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# Solvent-free anhydrous Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> salts of [B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sup>−</sup>, [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup>. Improved synthesis and solid-state structures†

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A modified, convenient, preparation of solvent-free, anhydrous, Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> salts of the ubiquitous [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> anion is reported, that involves a simple additional recrystallisation step. Anhydrous Na[BAr<sup>F</sup><sub>4</sub>], K[BAr<sup>F</sup><sub>4</sub>], and [Li(H<sub>2</sub>O)][BAr<sup>F</sup><sub>4</sub>], were characterised by single-crystal X-ray diffraction.

The use of weakly coordinating anions<sup>1</sup> 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,<sup>2</sup> both in solution and in the solid-state.<sup>3</sup> The anion [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>4</sup> Fig. 1, enjoys particular utility amongst the small suite of common anions used, e.g. [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>,<sup>5</sup> [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>−</sup> (R<sup>F</sup> = fluoroalkyl),<sup>6</sup> [B(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sup>−</sup>,<sup>7</sup> and [CB<sub>11</sub>X<sub>12</sub>]<sup>−</sup> (X = halogen)<sup>8</sup> 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<sup>F</sup><sub>4</sub>]<sup>−</sup> 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<sup>F</sup><sub>4</sub>] (M = Li, Na, K), although alternative activating cations are also known, e.g. [(Et<sub>2</sub>O)<sub>2</sub>H][BAr<sup>F</sup><sub>4</sub>] (Taubé and Brookhart)<sup>9</sup> and [Ph<sub>3</sub>C][BAr<sup>F</sup><sub>4</sub>] (Boudjouk).<sup>10</sup> The alkali salts have also been used as polymerisation initiators,<sup>11</sup> in electrochemistry,<sup>12</sup> as an additive in lithium ion batteries,<sup>13</sup> in ionic liquids,<sup>14</sup> and for the extraction of aqueous lanthanide ions.<sup>15</sup> While considered to be non-interacting, under appropriate conditions [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> can coordinate to metal centres through its arene ring,<sup>16,3a</sup> or *via* metal...F-CF<sub>2</sub> interactions.<sup>17</sup> It can also undergo B-C bond cleavage.<sup>18</sup>

The synthesis and use, as a phase transfer catalyst,<sup>4</sup> of the [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> anion was first reported by Kobayashi in 1981, fol-

lowed by the preparation of hydrated [Na(H<sub>2</sub>O)<sub>3</sub>][BAr<sup>F</sup><sub>4</sub>].<sup>19</sup> Brookhart subsequently reported the synthesis of Na[BAr<sup>F</sup><sub>4</sub>], by drying under vacuum and a cold CH<sub>2</sub>Cl<sub>2</sub> wash.<sup>9a</sup> Both these preparations used the Grignard reagent 1,3,5-XMg(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (X = Br, I). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture<sup>20</sup> for the preparation of anhydrous Na[BAr<sup>F</sup><sub>4</sub>],<sup>21</sup> but required prolonged drying under vacuum over P<sub>2</sub>O<sub>5</sub>. Synthetic protocols have been reported for hydrated Li<sup>+</sup> and K<sup>+</sup> salts;<sup>22</sup> or where the water content has not been reported.<sup>23</sup> To date, the synthesis (Li<sup>+</sup>, K<sup>+</sup>) and structures<sup>24</sup> (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) of anhydrous M[BAr<sup>F</sup><sub>4</sub>] have not been reported in the open literature. Such anhydrous salts are of importance when using the [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup>

## A Generation of a vacant site using M[BAr<sup>F</sup><sub>4</sub>]



## B Publications reporting the use of [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> (period 1981–2018)

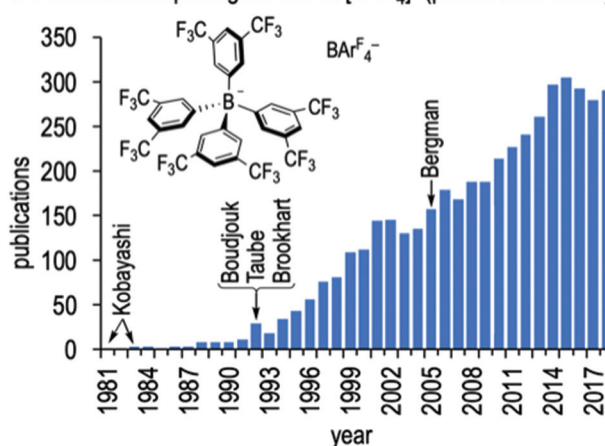


Fig. 1 (A) Generalised use of the [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> anion for the generation of low-coordinate metal centres. (B) Number of publications per year reporting use of the [BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> anion. Scifinder CAS (<https://scifinder.cas.org>) accessed 18/12/2018.

