



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 $\text{Li}^+$ , $\text{Na}^+$ and $\text{K}^+$ 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†

Antonio J. Martínez-Martínez \* and Andrew S. Weller \*

**A modified, convenient, preparation of solvent-free, anhydrous,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  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 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  $[\text{BAr}^{\text{F}}_4]^-$  ( $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ),<sup>4</sup> Fig. 1, enjoys particular utility amongst the small suite of common anions used, *e.g.*  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,<sup>5</sup>  $[\text{Al}(\text{OR}^{\text{F}})_4]^-$  ( $\text{R}^{\text{F}} = \text{fluoroalkyl}$ ),<sup>6</sup>  $[\text{B}(3,5\text{-Cl}_2\text{C}_6\text{H}_3)_4]^-$ ,<sup>7</sup> and  $[\text{CB}_{11}\text{X}_{12}]^-$  ( $\text{X} = \text{halogen}$ )<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, 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)<sup>9</sup> and  $[\text{Ph}_3\text{C}][\text{BAr}^{\text{F}}_4]$  (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  $[\text{BAr}^{\text{F}}_4]^-$  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>

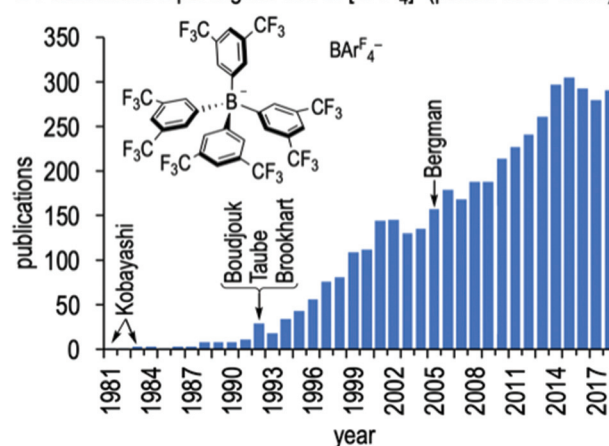
The synthesis and use, as a phase transfer catalyst,<sup>4</sup> of the  $[\text{BAr}^{\text{F}}_4]^-$  anion was first reported by Kobayashi in 1981, fol-

lowed by the preparation of hydrated  $[\text{Na}(\text{H}_2\text{O})_3][\text{BAr}^{\text{F}}_4]$ .<sup>19</sup> Brookhart subsequently reported the synthesis of  $\text{Na}[\text{BAr}^{\text{F}}_4]$ , by drying under vacuum and a cold  $\text{CH}_2\text{Cl}_2$  wash.<sup>9a</sup> 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 mixture<sup>20</sup> for the preparation of anhydrous  $\text{Na}[\text{BAr}^{\text{F}}_4]$ ,<sup>21</sup> but required prolonged drying under vacuum over  $\text{P}_2\text{O}_5$ . Synthetic protocols have been reported for hydrated  $\text{Li}^+$  and  $\text{K}^+$  salts;<sup>22</sup> or where the water content has not been reported.<sup>23</sup> To date, the synthesis ( $\text{Li}^+$ ,  $\text{K}^+$ ) and structures<sup>24</sup> ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) 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.

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



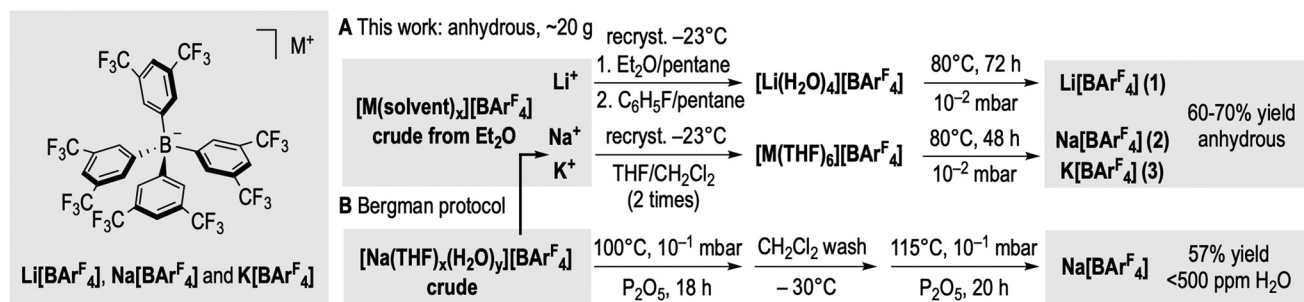


Fig. 2 Preparation and isolation of solvent-free anhydrous  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  salts of  $[\text{BARF}_4]^-$  and comparison with the Bergman synthesis.

