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Borylation of fluorinated arenes using the boron-centred nucleophile $\text{B}(\text{CN})_3^{2-}$ – a unique entry to aryltricyanoborates†

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The potassium salt of the boron-centred nucleophile $\text{B}(\text{CN})_3^{2-}$ (**1**) readily reacts with perfluorinated arenes, such as hexafluorobenzene, decafluorobiphenyl, octafluoronaphthalene and pentafluoropyridine, which results in KF and the K^+ salts of the respective borate anions with one $\{\text{B}(\text{CN})_3\}$ unit bonded to the (hetero)arene. An excess of $\text{K}_2\mathbf{1}$ leads to the successive reaction of two or, in the case of perfluoropyridine, even three C–F moieties and the formation of di- and trianions, respectively. Moreover, all of the 11 partially fluorinated benzene derivatives, $\text{C}_6\text{F}_{6-n}\text{H}_n$ ($n = 1-5$), generally react with $\text{K}_2\mathbf{1}$ to give new tricyano(phenyl)borate anions with high chemo- and regioselectivity. A decreasing number of fluorine substituents on benzene results in a decrease in the reaction rate. In the cases of partially fluorinated benzenes, the addition of LiCl is advantageous or even necessary to facilitate the reaction. Also, pentafluorobenzenes $\text{R}-\text{C}_6\text{F}_5$ ($\text{R} = -\text{CN}, -\text{OMe}, -\text{Me}, \text{ or } -\text{CF}_3$) react *via* C–F/C–B exchange that mostly occurs in the *para* position and to a lesser extent in the *meta* or *ortho* positions. Most of the reactions proceed *via* an $\text{S}_{\text{N}}\text{Ar}$ mechanism. The reaction of 1,4- $\text{F}_2\text{C}_6\text{H}_4$ with $\text{K}_2\mathbf{1}$ shows that an aryne mechanism has to be considered in some cases as well. In summary, a wealth of new stable tricyano(aryl)borates have been synthesised and fully characterized using multi-NMR spectroscopy and most of them were characterised using single-crystal X-ray diffraction.

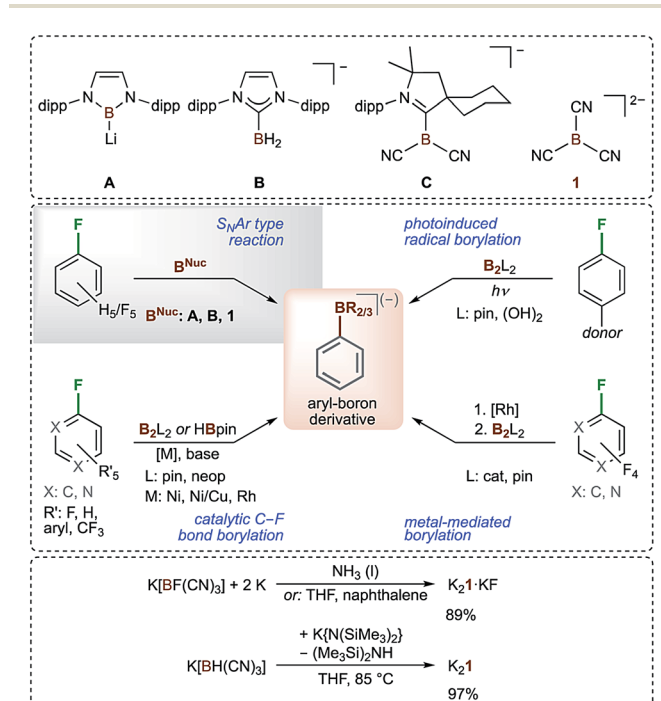
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Introduction

Anionic boron-centred nucleophiles are of growing interest as boron centres are usually electrophilic (Lewis-acidic). Therefore, boron-centred nucleophiles have unusual reactivity and are expected to have large synthetic potential.¹⁻⁴ The isolation of the first boron-centred nucleophile in 2006, the lithiated boryl anion **A** that is stable in THF at -45°C for months, was an important development in this field that stimulated intensive further research (Scheme 1).⁵ The chemistry of the lithiated boryl anion **A** and closely related species^{3,6-8} was studied in detail, and these compounds were found to be versatile starting compounds for the introduction of boryl moieties.^{1,3-14} Although some other boron-centred nucleophiles have been described, there is still a limited number of them.¹⁵⁻²⁶ Boryl anions were found to be stabilized by carbene ligands such as NHCs (NHC = N-heterocyclic carbene) and cAACs (cAAC =



Scheme 1 Selected boron-centred nucleophiles (top), the different types of conversion of C–F into C–B moieties of arenes and heteroarenes (middle), and convenient syntheses of $\text{K}_2\mathbf{1}$ (bottom); (dipp = 2,6-diisopropylphenyl, cat = catecholato, pin = pinacolato, and neop = neopentyl glycolato).

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cyclic (alkyl)(amino)carbene), as demonstrated in **B**²⁷ and **C**²⁸ (Scheme 1). An alternative approach for the stabilization of boron-centred nucleophiles is the introduction of cyano groups at the boron atom, as demonstrated in **C**²⁸ and the tricyanoborate dianion $\text{B}(\text{CN})_3^{2-}$ (**1**).^{29–32} The latter is the only dianionic boryl anion known to date, and its alkali metal salts are indefinitely stable at room temperature under an inert atmosphere. The first syntheses towards the alkali metal salts of **1** started from $\text{M}[\text{B}(\text{CN})_4]$ (M = alkali metal).²⁹ Recently, we reported convenient, high-yield and large-scale entries towards the salts of **1** starting from the readily available tricyanoborates $\text{M}[\text{BF}(\text{CN})_3]$ ^{33,34} and $\text{M}[\text{BH}(\text{CN})_3]$ ^{35,36} (Scheme 1).^{30–32} The unprecedented formation of dianion **1** from $[\text{BH}(\text{CN})_3]^-$ is the first example of the deprotonation of a hydridoborate anion.^{31,32} The conversion of a hydridoborane into monoanion **C** is the only related reaction²⁸ known to date.

