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Solvent-free anhydrous Li^+, Na^+ and K^+ salts of $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$, $[BAr^F_4]^-$. 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 $[BAr^F_4]^-$ anion is reported, that involves a simple additional recrystallisation step. Anhydrous $Na[BAr^F_4]$, $K[BAr^F_4]$, and $[Li(H_2O)][BAr^F_4]$, were characterised by single-crystal X-ray diffraction.

The use of weakly coordinating anions[1] 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 $[BAr^F_4]^-$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$),[4] Fig. 1, enjoys particular utility amongst the small suite of common anions used, *e.g.* $[B(C_6F_5)_4]^-$,[5] $[Al(OR^F)_4]^-$ (R^F = fluoroalkyl),[6] $[B(3,5\text{-}Cl_2C_6H_3)_4]^-$,[7] and $[CB_{11}X_{12}]^-$ (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, make $[BAr^F_4]^-$ 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 $M[BAr^F_4]$ (M = Li, Na, K), although alternative activating cations are also known, *e.g.* $[(Et_2O)_2H][BAr^F_4]$ (Taube and Brookhart)[9] and $[Ph_3C][BAr^F_4]$ (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 $[BAr^F_4]^-$ can coordinate to metal centres through its arene ring,[16,3a] or *via* metal⋯F–CF_2 interactions.[17] It can also undergo B–C bond cleavage.[18]

The synthesis and use, as a phase transfer catalyst,[4] of the $[BAr^F_4]^-$ anion was first reported by Kobayashi in 1981, followed by the preparation of hydrated $[Na(H_2O)_3][BAr^F_4]$.[19] Brookhart subsequently reported the synthesis of $Na[BAr^F_4]$, by drying under vacuum and a cold CH_2Cl_2 wash.[9a] Both these preparations used the Grignard reagent $1,3,5\text{-}XMg(CF_3)_2C_6H_3$ (X = Br, I). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture[20] for the preparation of anhydrous $Na[BAr^F_4]$,[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 structures[24] (Li^+, Na^+, K^+) of anhydrous $M[BAr^F_4]$ have not been reported in the open literature. Such anhydrous salts are of importance when using the $[BAr^F_4]^-$

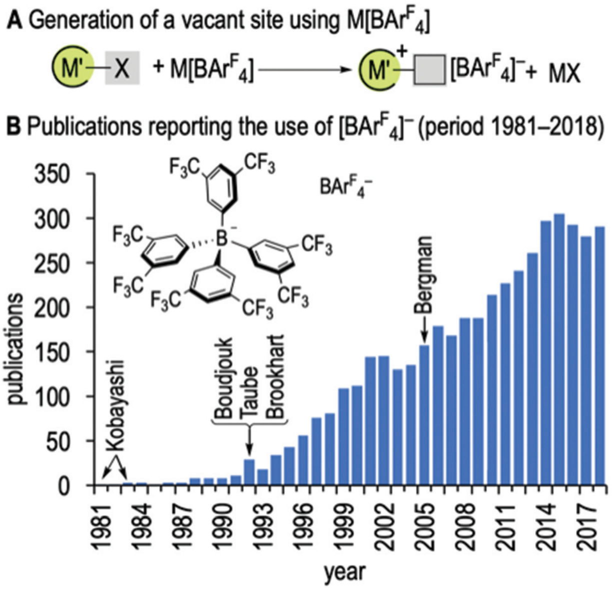

Fig. 1 (A) Generalised use of the $[BAr^F_4]^-$ anion for the generation of low-coordinate metal centres. (B) Number of publications per year reporting use of the $[BAr^F_4]^-$ anion. Scifinder CAS (https://scifinder.cas.org) accessed 18/12/2018.