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 = H<sub>2</sub>O and/or Et<sub>2</sub>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 °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 °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 °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/CH<sub>2</sub>Cl<sub>2</sub>. 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%).

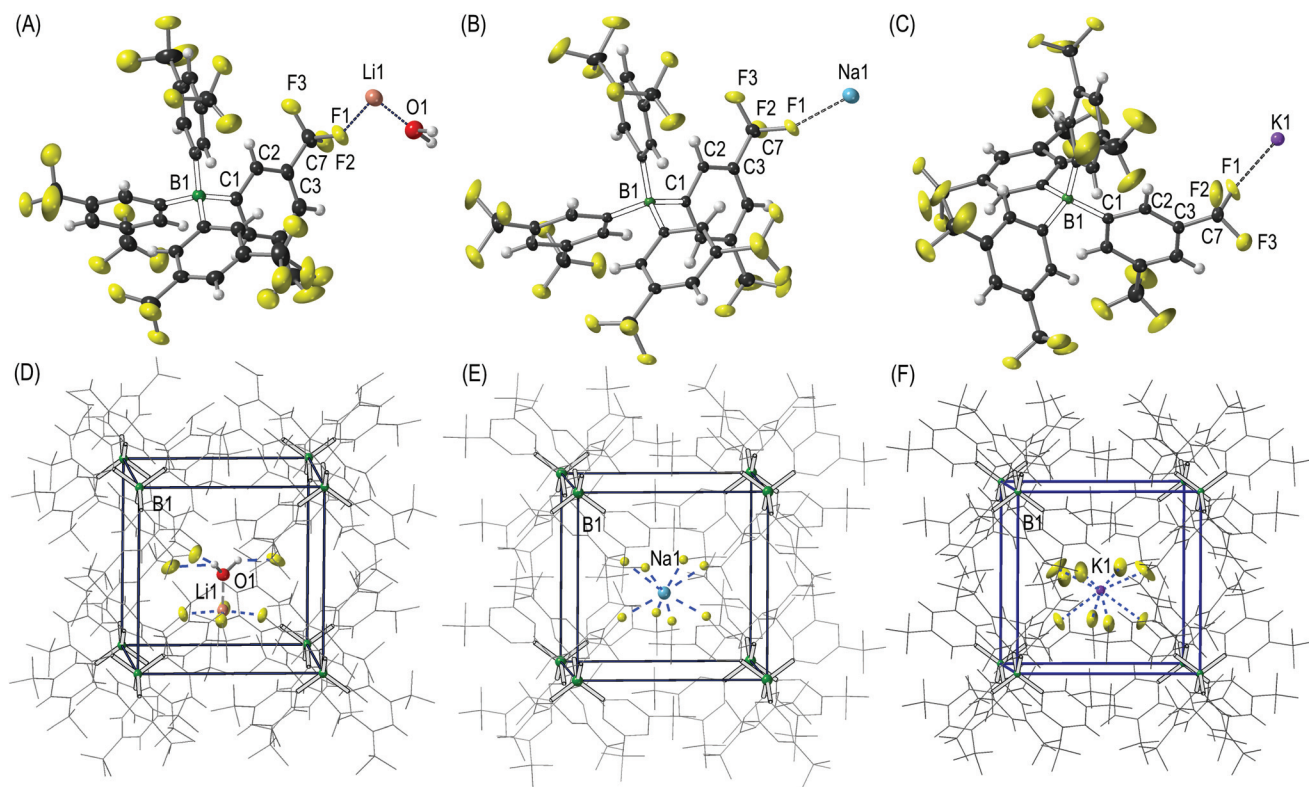
The  $[\text{BARF}_4]^-$  salts **1–4** were fully characterised in solution using multinuclear <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopy in THF-*d*<sub>8</sub> (298 K) and ESI-MS, and these data are consistent with previously reported examples (ESI†).<sup>21,22a,23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