As mentioned previously, boron-centred nucleophiles have large synthetic potential. Surprisingly, only very few examples of reactions of such nucleophiles with fluorinated arenes have been reported. Boryl lithium **A** was found to react with C_6F_6 or $\text{C}_6\text{H}_5\text{F}$ to obtain the corresponding monoborylated benzenes.⁶ Similar reactions have been reported for **B**²⁷ and **1**³⁰ with C_6F_6 only (Scheme 1). In general, only a limited number of transformations of C–F into C–B bonds of arenes or heteroarenes are known. They are either metal-catalyzed^{37–42} or metal-mediated⁴³ reactions, or photoinduced radical borylations^{44,45} (Scheme 1).

Herein, we report on the $\text{S}_{\text{N}}\text{Ar}$ reactions of the boryl dianion $\text{B}(\text{CN})_3^{2-}$ (**1**) with selected fully and partially fluorinated arenes^{46–51} including perfluorinated pyridine, naphthalene and biphenyl as well as fluorinated arenes with a functional group. All of the reactions proceeded *via* the exchange of fluorine with the tricyanoboryl moiety and most of them were chemo- and regioselective. Even multiple exchange reactions that provide access to bis- and tris(tricyanoborate) anions have been achieved.

Results and discussion

Reactions of $\text{K}_2\text{B}(\text{CN})_3$ (**K**₂**1**) with perfluoropyridine

As outlined in the introduction, $\text{K}_2\text{B}(\text{CN})_3$ (**K**₂**1**) was found to react with an excess of C_6F_6 at room temperature in THF to give the salts of the $[\text{C}_6\text{F}_5\text{B}(\text{CN})_3]^-$ anion (**B6a**) in 67% yield.³⁰ A related reaction of perfluoropyridine with **K**₂**1** was found to start at temperatures below 0 °C, as evidenced by the rapid decolorization of the suspension. The $[4-\{(\text{NC})_3\text{B}\}-\text{C}_5\text{F}_4\text{N}]^-$ anion (**Py1**) was obtained as the main product of the reaction with an excess of perfluoropyridine (Table 1 and Fig. 1). The exchange of the fluorine in the 4-position is typical for the $\text{S}_{\text{N}}\text{Ar}$ reactions of $\text{C}_5\text{F}_5\text{N}$.^{52–55} The dianion $[2,4-\{(\text{NC})_3\text{B}\}_2-\text{C}_5\text{F}_3\text{N}]^{2-}$ (**Py2**), a different isomer of **Py1**, most likely $[2-\{(\text{NC})_3\text{B}\}-\text{C}_5\text{F}_4\text{N}]^-$, and small amounts (<1%) of further tricyano(fluoropyridinyl)borate anions, including the trianion $[2,4,6-\{(\text{NC})_3\text{B}\}_3-\text{C}_5\text{F}_3\text{N}]^{3-}$ (**Py3**), were obtained as the side products.

An excess of **K**₂**1** yielded larger amounts of the dianion **Py2** and the trianion **Py3** and the reaction of perfluoropyridine with two equivalents of **K**₂**1** gave **K**₂**Py2** as the major product. Three equivalents of the potassium salt resulted in **K**₃**Py3** in 31% yield.

A related, successive replacement of 1, 2 and 3 fluorine substituents of perfluoropyridine *via* nucleophilic replacement has been previously reported for the methoxy anion.⁵⁴ In contrast, alkyl and aryl Grignard reagents were reported to result in only mono-substitutions in the *para* position of perfluoropyridine.⁵⁵ The decreasing solubility of the potassium borates **KPy1**, **K**₂**Py2** and **K**₃**Py3** with the increasing charge of the anion enabled the enrichment of **K**₂**Py2** and the purification of **K**₃**Py3** by precipitation from the THF solutions *via* the slow addition of CH_2Cl_2 . Pure **KPy1** and **K**₂**Py2** were obtained *via* crystallization. Single-crystals of **KPy1**, **K**₂**Py2**· $\text{OC}(\text{CH}_3)_2$ and **K**₃**Py3**· 3THF · $1.04\text{H}_2\text{O}$ were studied using X-ray diffraction (Fig. 1). Selected experimental bond distances of the three related anions **Py1**, **Py2** and **Py3** were compared to the calculated bond lengths in Table S3.†

Monosubstitution of partly fluorinated benzenes with **K**₂**1**

In addition to the reactions of **K**₂**1** with hexafluorobenzene³⁰ and pentafluoropyridine, **K**₂**1** was found to undergo C–F/C–B exchange reactions with all of the partly fluorinated benzenes $\text{C}_6\text{F}_{6-n}\text{H}_n$ ($n = 1–5$) (Table 1 and Fig. 2). Unprecedentedly, the nucleophilic attack of **1** at almost all of the partially fluorinated benzenes was regio- and chemoselective. As expected for electron deficient partly fluorinated benzenes, deprotonation was observed for the strong base **1**, yielding $[\text{BH}(\text{CN})_3]^-$ as a side product. The amount of $[\text{BH}(\text{CN})_3]^-$ formed reflects the Brønsted acidity of the hydrogen atoms of the respective fluorobenzene.^{56,57} 1,2,4,5-tetrafluoro- and pentafluorobenzene gave the largest amounts of $[\text{BH}(\text{CN})_3]^-$ with up to 48% for $\text{C}_6\text{F}_5\text{H}$ (Table 1). The addition of LiCl at the start of the reaction of **K**₂**1** with $\text{C}_6\text{F}_5\text{H}$ resulted in a reduction in the amount of $[\text{BH}(\text{CN})_3]^-$ to 10% and an increased yield of $[1-\{(\text{NC})_3\text{B}\}-2,3,5,6-\text{F}_4-\text{C}_6\text{H}]^-$ (**B5**) of 62%. Since the salts $[(\text{alkyl})_3\text{NH}][\text{BH}(\text{CN})_3]$ (alkyl = Me, Et) are water soluble, purification was achieved *via* the precipitation or extraction of the respective trimethyl- or triethylammonium phenylborates from aqueous solutions. The ammonium salts were easily back-converted into K^+ salts with K_2CO_3 .

