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

Antonio J. Martínez-Martínez\(\dagger\)* and Andrew S. Weller\(\dagger\)*

A modified, convenient, preparation of solvent-free, anhydrous, Li\(^+\), Na\(^+\) and K\(^+\) salts of the ubiquitous \([\text{BARF}_4]^−\) anion is reported, that involves a simple additional recrystallisation step. Anhydrous Na[\text{BARF}_4], K[\text{BARF}_4], and [\text{Li}(\text{H}_2\text{O})][\text{BARF}_4], were characterised by single-crystal X-ray diffraction.

The use of weakly coordinating anions 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, both in solution and in the solid-state. The anion \([\text{BARF}_4]^−\) (ArF = 3,5-(CF\(_3\))\text{C}_6\text{H}_3), Fig. 1, enjoys particular utility amongst the small suite of common anions used, e.g. \([\text{B}(\text{C}_6\text{F}_5)_4]^−\), \([\text{Al}(\text{ORF})_4]^−\) (RF = fluoroalkyl), \([\text{B}(3,5-\text{Cl}_2\text{C}_6\text{H}_3)_4]^−\), and \([\text{CB}_{11}\text{X}_{12}]^−\) (X = halogen) derivatives. A combination of synthetic accessibility, desirable properties of the resulting salts, i.e. solubility and crystallinity, and simple NMR-reporter groups, make \([\text{BARF}_4]^−\) 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[\text{BARF}_4] (M = Li, Na, K), although alternative activating cations are also known, e.g. [[\text{Et}_2\text{O}]\text{H}][\text{BARF}_4] (Taube and Brookhart)\(^a\) and [\text{Ph}_3\text{C}][\text{BARF}_4] (Boudjouk).\(^b\) The alkali salts have also been used as polymerisation initiators,\(^c\) in electrochemistry,\(^d\) as an additive in lithium ion batteries,\(^e\) in ionic liquids,\(^f\) and for the extraction of aqueous lanthanide ions.\(^g\) While considered to be non-interacting, under appropriate conditions \([\text{BARF}_4]^−\) can coordinate to metal centres through its arene ring,\(^h\) or via metal...F–CF\(_2\) interactions.\(^i\) It can also undergo B–C bond cleavage.\(^j\)

The synthesis and use, as a phase transfer catalyst, of the \([\text{BARF}_4]^−\) anion was first reported by Kobayashi in 1981, followed by the preparation of hydrated \([\text{Na}(\text{H}_2\text{O})_3][\text{BARF}_4]\).\(^k\) Brookhart subsequently reported the synthesis of Na[\text{BARF}_4], by drying under vacuum and a cold CH\(_2\text{Cl}_2\) wash.\(^l\) Both these preparations used the Grignard reagent 1,3,5-XMg(\text{CF}_3)\text{C}_6\text{H}_3 (X = Br, I). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture for the preparation of anhydrous Na[\text{BARF}_4],\(^m\) but required prolonged drying under vacuum over P\(_2\)O\(_5\). Synthetic protocols have been reported for hydrated Li\(^+\) and K\(^+\) salts;\(^n\) or where the water content has not been reported.\(^o\) To date, the synthesis (Li\(^+\), K\(^+\)) and structures (Li\(^+\), Na\(^+\), K\(^+\)) of anhydrous M[\text{BARF}_4] have not been reported in the open literature. Such anhydrous salts are of importance when using the \([\text{BARF}_4]^−\) anion.

The synthesis and use, as a phase transfer catalyst, of the \([\text{BARF}_4]^−\) anion was first reported by Kobayashi in 1981, followed by the preparation of hydrated \([\text{Na}(\text{H}_2\text{O})_3][\text{BARF}_4]\).\(^k\) Brookhart subsequently reported the synthesis of Na[\text{BARF}_4], by drying under vacuum and a cold CH\(_2\text{Cl}_2\) wash.\(^l\) Both these preparations used the Grignard reagent 1,3,5-XMg(\text{CF}_3)\text{C}_6\text{H}_3 (X = Br, I). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture for the preparation of anhydrous Na[\text{BARF}_4],\(^m\) but required prolonged drying under vacuum over P\(_2\)O\(_5\). Synthetic protocols have been reported for hydrated Li\(^+\) and K\(^+\) salts;\(^n\) or where the water content has not been reported.\(^o\) To date, the synthesis (Li\(^+\), K\(^+\)) and structures (Li\(^+\), Na\(^+\), K\(^+\)) of anhydrous M[\text{BARF}_4] have not been reported in the open literature. Such anhydrous salts are of importance when using the \([\text{BARF}_4]^−\) anion.