–0.54, which shifts to  $\delta$  –0.38 in **4**. The H<sub>2</sub>O ligand in complex **4** is observed at  $\delta$  4.02 as a sharp singlet (2 H) in the <sup>1</sup>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 H<sub>2</sub>O content, using <sup>1</sup>H NMR spectroscopy to measure the thus formed oxo-bridged complex (and CH<sub>4</sub>).<sup>21</sup> No evidence of residual H<sub>2</sub>O was observed in any of the dried salts. Importantly, this <sup>1</sup>H NMR titration method confirmed the presence of one molecule of H<sub>2</sub>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 C<sub>6</sub>H<sub>5</sub>F/CH<sub>2</sub>Cl<sub>2</sub> (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 *P*4/*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 CF<sub>3</sub>...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 CF<sub>3</sub> groups from four distinct  $[\text{BARF}_4]^-$  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<sub>3</sub>...H<sub>2</sub>O interactions are also present in **4** (F...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 CF<sub>3</sub> groups from the  $[\text{BARF}_4]^-$  anions that surround each cation (Fig. 3E and F) through M...F interactions. The increase in the ionic radius,<sup>26</sup> in the series  $\text{Li} < \text{Na} < \text{K}$ , 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  $\text{Li}[\text{BARF}_4]$ ,  $\text{Na}[\text{BARF}_4]$  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.

## Acknowledgements

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

## References

- (a) S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927–942; (b) C. A. Reed, *Acc. Chem. Res.*, 1998, **31**, 133–139;
- (c) I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066–2090.
- (a) W. Beck and K. Suenkel, *Chem. Rev.*, 1988, **88**, 1405–1421; (b) T. A. Engesser, M. R. Lichtenthaler, M. Schleep and I. Krossing, *Chem. Soc. Rev.*, 2016, **45**, 789–899; (c) S. D. Pike, M. R. Crimmin and A. B. Chaplin, *Chem. Commun.*, 2017, **53**, 3615–3633; (d) I. M. Riddlestone, A. Kraft, J. Schaefer and I. Krossing, *Angew. Chem., Int. Ed.*, 2018, **57**, 13982–14024.
- (a) S. D. Pike, F. M. Chadwick, N. H. Rees, M. P. Scott, A. S. Weller, T. Krämer and S. A. Macgregor, *J. Am. Chem. Soc.*, 2015, **137**, 820–833; (b) A. J. Martínez-Martínez, B. E. Tegner, A. I. McKay, A. J. Bukvic, N. H. Rees, G. J. Tizzard, S. J. Coles, M. R. Warren, S. A. Macgregor and A. S. Weller, *J. Am. Chem. Soc.*, 2018, **140**, 14958–14970.
- H. Kobayashi, T. Sonoda, H. Iwamoto and M. Yoshimura, *Chem. Lett.*, 1981, **10**, 579–580.
- (a) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245–250; (b) E. Martin, D. L. Hughes and S. J. Lancaster, *Inorg. Chim. Acta*, 2010, **363**, 275–278.
- (a) S. M. Ivanova, B. G. Nolan, Y. Kobayashi, S. M. Miller, O. P. Anderson and S. H. Strauss, *Chem. – Eur. J.*, 2001, **7**, 503–510; (b) I. Krossing, *Chem. – Eur. J.*, 2001, **7**, 490–502;