The regioselectivities of the C–F/C–B exchange reactions were found to be high, and in most cases one major isomer had formed (Table 1). Most of the new tricyanoborates were characterized using single-crystal X-ray diffraction (Fig. 2) and the details of the experimental and calculated bond parameters are summarized in Table S3.† The exchange of a fluorine with a tricyanoboryl group in the *para* position to a fluorine substituent is unfavoured. Replacement was found to be preferred for fluorine substituents in the *meta* position to one or two further fluorine substituents, which is typical for the $\text{S}_{\text{N}}\text{Ar}$ reactions of fluorobenzenes.^{52,53} 1,4-difluorobenzene gave a mixture of $[1-\{(\text{NC})_3\text{B}\}-4-\text{F}-\text{C}_6\text{H}_4]^-$ (**B2c**) and $[1-\{(\text{NC})_3\text{B}\}-3-\text{F}-\text{C}_6\text{H}_4]^-$ (**B2b**) in conjunction with 25% of $[\text{BH}(\text{CN})_3]^-$ (Scheme 2). The formation of anion **B2b** is rationalized by an aryne mechanism that is similar to related reactions.⁵⁸ In summary, the high regioselectivities that were observed show that an $\text{S}_{\text{N}}\text{Ar}$ mechanism dominates for the C–F/C–B exchange presented herein.



Table 1 Reactions of K₂1 with selected fluoro(hetero)arenes

Entry	Substrate	LiCl ^a	K ₂ 1 ^b	Conditions	[BH(CN) ₃] ^{-c}	Major tricyanoborate anion(s) formed	Isolated yield
1	C ₆ FH ₅	Yes	<1	80 °C, 2 d	25%	[1-(NC) ₃ B]-C ₆ H ₅] ⁻ (B1)	Sole isomer 45%
2	1,2-C ₆ F ₂ H ₄	Yes	<1	r.t., 16 h	9%	[1-(NC) ₃ B]-2-F-C ₆ H ₄] ⁻ (B2a)	Sole isomer 58%
3	1,3-C ₆ F ₂ H ₄	Yes	<1	r.t., 3 d	<5%	[1-(NC) ₃ B]-3-F-C ₆ H ₄] ⁻ (B2b)	Sole isomer 70%
4	1,4-C ₆ F ₂ H ₄	Yes	<1	75 °C, 30 h	28%	[1-(NC) ₃ B]-4-F-C ₆ H ₄] ⁻ (B2c) + B2b (6 : 4) ^d ^e	45% ^e
5	1,2,3-C ₆ F ₃ H ₃	Yes	<1	r.t., 3 d	<5%	[1-(NC) ₃ B]-2,3-F ₂ -C ₆ H ₃] ⁻ (B3a) + [1-(NC) ₃ B]-2,6-F ₂ -C ₆ H ₃] ⁻ (B3b) (4 : 1)	66%
6	1,2,4-C ₆ F ₃ H ₃	Yes	<1	r.t., 2 h	<5%	[1-(NC) ₃ B]-2,5-F ₂ -C ₆ H ₃] ⁻ (B3c)	Sole isomer 76%
7	1,3,5-C ₆ F ₃ H ₃	Yes	<1	r.t., 16 h	<5%	[1-(NC) ₃ B]-3,5-F ₂ -C ₆ H ₃] ⁻ (B3d)	Sole isomer 63%
8	1,2,3,4-C ₆ F ₄ H ₂	Yes	<1	r.t., <1 h	<5%	[1-(NC) ₃ B]-2,3,6-F ₃ -C ₆ H ₂] ⁻ (B4a)	Sole isomer 77%
9	1,2,3,5-C ₆ F ₄ H ₂	Yes	<1	r.t., 2 h	<5%	[1-(NC) ₃ B]-2,3,5-F ₃ -C ₆ H ₂] ⁻ (B4b)	Sole isomer 63%
10	1,2,3,5-C ₆ F ₄ H ₂	No	<1	75 °C, 30 h	10%	B4b	8% of other isomers 51%
11	1,2,4,5-C ₆ F ₄ H ₂	Yes	<1	r.t., 30 min	30%	[1-(NC) ₃ B]-2,4,5-F ₃ -C ₆ H ₂] ⁻ (B4c)	Sole isomer 50%
12	1,2,4,5-C ₆ F ₄ H ₂	Yes	2	r.t., 16 h	n.d.	[1,4-(NC) ₃ B] ₂ -2,5-F ₂ -C ₆ H ₂] ²⁻ (B4d)	Sole isomer 42% ^f
13	C ₆ F ₅ H	Yes	<1	r.t., 10 min	10%	[1-(NC) ₃ B]-2,3,5,6-F ₄ -C ₆ H] ⁻ (B5)	6% of one other isomer 62%
14	C ₆ F ₅ H	No	<1	r.t., 2 d	48%	B5	20% of other anions 39%
15	C ₆ F ₆	No	<1	0 °C	—	[1-(NC) ₃ B]-C ₆ F ₅] ⁻ (B6a) ²⁹	Sole isomer 67% (ref. 30)
16	C ₆ F ₆	No	2.2	Reflux, 20 h	—	[1,4-(NC) ₃ B] ₂ -C ₆ F ₄] ²⁻ (B6b)	Sole isomer 74%
17	C ₅ F ₅ N	No	0.33	r.t., 12 h	—	[4-(NC) ₃ B]-C ₅ F ₄ N] ⁻ (Py1) ^g	Other isomer(s), Py2 , Py3 81% ^h
18	C ₅ F ₅ N	No	2	r.t., 4 d	—	[2,4-(NC) ₃ B] ₂ -C ₅ F ₃ N] ²⁻ (Py2) ⁱ	Other isomer(s), Py3 59% ^j
19	C ₅ F ₅ N	No	3	r.t., 4 d	—	[2,4,6-(NC) ₃ B] ₃ -C ₅ F ₂ N] ³⁻ (Py3)	<10% Py1 and Py2 31%
20	C ₁₂ F ₁₀	No	0.8	r.t., 2 h	—	[4-(NC) ₃ B]-C ₁₂ F ₉] ⁻ (BP1)	<20% of BP2 49%
21	C ₁₂ F ₁₀	No	2.2	50 °C, 1 h	—	[4,4'-(NC) ₃ B] ₂ -C ₁₂ F ₈] ²⁻ (BP2)	Sole isomer 90%
22	C ₁₀ F ₈	No	0.5	r.t., 3 d	—	[2-(NC) ₃ B]-C ₁₀ F ₇] ⁻ (N1)	8% of other isomers ^k 55%
23	C ₁₀ F ₈	No	2	60 °C, 16 h	—	[2,6-(NC) ₃ B] ₂ -C ₁₀ F ₆] ²⁻ (N2)	Mixture of N1 , N2 and N3 ^l 24%
24	F ₃ C-C ₆ F ₅	No	<1	r.t., 3 h	—	[1-F ₃ C-4-(NC) ₃ B]-C ₆ F ₄] ⁻ (B7)	Sole isomer 68%
25	Me-C ₆ F ₅	No	<1	90 °C, 3 d	—	[1-Me-4-(NC) ₃ B]-C ₆ F ₄] ⁻ (B8a) + [1-Me-3-(NC) ₃ B]-C ₆ F ₄] ⁻ (B8b) (9 : 1)	n.d.
26	1-F ₃ C-4-H-C ₆ F ₄	No	<1	r.t., 2 h	75%	Unidentified borate anions	n.d.
27	1-F ₃ C-6-H-C ₆ F ₄	No	<1	r.t., 4 d	2%	[1-F ₃ C-4-(NC) ₃ B]-2,3,5-F ₃ -C ₆ H] ⁻ (B9)	7% of other isomers 78%
28	MeO-C ₆ F ₅	No	<1	60 °C, 16 h	—	[1-MeO-4-(NC) ₃ B]-C ₆ F ₄] ⁻ (B10a) + [1-MeO-3-(NC) ₃ B]-C ₆ F ₄] ⁻ (B10b) (1 : 1)	82%
29	NC-C ₆ F ₅	No	<1	r.t., <1 h	—	[1-NC-4-(NC) ₃ B]-C ₆ F ₄] ⁻ (B11a) + [1-NC-2-(NC) ₃ B]-C ₆ F ₄] ⁻ (B11b) + [B(CN) ₄] ⁻ (2.5 : 1.5 : 1) ^m	n.d.
30	Cl-C ₆ F ₅	No	<1	r.t., <1 h	—	[BCl(CN) ₃] ⁻ , [B ₂ (CN) ₆] ²⁻ , ...	n.d.
31	O ₂ N-C ₆ F ₅	No	<1	r.t., 16 h	—	[B ₂ (CN) ₆] ²⁻ , ...	n.d.