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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

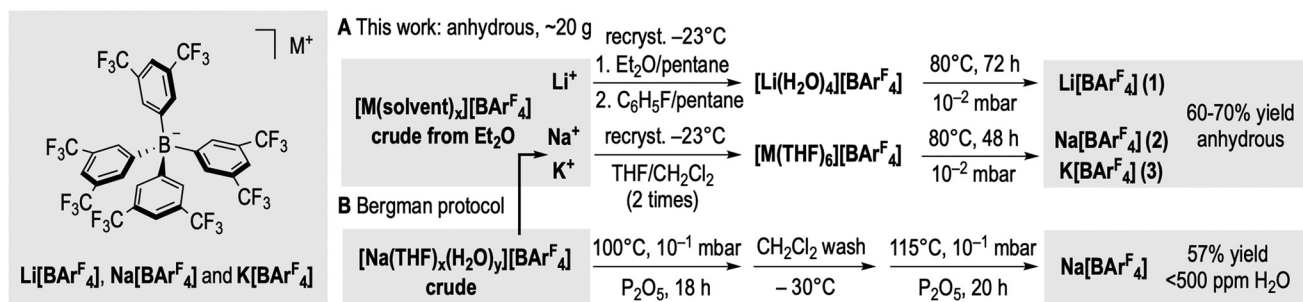


Fig. 2 Preparation and isolation of solvent-free anhydrous  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  salts of  $[\text{BARF}_4]^-$  and comparison with the Bergman synthesis.

anion to access highly Lewis-acidic, and low-coordinate, complexes.<sup>25</sup>

We now detail here a robust multigram protocol to prepare solvent-free anhydrous  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  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  $\text{Na}^+$  and  $\text{K}^+$ , and mono aquo  $\text{Li}^+$  salts of  $[\text{BARF}_4]^-$  to be determined.

Following a modified Kobayashi synthesis,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  salts of  $[\text{BARF}_4]^-$  (Fig. 2) were prepared from 1,3,5-BrMg ( $\text{CF}_3$ )<sub>2</sub>C<sub>6</sub>H<sub>3</sub>/BF<sub>3</sub> followed by treatment with the aqueous alkali metal carbonate of choice ( $\text{M}_2\text{CO}_3$ ,  $\text{M} = \text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ). Extraction into diethyl ether gave the corresponding crude  $[\text{M}(\text{solvent})_x][\text{BARF}_4]$  (solvent =  $\text{H}_2\text{O}$  and/or  $\text{Et}_2\text{O}$ ). 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  $-23^{\circ}\text{C}$  to give  $[\text{Li}(\text{H}_2\text{O})_4][\text{BARF}_4]$ <sup>22a</sup> 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  $80^{\circ}\text{C}$  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 ( $80^{\circ}\text{C}$ , 48 h).<sup>22c</sup>  $[\text{M}(\text{THF})_6][\text{BARF}_4]$  were themselves isolated by two consecutive recrystallisations of crude  $[\text{M}(\text{solvent})_x][\text{BARF}_4]$  from THF/ $\text{CH}_2\text{Cl}_2$ . These two recrystallisation steps ensure high purity of the final anhydrous salts. These procedures routinely yield ~20 g of anhydrous hygroscopic  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  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%).