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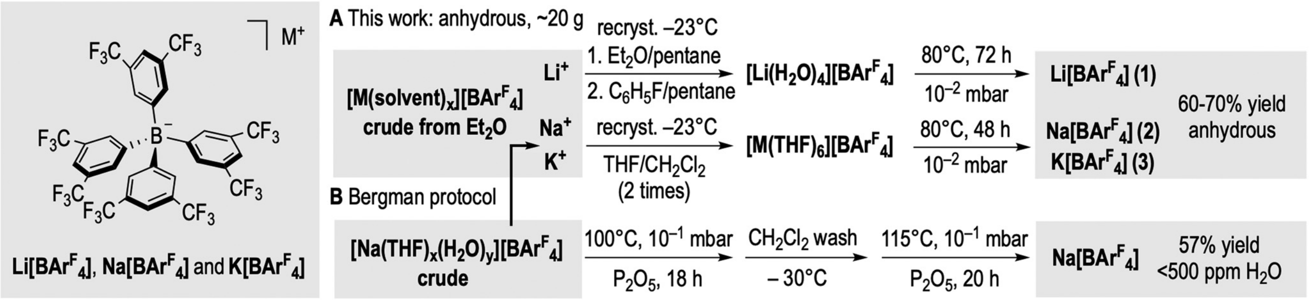

Fig. 2 Preparation and isolation of solvent-free anhydrous Li^+, Na^+ and K^+ salts of $[BAr^F{}_4]^-$ and comparison with the Bergman synthesis.

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 $[BAr^F{}_4]^-$ 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 $[BAr^F{}_4]^-$ to be determined.

Following a modified Kobayashi synthesis, Li^+, Na^+ and K^+ salts of $[BAr^F{}_4]^-$ (Fig. 2) were prepared from 1,3,5-BrMg$(CF_3)_2C_6H_3/BF_3$ followed by treatment with the aqueous alkali metal carbonate of choice (M_2CO_3, M = Li^+, Na^+ and K^+). Extraction into diethyl ether gave the corresponding crude $[M(solvent)_x][BAr^F{}_4]$ (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. $[Li(solvent)_x][BAr^F{}_4]$ was successively recrystallised from undried diethyl ether/*n*-pentane and then undried fluorobenzene/*n*-pentane at −23 °C to give $[Li(H_2O)_4][BAr^F{}_4]$[22a] as determined by NMR spectroscopy and single-crystal X-ray diffraction (ESI). Anhydrous $Li[BAr^F{}_4]$ **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 $[Li(H_2O)][BAr^F{}_4]$ **4**. Using $[Li(H_2O)_4]^+$ is crucial, as any bound ether results in decomposition on drying. Anhydrous $Na[BAr^F{}_4]$, **2** (68%, white solid), and $K[BAr^F{}_4]$, **3** (58%, off-white solid), were obtained from drying the pure THF solvates $[M(THF)_6][BAr^F{}_4]$ under vacuum (80 °C, 48 h).[22c] $[M(THF)_6][BAr^F{}_4]$ were themselves isolated by two consecutive recrystallisations of crude $[M(solvent)_x][BAr^F{}_4]$ 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 hydroscopic Li^+, Na^+ and K^+ salts of $[BAr^F{}_4]^-$. This method also works for the Bergman synthesis, by recrystalising crude $[Na(solvent)_x][BAr^F{}_4]$ prior to drying, to give anhydrous $Na[BAr^F{}_4]$ (12.3 g isolated yield, 58%).

The $[BAr^F{}_4]^-$ 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 δ −0.38 in **4**. The H_2O 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, $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ 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 $Na[BAr^F{}_4]$ **2** and $K[BAr^F{}_4]$ **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_6H_5F/CH_2Cl_2 (Fig. 3). For $Li[BAr^F{}_4]$ **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 $[Li(H_2O)][BAr^F{}_4]$ **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 $[BAr^F{}_4]^-$ anion (S_4 symmetry), with an additional quarter of one molecule of water for **4**. The $[BAr^F{}_4]^-$ anions dictate the microenvironment around the $[Li(H_2O)]^+$, Na^+ and K^+ cations, and eight $[BAr^F{}_4]^-$ anions encapsulate each alkali metal cation through $CF_3\cdots$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 $[BAr^F{}_4]^-$ 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 $CF_3\cdots H_2O$ 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 $[BAr^F{}_4]^-$ 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 $Li[BAr^F{}_4]$, $Na[BAr^F{}_4]$ and $K[BAr^F{}_4]$ has been prepared in multigram scale following a revised protocol, that rests upon a simple recrystallisation