^a Whether LiCl was added to the reaction mixture. ^b Equivalents of K₂1. ^c The percentage that was formed as a side product; [BH(CN)₃]⁻ was removed during the work-up. ^d The ratio **B2c** : **B2b** was 6 : 4 in the reaction mixture and 7 : 3 in the isolated material. ^e 11% of K[BH(CN)₃]⁻ [Et₃NH]⁺ salt. ^f The internal yield was 75% **Py1**, 16% **Py2**, 8% another isomer (probably [2-(NC)₃B]-C₅F₄N]⁻), and 1% **Py3** and unknown tricyano(fluoropyridinyl)borate anions. ^g Purity ca. 85% (¹¹B/¹⁹F NMR); it contained 15% other tricyano(fluoropyridinyl)borates. ^h The internal yield (¹¹B/¹⁹F NMR) was 60% **Py2**, 30% **Py3**, and 10% another tricyano(fluoropyridinyl)borate anion. ⁱ Purity ca. 75% (¹¹B/¹⁹F NMR); it contained 15% **K₃Py3** and 10% another tricyano(fluoropyridinyl)borate. ^j **N2** : **N3** = 1.0 : 0.8 (**N3** = [2,7-(NC)₃B]₂-C₁₀F₆]²⁻). ^k The ratio of the reaction mixture: **N1** : **N2** : **N3** = 0.4 : 1.0 : 0.7; **N2** is hardly soluble and was obtained as a pure K⁺ salt. ^l **K[B(CN)₄]** was mostly removed *via* fractional precipitation.

The reaction rate of the C-F/C-B exchange strongly depended on the degree of fluorination and therefore on the electron density of the aromatic ring system. C₆F₆ reacted within minutes at room temperature, whereas the conversion of C₆F₅H required two days. In the cases of mono-, di- and trifluorobenzenes, no reaction was observed with K₂1 in THF even at 80 °C. Tetrafluorobenzenes showed some reactivity towards K₂1 in THF depending on the substitution scheme. 1,2,3,5-tetrafluorobenzene reacted at 75 °C within 3 days. The reaction of the 1,2,4,5-isomer required 120 °C, yielding an inseparable brownish mixture. The addition of anhydrous LiCl was found to result in a tremendous increase in the reaction rate. For example, upon the addition of LiCl, a mixture of 1,2,4,5-tetrafluorobenzene and K₂1 immediately became warm and the reaction was complete within minutes. Similarly, the reaction

time of the conversion of C₆F₅H into **B5** was reduced from 2 days to 10 minutes. The shorter reaction time was accompanied by enhanced chemo- and regioselectivity (Table 1). The LiCl-induced reaction was successfully applied for all of the di- and trifluorobenzenes and C₆FH₅ (Fig. 1). The reactions of all three trifluorobenzene isomers and of 1,2- and 1,3-difluorobenzene were conducted at room temperature. Only for 1,4-F₂-C₆H₄ and C₆FH₅ were higher temperatures necessary. Three different effects may be responsible for the faster reactions and the higher chemo- and regioselectivities in the presence of LiCl: (i) Li₂1 is more soluble in THF than K₂1,³¹ which results in an enhanced availability of the dianion **1**; (ii) the high fluoride ion affinity of Li⁺ may lead to a Li...F interaction, a weakening of the C-F bond and a lowering of the activation barrier for the nucleophilic replacement; and (iii) a weak Li...B or Li...N



