Dalton
Transactions

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2019, **48**, 3551

Received 17th January 2019,
Accepted 30th January 2019

DOI: 10.1039/c9dt00235a

rsc.li/dalton

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-$XMg(CF_3)_2C_6H_3$ (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 $[BAr^F{}_4]^-$

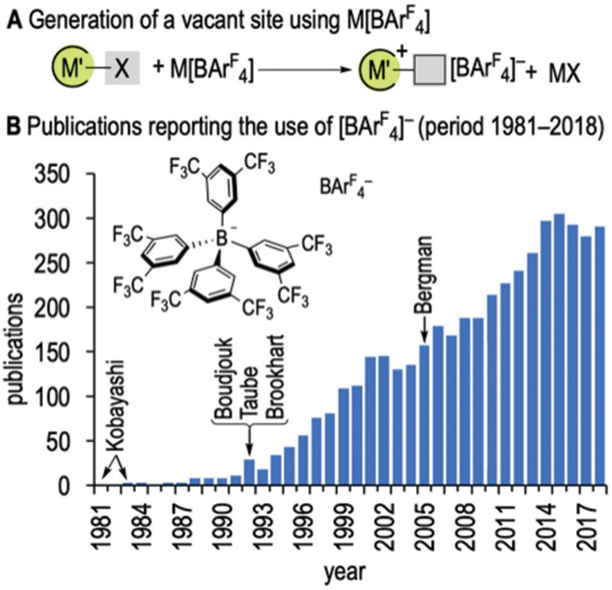

Fig. 1 (A) Generalised use of the $[BAr^F{}_4]^-$ anion for the generation of low-coordinate metal centres. (B) Number of publications per year reporting use of the $[BAr^F{}_4]^-$ anion. Scifinder CAS (https://scifinder.cas.org) accessed 18/12/2018.

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† 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

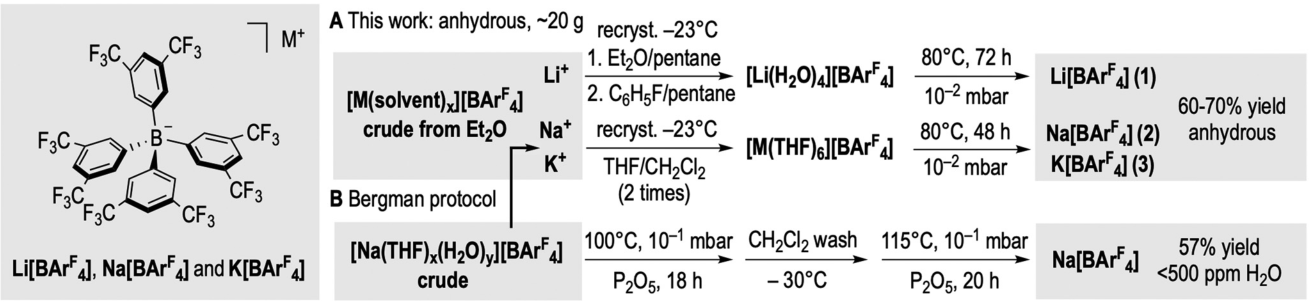

Fig. 2 Preparation and isolation of solvent-free anhydrous Li^+, Na^+ and K^+ salts of $[BAr^F{}_4]^-$ and comparison with the Bergman synthesis.

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

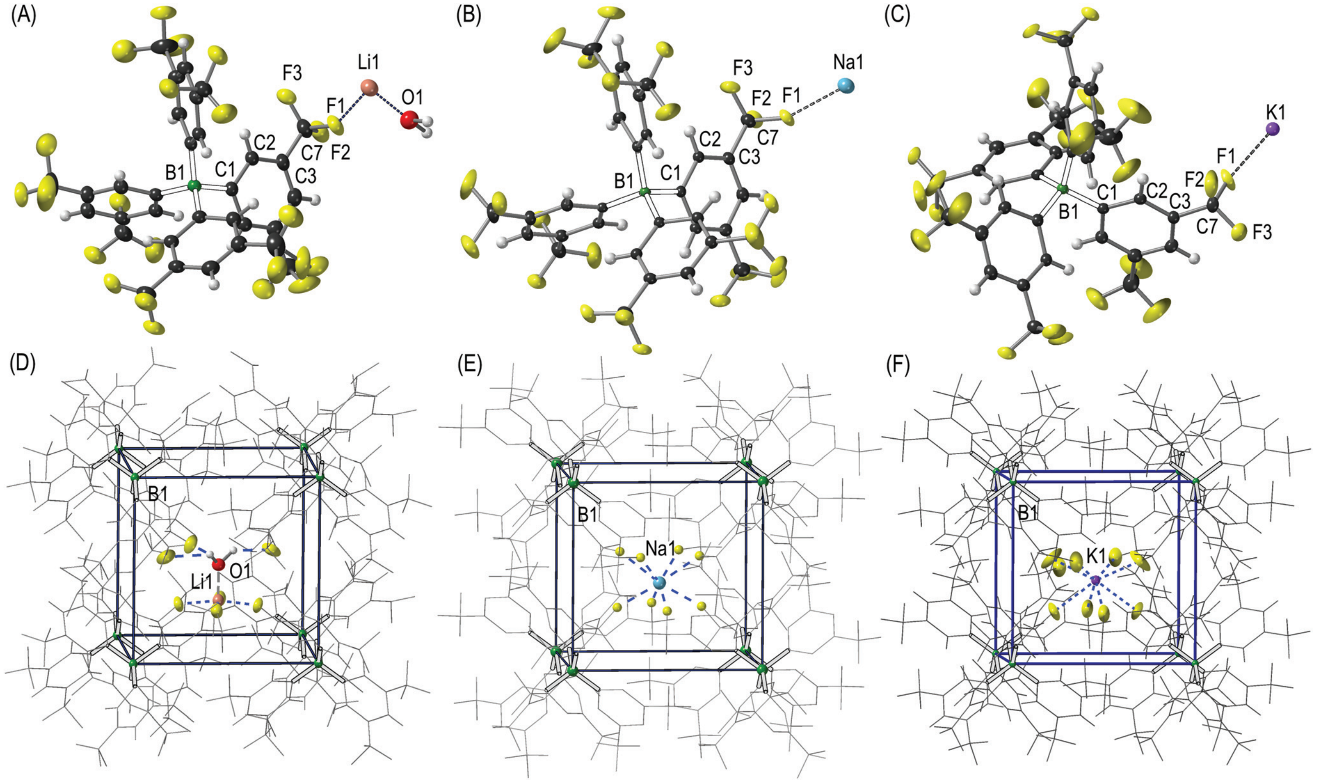

Fig. 3 Molecular structures of (A) $[Li(H_2O)][BAr^F{}_4]$ **4**, (B) anhydrous $Na[BAr^F{}_4]$ **2** and (C) $K[BAr^F{}_4]$ **3**. Crystal packing diagrams showing the cubic arrangement of $[BAr^F{}_4]^-$ anions around (D) $[Li(H_2O)]^+$, (E) Na^+ and (F) K^+ cations. Minor disordered components for 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

EPSRC EP/M024210/1 and SCG Chemicals Co. Ltd. Radleys UK for the laboratory equipment used in the synthetic protocols.

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