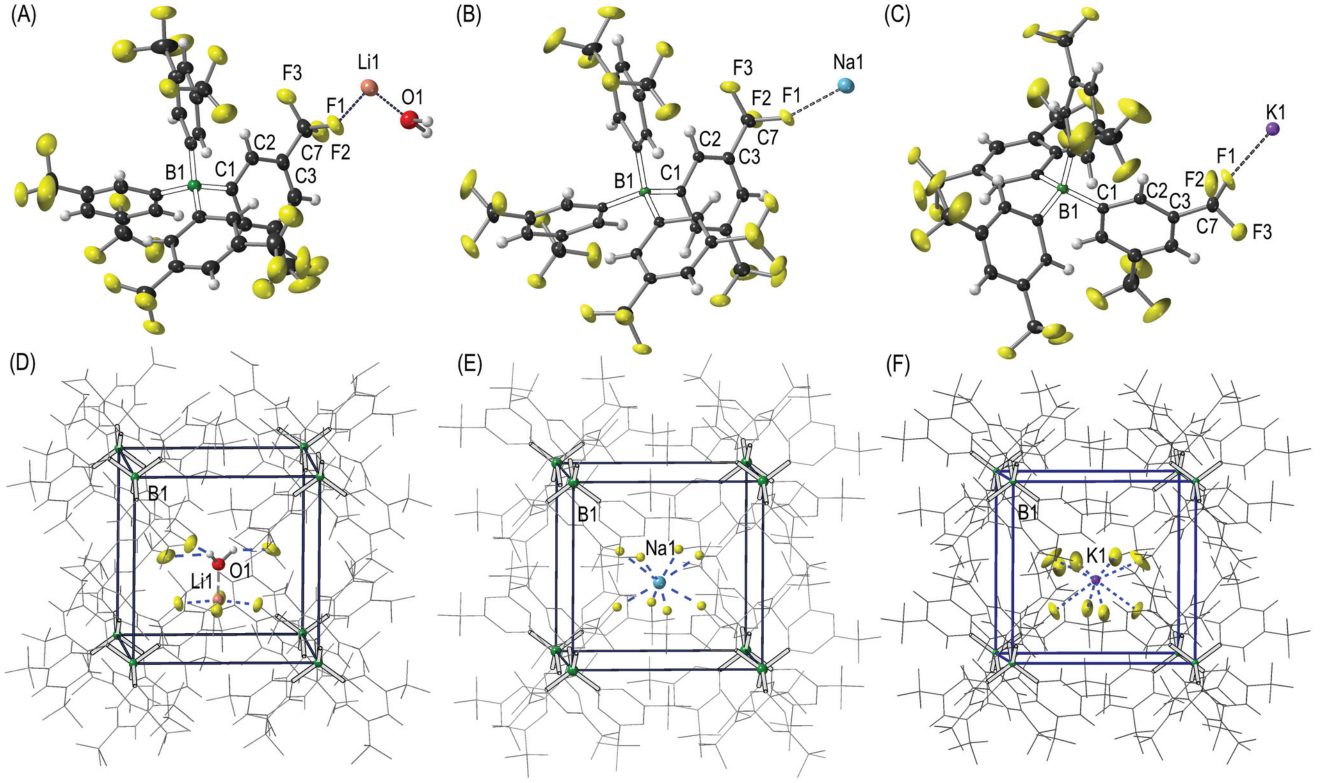

Fig. 3 Molecular structures of (A) [Li(H$_2$O)][BAr$^F{}_4$] **4**, (B) anhydrous Na[BAr$^F{}_4$] **2** and (C) K[BAr$^F{}_4$] **3**. Crystal packing diagrams showing the cubic arrangement of [BAr$^F{}_4$]$^-$ anions around (D) [Li(H$_2$O)]$^+$, (E) Na$^+$ and (F) K$^+$ cations. Minor disordered components for the CF$_3$ groups have been omitted for clarity. Displacement ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): **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 [BAr$^F{}_4$]$^-$ 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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