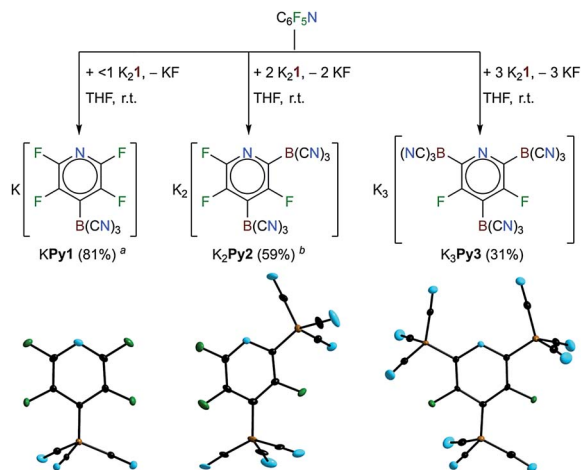
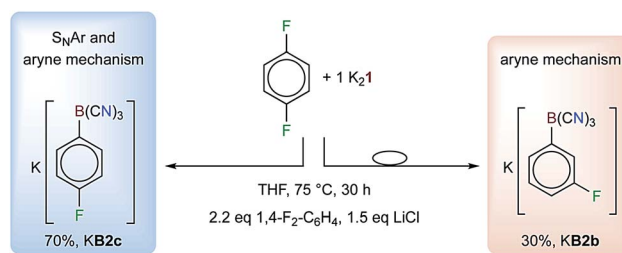


Fig. 1 Top: the reactions of K_21 with pentafluoropyridine to give Py1, Py2 and Py3 (^acontained 15% other tricyano(fluoropyridinyl)borates; ^bcontained 15% K_3Py3 and 10% another tricyano(fluoropyridinyl)borate). Bottom: the anions in crystals of their K^+ salts (the displacement ellipsoids are at the 25% probability level, except for Py3 where they are at 50%).

interaction between Li^+ and the boryl dianion **1** may influence the reactivity of **1**.

Disubstitution of fluorinated benzenes with K_21

C_6F_6 and 1,2,4,5- $F_4-C_6H_2$ were reacted with an excess of K_21 to give salts of the dianions $[1,4-\{(NC)_3B\}_2-C_6F_4]^{2-}$ (**B6b**) and $[1,4-$



Scheme 2 Reaction of 1,4- $F_2-C_6H_4$ with K_21 in the presence of LiCl to give a mixture of KB2 and KB3 (ratio 7 : 3). The $[BH(CN)_3]^-$ that formed (25%) is not shown.

$\{(NC)_3B\}_2-2,6-F_2-C_6H_2]^{2-}$ (**B4d**) (Table 1 and Fig. 2). In the case of the reaction of 1,2,4,5- $F_4-C_6H_2$, anhydrous LiCl was added to enhance the rate of the reaction. Both of the reactions were found to be highly regioselective and in accordance with an S_NAr mechanism. Therefore, the second C-F/C-B exchange gave the *para*- $\{B(CN)_3\}_2$ derivatives as the sole isomers.

In addition to the multiple C-F/C-B exchange reactions of C_5F_5N (Fig. 1), C_6F_6 and 1,2,4,5- $F_4-C_6H_2$ (Fig. 2), perfluorobiphenyl and perfluoronaphthalene were successfully applied in related reactions with K_21 . Stoichiometric amounts or a slight excess of K_21 yielded $K_2[4,4'-\{(NC)_3B\}_2-C_{12}F_8]$ (**K2BP2**) and $K_2[2,6-\{(NC)_3B\}_2-C_{10}F_6]$ (**K2N2**), respectively. In contrast, an excess of the perfluorinated arene predominantly gave the corresponding monoanions $[4-\{(NC)_3B\}-C_{12}F_9]^-$ (**BP1**) and $[2-\{(NC)_3B\}-C_{10}F_7]^-$ (**N1**) (Table 1). The successive reactions of perfluorobiphenyl that gave **BP1** and **BP2** were fully

