3,5\text{-Cl}_2\text{C}_6\text{H}_3)_4]^-$,⁷ and $[\text{CB}_{11}\text{X}_{12}]^-$ ($\text{X} = \text{halogen}$)⁸ derivatives. A combination of synthetic accessibility, desirable properties of the resulting salts, *i.e.* solubility and crystallinity, and simple NMR-reporter groups, make $[\text{BAr}^{\text{F}}_4]^-$ 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 $\text{M}[\text{BAr}^{\text{F}}_4]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$), although alternative activating cations are also known, *e.g.* $[(\text{Et}_2\text{O})_2\text{H}][\text{BAr}^{\text{F}}_4]$ (Taubé and Brookhart)⁹ and $[\text{Ph}_3\text{C}][\text{BAr}^{\text{F}}_4]$ (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 $[\text{BAr}^{\text{F}}_4]^-$ 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 $[\text{BAr}^{\text{F}}_4]^-$ anion was first reported by Kobayashi in 1981, fol-

lowed by the preparation of hydrated $[\text{Na}(\text{H}_2\text{O})_3][\text{BAr}^{\text{F}}_4]$.¹⁹ Brookhart subsequently reported the synthesis of $\text{Na}[\text{BAr}^{\text{F}}_4]$, by drying under vacuum and a cold CH_2Cl_2 wash.^{9a} Both these preparations used the Grignard reagent $1,3,5\text{-XMg}(\text{CF}_3)_2\text{C}_6\text{H}_3$ ($\text{X} = \text{Br}, \text{I}$). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture²⁰ for the preparation of anhydrous $\text{Na}[\text{BAr}^{\text{F}}_4]$,²¹ but required prolonged drying under vacuum over P_2O_5 . 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 $\text{M}[\text{BAr}^{\text{F}}_4]$ have not been reported in the open literature. Such anhydrous salts are of importance when using the $[\text{BAr}^{\text{F}}_4]^-$

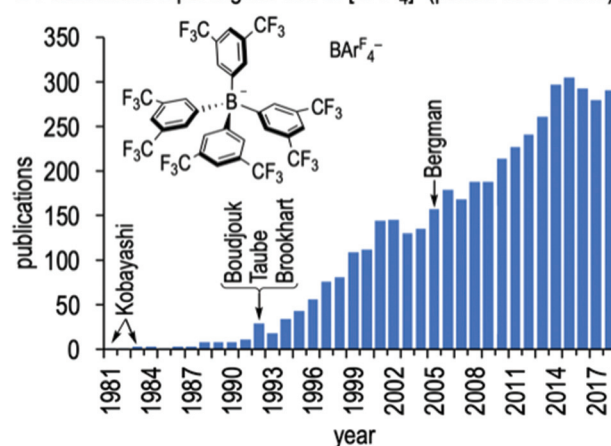
A Generation of a vacant site using $\text{M}[\text{BAr}^{\text{F}}_4]$ B Publications reporting the use of $[\text{BAr}^{\text{F}}_4]^-$ (period 1981–2018)

Fig. 1 (A) Generalised use of the $[\text{BAr}^{\text{F}}_4]^-$ anion for the generation of low-coordinate metal centres. (B) Number of publications per year reporting use of the $[\text{BAr}^{\text{F}}_4]^-$ anion. Scifinder CAS (<https://scifinder.cas.org>) accessed 18/12/2018.

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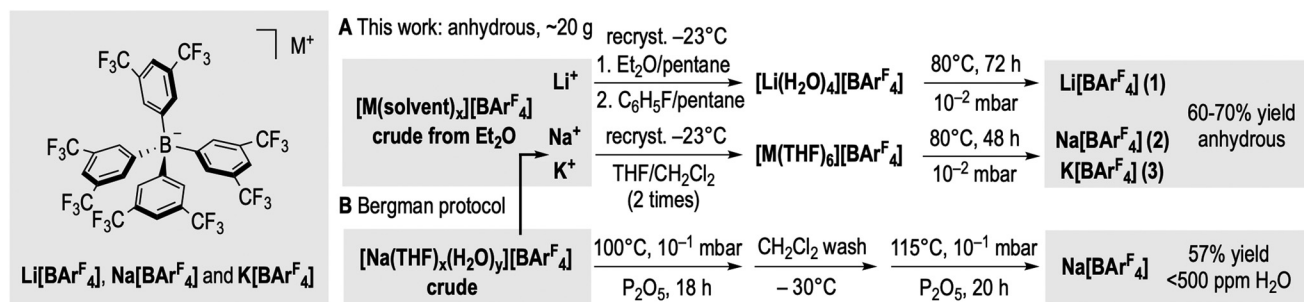


Fig. 2 Preparation and isolation of solvent-free anhydrous Li $^+$, Na $^+$ and K $^+$ salts of [BArF $_4$] $^-$ and comparison with the Bergman synthesis.

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 [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 [BArF $_4$] $^-$ to be determined.

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

The [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 $_2$ O ligand in complex **4** is observed at δ 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, ($\eta^5\text{-C}_5\text{H}_5$) $_2\text{ZrMe}_2$ was used to determine H $_2$ O content, using ^1H NMR spectroscopy to measure the thus formed oxo-bridged complex (and CH $_4$).²¹ No evidence of residual H $_2$ O was observed in any of the dried salts. Importantly, this ^1H NMR titration method confirmed the presence of one molecule of H $_2$ O in **4**.