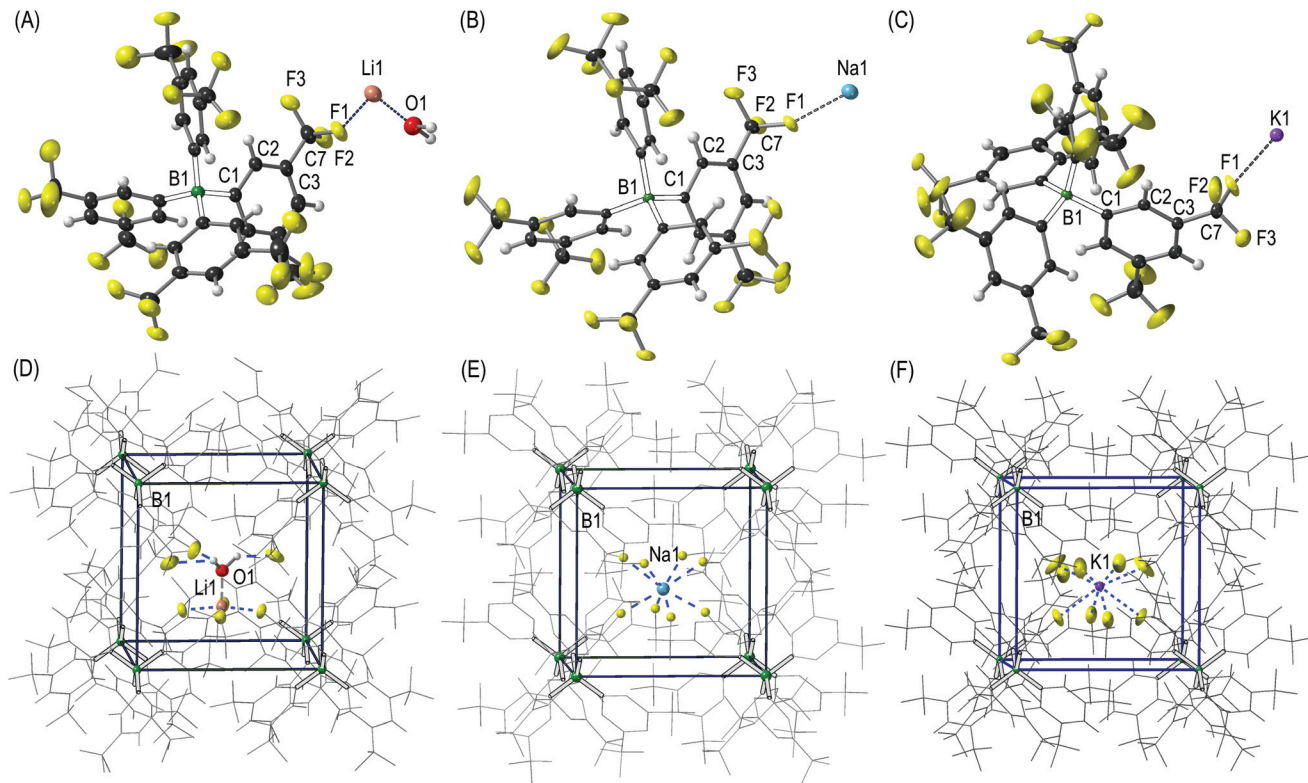
The  $[\text{BARF}_4]^-$  salts **1–4** were fully characterised in solution using multinuclear  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectroscopy in THF-*d*<sub>8</sub> (298 K) and ESI-MS, and these data are consistent with previously reported examples (ESI†).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

$-0.54$ , which shifts to  $\delta -0.38$  in **4**. The  $\text{H}_2\text{O}$  ligand in complex **4** is observed at  $\delta 4.02$  as a sharp singlet (2 H) in the  $^1\text{H}$  NMR spectrum. While elemental analysis did not suggest the presence of water in **1–3**, following Bergman's procedure, ( $\eta^5\text{-C}_5\text{H}_5$ )<sub>2</sub>ZrMe<sub>2</sub> was used to determine  $\text{H}_2\text{O}$  content, using  $^1\text{H}$  NMR spectroscopy to measure the thus formed oxo-bridged complex (and  $\text{CH}_4$ ).<sup>21</sup> No evidence of residual  $\text{H}_2\text{O}$  was observed in any of the dried salts. Importantly, this  $^1\text{H}$  NMR titration method confirmed the presence of one molecule of  $\text{H}_2\text{O}$  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*<sub>4</sub> symmetry), with an additional quarter of one molecule of water for **4**. The  $[\text{BARF}_4]^-$  anions dictate the microenvironment around the  $[\text{Li}(\text{H}_2\text{O})]^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  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  $\text{Li}^+$  ion in **4** has a square pyramidal geometry, interacting with  $\text{CF}_3$  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  $\text{Na}^+$  and  $\text{K}^+$  centres, respectively, interact with a total of eight  $\text{CF}_3$  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,<sup>26</sup> in the series  $\text{Li} < \text{Na} < \text{K}$ , translates into correspondingly longer  $\text{M}\cdots\text{F}$  distances [ $\text{Li}$ : 1.995(7)–2.045(4);  $\text{Na}$ : 2.473(2)–2.631(3); and  $\text{K}$ : 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)  $\text{Na}^+$  and (F)  $\text{K}^+$  cations. Minor disordered components for the  $\text{CF}_3$  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  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  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.

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