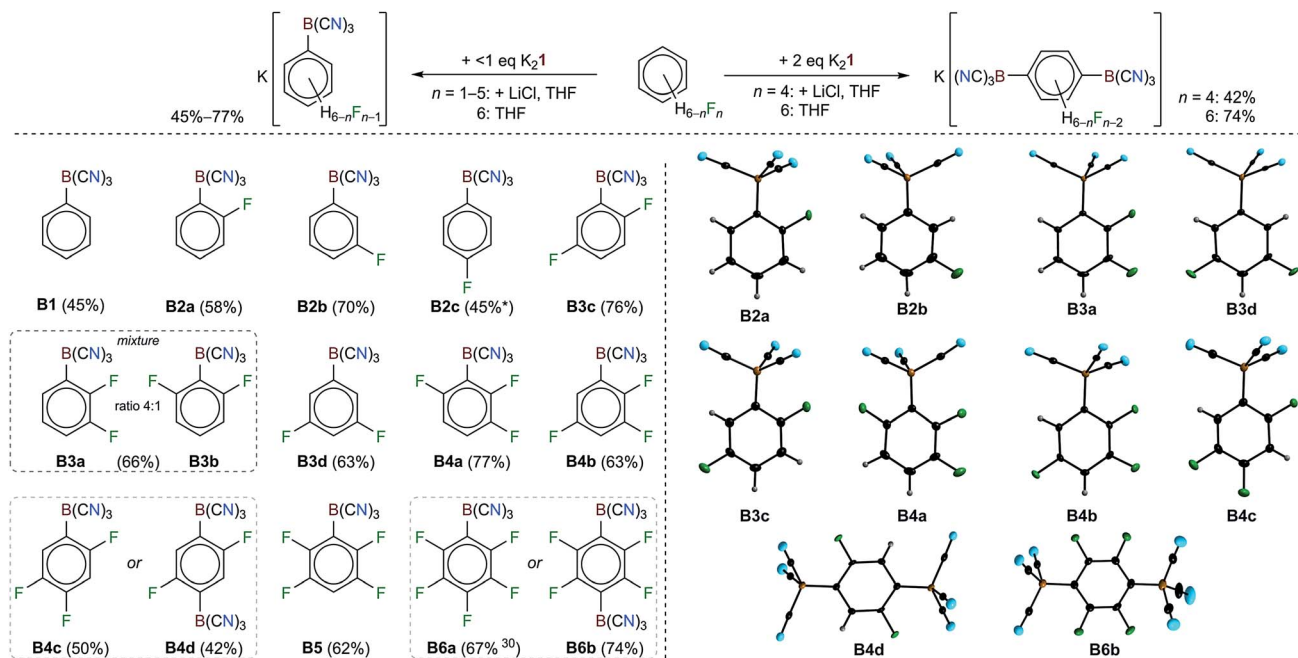


Fig. 2 Reactions of K_21 with fluorinated benzenes (top). The main products; dashed boxes show the anions that were derived from the same arene. In the cases of C_6F_6 and 1,2,4,5- $F_4-C_6H_2$, the different anions were obtained from different entries (bottom left). The tricyanophenylborate anions in the crystal structures of their K^+ (**B2a**, **B2b**, **B3a**, **B3c**, **B3d**, **B4a**, and **B4b**), $[Et_4N]^+$ (**B6b**), $[Et_3NH]^+$ (**B4d**) and $[Me_3NH]^+$ (**B4c**) salts (the displacement ellipsoids are at the 50% probability level, except for **B3a** where they are at 25%, and the H atoms are depicted with arbitrary radii) (bottom right).



regioselective. K_2BP2 was isolated in an excellent yield of 90% and a single crystal was investigated using X-ray diffraction (Fig. 3 and Table S3†). A slightly lower but still high regioselectivity was found for the first replacement of fluorine with **1** in perfluoronaphthalene to give **N1**. The introduction of a second $\{B(CN)_3\}$ moiety resulted in a mixture of **N1**, **N2** and $[2,7-\{(NC)_3B\}_2-C_{10}F_6]^{2-}$ (**N3**) with the ratio 0.4 : 1.0 : 0.7. The formation of **N2** as the major isomer agrees with the typical substitution scheme for the S_NAr reactions of perfluoronaphthalene.⁵³

Reactions of K_21 with fluorinated benzenes with functional groups

The reactions described so far (*vide supra*) demonstrate the regioselectivity of the S_NAr reaction of fluorinated (hetero)arenes with K_21 and show the possibility of synthesising multiple charged tricyanoborate anions. The multiple C–F/C–B exchange reactions are the first examples of the transformations of functionalized fluorinated (hetero)arenes with **1**. A series of further selected reactions of polyfluorinated benzenes with a functional group bonded to the benzene ring have been studied (Fig. 4 and Table 1, entries 24–31).

Perfluorotoluene was found to give $[1-F_3C-4-\{(NC)_3B\}-C_6F_4]^-$ (**B7**) as the sole isomer and $KB7$ was isolated in 68% yield. 4-Me- C_6F_5 resulted in a mixture of the isomers $[1-Me-4-\{(NC)_3B\}-C_6F_4]^-$ (**B8a**) and $[1-Me-3-\{(NC)_3B\}-C_6F_4]^-$ (**B8b**) in a 9 : 1 ratio and pentafluoroanisole gave $[1-MeO-4-\{(NC)_3B\}-C_6F_4]^-$ (**B10a**) and $[1-MeO-3-\{(NC)_3B\}-C_6F_4]^-$ (**B10b**) in equal amounts. The decrease in the regioselectivity in the order $F_3C-C_6F_5$, Me- C_6F_5 and MeO- C_6F_5 reflects the influence of the electronic properties of the $-CF_3$, $-Me$ and $-OMe$ substituents on the reactivity of the corresponding fluoroarenes. The trifluoromethyl group is a strong electron withdrawing group, while the methoxy group is an electron donating group. Strong electron withdrawing groups are usually *para* and *ortho* directing. It is most likely that steric effects are the reason that the *ortho*-substituted product $[1-F_3C-2-\{(NC)_3B\}-C_6F_4]^-$ was not observed. The reaction of K_21 with NC- C_6F_5 , which contains the strong electron withdrawing cyano group that is sterically less demanding than the CF_3 group, gave the *ortho*-substituted anion $[1-NC-2-\{(NC)_3B\}-C_6F_4]^-$ (**B11b**) together with $[1-NC-4-\{(NC)_3B\}-C_6F_4]^-$ (**B11a**) and $[B(CN)_4]^-$ in a ratio of 1.5 : 2.5 : 1. The formation of the tetracyanoborate anion is due to the nucleophilic attack at the carbon atom of the cyano group. The formation of $[B(CN)_4]^-$ starting from K_21 was reported previously, *e.g.* from reactions with $(CN)_2$ and PhOCN.³¹ Single crystals of the potassium salts

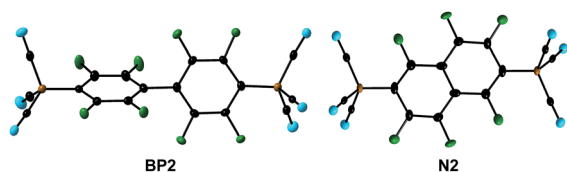


Fig. 3 The bis(tricyanoborate) dianions **BP2** and **N2** in the crystal structures of their K^+ salts (the displacement ellipsoids are at the 50% probability level).

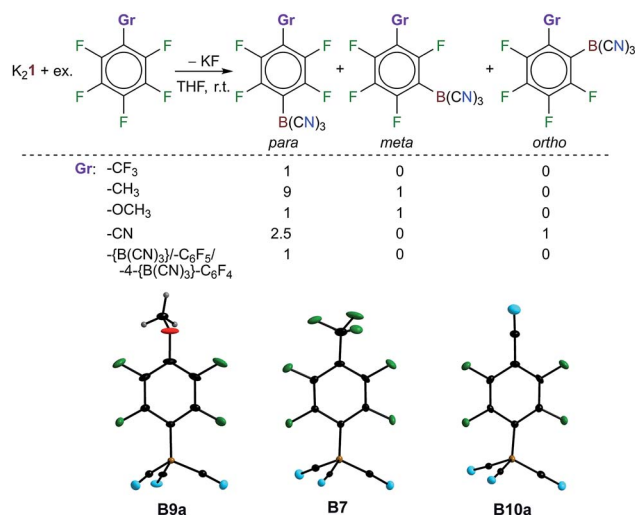


Fig. 4 Reactions of K_21 with functionalized fluorinated benzenes. Borate anions **B9a**, **B7** and **B10a** in the crystal structures of their K^+ salts (the displacement ellipsoids are at the 25% probability level, except for **B10a** where they are at 50%, and the H atoms are depicted with arbitrary radii).

of $[1-F_3C-4-\{(NC)_3B\}-C_6F_4]^-$ (**B7**), $[1-MeO-4-\{(NC)_3B\}-C_6F_4]^-$ (**B10a**) and $[1-NC-4-\{(NC)_3B\}-C_6F_4]^-$ (**B11a**) were characterized using diffraction experiments (Fig. 4 and Table S3†).