- (c) I. Krossing and A. Reisinger, *Eur. J. Inorg. Chem.*, 2005, **2005**, 1979–1989.
- 7 A. B. Chaplin and A. S. Weller, *Eur. J. Inorg. Chem.*, 2010, **2010**, 5124–5128.
- 8 C. Douvris and J. Michl, *Chem. Rev.*, 2013, **113**, PR179–PR233.
- 9 (a) M. Brookhart, B. Grant and A. F. Volpe, *Organometallics*, 1992, **11**, 3920–3922; (b) R. Taube and S. Wache, *J. Organomet. Chem.*, 1992, **428**, 431–442.
- 10 S. R. Bahr and P. Boudjouk, *J. Org. Chem.*, 1992, **57**, 5545–5547.
- 11 C.-T. Chang, C.-L. Chen, Y.-H. Liu, S.-M. Peng, P.-T. Chou and S.-T. Liu, *Inorg. Chem.*, 2006, **45**, 7590–7592.
- 12 F. Barrière, N. Camire, W. E. Geiger, U. T. Mueller-Westerhoff and R. Sanders, *J. Am. Chem. Soc.*, 2002, **124**, 7262–7263.
- 13 F. Kita, H. Sakata, S. Sinomoto, A. Kawakami, H. Kamizori, T. Sonoda, H. Nagashima, J. Nie, N. V. Pavlenko and Y. L. Yagupolskii, *J. Power Sources*, 2000, **90**, 27–32.
- 14 A. Bösmann, G. Franciò, E. Janssen, M. Solinas, W. Leitner and P. Wasserscheid, *Angew. Chem., Int. Ed.*, 2001, **40**, 2697–2699.
- 15 H. Suzuki, H. Naganawa and S. Tachimori, *Phys. Chem. Chem. Phys.*, 2003, **5**, 726–733.
- 16 (a) J. Powell, A. Lough and T. Saeed, *J. Chem. Soc., Dalton Trans.*, 1997, 4137–4138; (b) T. M. Douglas, E. Molinos, S. K. Brayshaw and A. S. Weller, *Organometallics*, 2007, **26**, 463–465.
- 17 (a) P. Holze, T. Corona, N. Frank, B. Braun-Cula, C. Herwig, A. Company and C. Limberg, *Angew. Chem., Int. Ed.*, 2017, **56**, 2307–2311; (b) M. Everett, A. Jolleys, W. Levason, D. Pugh and G. Reid, *Chem. Comm.*, 2014, **50**, 5843–5846; (c) J. B. Smith, S. H. Kerr, P. S. White and A. J. M. Miller, *Organometallics*, 2017, **36**, 3094–3103.
- 18 (a) W. V. Konze, B. L. Scott and G. J. Kubas, *Chem. Commun.*, 1999, 1807–1808; (b) H. Salem, L. J. W. Shimon, G. Leitens, L. Weiner and D. Milstein, *Organometallics*, 2008, **27**, 2293–2299.
- 19 H. Nishida, N. Takada, M. Yoshimura, T. Sonoda and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2600–2604.
- 20 J. L. Leazer, R. Cvetovich, F.-R. Tsay, U. Dolling, T. Vickery and D. Bachert, *J. Org. Chem.*, 2003, **68**, 3695–3698.
- 21 N. A. Yakelis and R. G. Bergman, *Organometallics*, 2005, **24**, 3579–3581.
- 22 (a) J. H. Golden, P. F. Mutolo, E. B. Lobkovsky and F. J. DiSalvo, *Inorg. Chem.*, 1994, **33**, 5374–5375; (b) M. R. Kita and A. J. M. Miller, *J. Am. Chem. Soc.*, 2014, **136**, 14519–14529; (c) L. Carreras, L. Rovira, M. Vaquero, I. Mon, E. Martin, J. Benet-Buchholz and A. Vidal-Ferran, *RSC Adv.*, 2017, **7**, 32833–32841.
- 23 W. E. Buschmann, J. S. Miller, K. Bowman-James and C. N. Miller, *Inorg. Synth.*, 2002, **33**, 85.
- 24 The structure of solvent-free Na[BAR<sup>F</sup><sub>4</sub>] 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.
- 25 A. D. Piascik, R. Li, H. J. Wilkinson, J. C. Green and A. E. Ashley, *J. Am. Chem. Soc.*, 2018, **140**, 10691–10694.
- 26 M. Rahm, R. Hoffmann and N. W. Ashcroft, *Chem. – Eur. J.*, 2016, **22**, 14625–14632.