The synthesis and use, as a phase transfer catalyst, of the \([\text{BARF}_4]^−\) anion was first reported by Kobayashi in 1981, followed by the preparation of hydrated \([\text{Na}(\text{H}_2\text{O})_3][\text{BARF}_4]\).\(^k\) Brookhart subsequently reported the synthesis of Na[\text{BARF}_4], by drying under vacuum and a cold CH\(_2\text{Cl}_2\) wash.\(^l\) Both these preparations used the Grignard reagent 1,3,5-XMg(\text{CF}_3)\text{C}_6\text{H}_3 (X = Br, I). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture for the preparation of anhydrous Na[\text{BARF}_4],\(^m\) but required prolonged drying under vacuum over P\(_2\)O\(_5\). Synthetic protocols have been reported for hydrated Li\(^+\) and K\(^+\) salts;\(^n\) or where the water content has not been reported.\(^o\) To date, the synthesis (Li\(^+\), K\(^+\)) and structures (Li\(^+\), Na\(^+\), K\(^+\)) of anhydrous M[\text{BARF}_4] have not been reported in the open literature. Such anhydrous salts are of importance when using the \([\text{BARF}_4]^−\) anion.

The synthesis and use, as a phase transfer catalyst, of the \([\text{BARF}_4]^−\) anion was first reported by Kobayashi in 1981, followed by the preparation of hydrated \([\text{Na}(\text{H}_2\text{O})_3][\text{BARF}_4]\).\(^k\) Brookhart subsequently reported the synthesis of Na[\text{BARF}_4], by drying under vacuum and a cold CH\(_2\text{Cl}_2\) wash.\(^l\) Both these preparations used the Grignard reagent 1,3,5-XMg(\text{CF}_3)\text{C}_6\text{H}_3 (X = Br, I). In 2005, Bergman described an alternative protocol that avoided the use of the Grignard/magnesium metal mixture for the preparation of anhydrous Na[\text{BARF}_4],\(^m\) but required prolonged drying under vacuum over P\(_2\)O\(_5\). Synthetic protocols have been reported for hydrated Li\(^+\) and K\(^+\) salts;\(^n\) or where the water content has not been reported.\(^o\) To date, the synthesis (Li\(^+\), K\(^+\)) and structures (Li\(^+\), Na\(^+\), K\(^+\)) of anhydrous M[\text{BARF}_4] have not been reported in the open literature. Such anhydrous salts are of importance when using the \([\text{BARF}_4]^−\) anion.

Department of Chemistry, Chemistry Research Laboratories, Mansfield Road, University of Oxford, Oxford, OX1 3TA, UK.
E-mail: antonio.martinez@chem.ox.ac.uk, andrew.weller@chem.ox.ac.uk
†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. 1 (A) Generalised use of the [\text{BARF}_4]^− anion for the generation of low-coordinate metal centres. (B) Number of publications per year reporting use of the [\text{BARF}_4]^− anion. SciFinder CAS (https://scifinder.cas.org) accessed 18/12/2018.
Anhydrous Li\([\text{BArF}_4]\) 1 was then conveniently obtained as a highly hygroscopic off-white solid (64% yield) after drying under dynamic vacuum (10^-3 mbar) at 80 °C for 72 h. Shorter drying times (24 h) gave \([\text{Li(H}_2\text{O})_4]\)[\text{BArF}_4]\]. Using \([\text{Li(H}_2\text{O})_4]\) is crucial, as any bound ether results in decomposition on drying. Anhydrous Na\([\text{BArF}_4]\), 2 (68%, white solid), and K\([\text{BArF}_4]\), 3 (58%, off-white solid), were obtained from drying the pure THF solvates \([\text{M(THF)}_n][\text{BArF}_4]\) under vacuum (80 °C, 48 h).\(^{22c}\) [\text{M(THF)}_n][\text{BArF}_4]\] were themselves isolated by two consecutive recrystallisations of crude \([\text{M(solvent)}][\text{BArF}_4]\) from THF/CH\(_2\)Cl\(_2\). 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 \([\text{BArF}_4]\)^-. This method also works for the Bergman synthesis, by recrystallising crude \([\text{Na(solvent)}][\text{BArF}_4]\) prior to drying, to give anhydrous 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-\(_d_8\) (298 K) and ESI-MS, and these data are consistent with previously reported examples (ESI†).\(^{21,22a,23}\) Additionally, 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, \((\eta^5\text{C}_5\text{H}_5)\text{ZrMe}_2\) 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 CH\(_4\)).\(^{21}\) 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 Na[\text{BArF}_4] 2 and 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 Li[\text{BArF}_4] 4, 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(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(H}_2\text{O)}]\^+, Na\(^+\) and K\(^+\) cations, and eight [\text{BArF}_4]\^- anions encapsulate each alkali metal cation through \(\text{CF}_3\)···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 \(\text{CF}_3\) groups from four distinct [\text{BArF}_4]\^- anions [\(S_4\) symmetry], with an additional quarter of one molecule of water for 4. The [\text{BArF}_4]\^- anions dictate the microenvironment around the [\text{Li(H}_2\text{O)}]\^+, Na\(^+\) and K\(^+\) cations, and eight [\text{BArF}_4]\^- anions encapsulate each alkali metal cation through \(\text{CF}_3\)···alkali metal interactions forming an essentially cubic environment (Fig. 3D–F).
step. Our method stands by its simplicity to obtain the Li\(^+\), Na\(^+\) and K\(^+\) salts of the [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

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

References


24 The structure of solvent-free Na[BArF$_4$] has been deposited as a private communication to the Cambridge Structural Database (VEGDAP, DOI: 10.5517/ccdc.csd.cc1ptr7h). Detailed synthesis and structural discussion were not reported.