The deprotonation of 1- $F_3C-4-H-C_6F_4$ to give $[BH(CN)_3]^-$ was found to be the most relevant reaction with K_21 , and other unidentified borate anions had formed. In contrast, 1- $F_3C-2-H-C_6F_4$ and K_21 gave the $[1-F_3C-4-\{(NC)_3B\}-2,3,5-F_3-C_6H]^-$ anion (**B9**) in 78% yield and only 2% of $[BH(CN)_3]^-$ was observed (Table 1).

The reactions of K_21 with Cl- C_6F_5 and O₂N- C_6F_5 gave complex product mixtures, and the hexacyanoborate dianion $[B_2(CN)_6]^{2-}$ (ref. 59) was identified. Additionally, the tricyanohaloborate anion $[BCl(CN)_3]^-$ (ref. 60) formed from Cl- C_6F_5 (Table 1).

Conclusions

Boron-centred nucleophiles are an emerging class of compounds and are of growing importance for synthetic chemistry because they provide a very convenient entry to boron-functionalized compounds and materials.^{1–28} The unprecedented, straightforward, regioselective and transition-metal-free introduction of one, two or even three $\{B(CN)_3\}^-$ units into fluoro(hetero)arenes starting from readily accessible K_21 ^{30–32} opens unique and convenient access to single and multiple charged anions with tricyanoborate moieties. The observed regioselectivities for the C–F/C–B exchange reactions are almost all in accordance with an S_NAr mechanism, which showed the boron-centred nucleophilic character of the dianion **1**, as previously observed for the formation of $[B_2(CN)_6]^{2-}$ starting from K_21 and $K[BF(CN)_3]$.⁵⁹ So, an alternative radical reaction pathway is highly unlikely, although this type of reactivity was observed for other boron-centred nucleophiles.^{61,62} Furthermore, the syntheses highlight the value of K_21 for the



general preparation of a wealth of tricyanoborate anions. Since the salts of the tricyanoborate anions such as the ones described herein are promising building blocks for materials science, for example as components of ionic liquids that are used in electrochemical devices,⁶³ convenient and high yield syntheses are necessary to facilitate applications.