Single-crystals of solvent-free anhydrous Na[BArF $_4$] **2** and K[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 C $_6$ H $_5$ F/ CH_2Cl_2 (Fig. 3). For Li[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 [Li(H $_2$ O)][BArF $_4$] **4** being isolated (Fig. 3A). Complexes **2**, **3**, and **4** crystallise in the tetragonal space group *P*4/*n* as contact ion-pairs (Fig. 3A–C). The contents of asymmetric units include 1/4 of the alkali metal and [BArF $_4$] $^-$ anion (*S* $_4$ symmetry), with an additional quarter of one molecule of water for **4**. The [BArF $_4$] $^-$ anions dictate the microenvironment around the [Li(H $_2$ O)] $^+$, Na $^+$ and K $^+$ cations, and eight [BArF $_4$] $^-$ anions encapsulate each alkali metal cation through CF $_3$...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 [BArF $_4$] $^-$ anions [Li...F, 1.995(7)–2.045(4) Å] with the water molecule [Li–O, 1.842(8) Å] in the apical position (Fig. 3D). Additional CF $_3$...H $_2$ O interactions are also present in **4** (F...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 [BArF $_4$] $^-$ anions that surround each cation (Fig. 3E and F) through M...F interactions. The increase in the ionic radius,²⁶ in the series Li < Na < K, translates into correspondingly longer M...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 Li[BArF $_4$], Na[BArF $_4$] and K[BArF $_4$] has been prepared in multigram scale following a revised protocol, that rests upon a simple recrystallisation



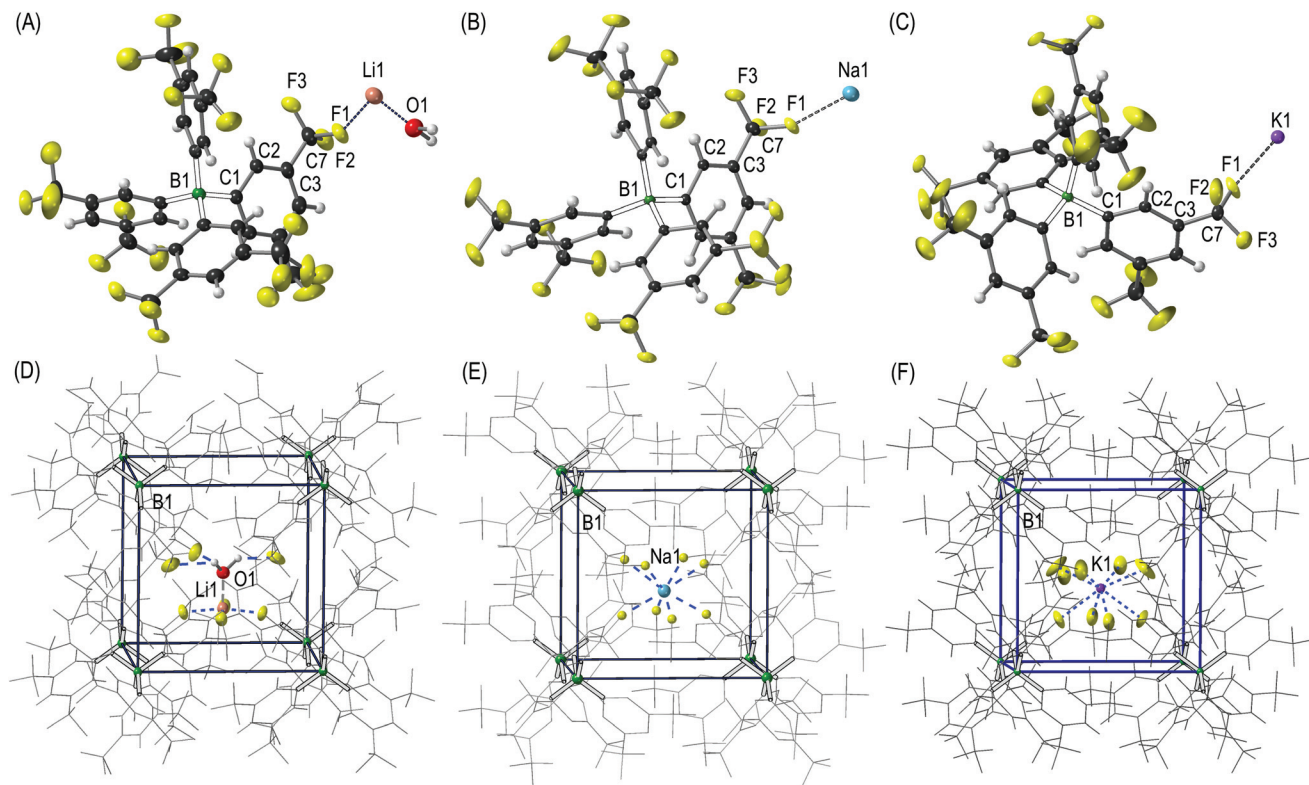


Fig. 3 Molecular structures of (A) $[\text{Li}(\text{H}_2\text{O})][\text{BARF}_4]$ **4**, (B) anhydrous $\text{Na}[\text{BARF}_4]$ **2** and (C) $\text{K}[\text{BARF}_4]$ **3**. Crystal packing diagrams showing the cubic arrangement of $[\text{BARF}_4]^-$ anions around (D) $[\text{Li}(\text{H}_2\text{O})]^+$, (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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