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Notes and references

- M. Yamashita and K. Nozaki, in *Topics in Organometallic Chemistry: Synthesis and Application of Organoboron Compounds*, ed. E. Fernández and A. Whiting, Springer, Cham, Switzerland, 2015, pp. 1–37.
- J. Cid, H. Gulyás, J. J. Carbó and E. Fernández, *Chem. Soc. Rev.*, 2012, **41**, 3558–3570.
- M. Yamashita, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 983–999.
- L. Weber, *Eur. J. Inorg. Chem.*, 2012, 5595–5609.
- Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113–115.
- Y. Segawa, Y. Suzuki, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **130**, 16069–16079.
- M. Yamashita, Y. Suzuki, Y. Segawa and K. Nozaki, *J. Am. Chem. Soc.*, 2007, **129**, 9570–9571.
- Y. Okuno, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2011, **50**, 920–923.
- N. Dettenrieder, Y. Aramaki, B. M. Wolf, C. Maichle-Mössmer, X. Zhao, M. Yamashita, K. Nozaki and R. Anwander, *Angew. Chem., Int. Ed.*, 2014, **53**, 6259–6262.
- H. Hayashi, Y. Segawa, M. Yamashita and K. Nozaki, *Chem. Commun.*, 2011, **47**, 5888–5890.
- K. Nozaki, Y. Aramaki, M. Yamashita, S.-H. Ueng, M. Malacria, E. Lacôte and D. P. Curran, *J. Am. Chem. Soc.*, 2010, **132**, 11449–11451.
- A. Rit, J. Campos, H. Niu and S. Aldridge, *Nat. Chem.*, 2016, **8**, 1022–1026.
- A. V. Protchenko, D. Dange, A. D. Schwarz, C. Y. Tang, N. Phillips, P. Mountford, C. Jones and S. Aldridge, *Chem. Commun.*, 2014, **50**, 3841–3844.
- A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birj Kumar, C. Jones, N. Kalsoyannis, P. Mountford and S. Aldridge, *Nat. Chem.*, 2014, **6**, 315–319.
- B. Wang, Y. Li, R. Ganguly, H. Hirao and R. Kinjo, *Nat. Commun.*, 2016, **7**, 11871.
- W. Lu, H. Hu, Y. Li, R. Ganguly and R. Kinjo, *J. Am. Chem. Soc.*, 2016, **138**, 6650–6661.
- H. Braunschweig, C.-W. Chiu, K. Radacki and T. Kupfer, *Angew. Chem., Int. Ed.*, 2010, **49**, 2041–2044.
- H. Braunschweig, M. Buzler, R. D. Dewhurst and K. Radacki, *Angew. Chem., Int. Ed.*, 2008, **47**, 5650–5653.
- H. Braunschweig, R. D. Dewhurst, L. Pentecost, K. Radacki, A. Vargas and Q. Ye, *Angew. Chem., Int. Ed.*, 2016, **55**, 436–440.
- R. Kinjo, B. Donnadiou, M. A. Celik, G. Frenking and G. Bertrand, *Science*, 2011, **333**, 610–613.
- D. A. Ruiz, M. Melaimi and G. Bertrand, *Chem. Commun.*, 2014, **50**, 7837–7839.
- L. Kong, Y. Li, R. Ganguly, D. Vidovic and R. Kinjo, *Angew. Chem., Int. Ed.*, 2014, **53**, 9280–9283.
- L. Kong, R. Ganguly, Y. Li and R. Kinjo, *Chem. Sci.*, 2015, **6**, 2893–2902.
- D. Wu, L. Kong, Y. Li, R. Ganguly and R. Kinjo, *Nat. Commun.*, 2015, **6**, 7340.
- T. Imamoto and T. Hikosaka, *J. Org. Chem.*, 1994, **59**, 6753–6759.
- L. Kong, W. Lu, L. Yongxin, R. Ganguly and R. Kinjo, *Inorg. Chem.*, 2017, **56**, 5586–5593.
- J. Monot, A. Solovyev, H. Bonin-Dubarle, É. Derat, D. P. Curran, M. Robert, L. Fensterbank, M. Malacria and E. Lacôte, *Angew. Chem., Int. Ed.*, 2010, **49**, 9166–9169.
- D. A. Ruiz, G. Ung, M. Melaimi and G. Bertrand, *Angew. Chem., Int. Ed.*, 2013, **52**, 7590–7592.
- E. Bernhardt, V. Bernhardt-Pitchougina, H. Willner and N. V. Ignatiev, *Angew. Chem., Int. Ed.*, 2011, **50**, 12085–12088.
- J. Landmann, J. A. P. Sprenger, R. Bertermann, N. Ignat'ev, V. Bernhardt-Pitchougina, E. Bernhardt, H. Willner and M. Finze, *Chem. Commun.*, 2015, **51**, 4989–4992.
- J. Landmann, F. Keppner, D. B. Hofmann, J. A. P. Sprenger, M. Häring, S. H. Zottnick, K. Müller-Buschbaum, N. V. Ignat'ev and M. Finze, *Angew. Chem., Int. Ed.*, 2017, **56**, 2795–2799.
- J. Landmann, F. Keppner, J. A. P. Sprenger, M. Finze and N. Ignat'ev, DE102014018103A1, Julius-Maximilians-Universität Würzburg, Merck Patent GmbH, 2016.
- J. A. P. Sprenger, J. Landmann, M. Drisch, N. Ignat'ev and M. Finze, *Inorg. Chem.*, 2015, **54**, 3403–3412.
- N. Ignatyev, J. A. P. Sprenger, J. Landmann and M. Finze, WO2014198401, Merck Patent GmbH, 2014.
- L. A. Bischoff, M. Drisch, C. Kerpen, P. T. Hennig, J. Landmann, J. A. P. Sprenger, N. Ignat'ev and M. Finze, in preparation.
- M. Drisch, L. A. Bischoff, L. Herkert, J. A. P. Sprenger, M. Finze, N. Ignatyev and R. van Hal, WO2016074760, Merck Patent GmbH, 2016.
- W.-H. Guo, Q.-Q. Min, J.-W. Gu and X. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 9075–9078.
- J. Zhou, M. W. Kuntze-Fechner, R. Bertermann, U. S. D. Paul, J. H. J. Berthel, A. Friedrich, Z. Du, T. B. Marder and U. Radius, *J. Am. Chem. Soc.*, 2016, **138**, 5250–5253.
- T. Niwa, H. Ochiai, Y. Watanabe and T. Hosoya, *J. Am. Chem. Soc.*, 2015, **137**, 14313–14318.
- X.-W. Liu, J. Echavarren, C. Zarate and R. Martin, *J. Am. Chem. Soc.*, 2015, **137**, 12470–12473.
- S. I. Källäne, M. Teltewskoi, T. Braun and B. Braun, *Organometallics*, 2015, **34**, 1156–1169.
- M. Teltewskoi, J. A. Panetier, S. A. Macgregor and T. Braun, *Angew. Chem., Int. Ed.*, 2010, **49**, 3947–3951.



- 43 R. J. Lindup, T. B. Marder, R. N. Perutz and A. C. Whitwood, *Chem. Commun.*, 2007, 3664–3666.
- 44 A. M. Mfuh, J. D. Doyle, B. Chhetri, H. D. Arman and O. V. Larionov, *J. Am. Chem. Soc.*, 2016, **138**, 2985–2988.
- 45 K. Chen, M. S. Cheung, Z. Lin and P. Li, *Org. Chem. Front.*, 2016, **3**, 875–879.
- 46 T. Ahrens, J. Kohlmann, M. Ahrens and T. Braun, *Chem. Rev.*, 2015, **115**, 931–972.
- 47 E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady and R. N. Perutz, *Acc. Chem. Res.*, 2011, **44**, 333–348.
- 48 H. Amii and K. Uneyama, *Chem. Rev.*, 2009, **109**, 2119–2183.
- 49 D. O'Hagan, *Chem. Soc. Rev.*, 2008, **37**, 308–319.
- 50 T. G. Richmond, *Angew. Chem., Int. Ed.*, 2000, **39**, 3241–3244.
- 51 W. Chen, C. Bakewell and M. R. Crimmin, *Synthesis*, 2017, **49**, 810–821.
- 52 G. M. Brooke, *J. Fluorine Chem.*, 1997, **86**, 1–76.
- 53 R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse and D. L. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1974, 239–240.
- 54 V. V. Aksenov, V. M. Vlasov and G. G. Yakobson, *J. Fluorine Chem.*, 1982, **20**, 439–458.
- 55 Y. Sun, H. Sun, J. Jia, A. Du and X. Li, *Organometallics*, 2014, **33**, 1079–1081.
- 56 M. Schlosser and E. Marzi, *Chem.–Eur. J.*, 2005, **11**, 3449–3454.
- 57 H. H. Büker, N. M. M. Nibbering, D. Espinosa, F. Mongin and M. Schlosser, *Tetrahedron Lett.*, 1997, **38**, 8519–8522.
- 58 C. Wu and F. Shi, *Asian J. Org. Chem.*, 2013, **2**, 116–125.
- 59 J. Landmann, J. A. P. Sprenger, M. Hailmann, V. Bernhardt-Pitchougina, H. Willner, N. Ignat'ev, E. Bernhardt and M. Finze, *Angew. Chem., Int. Ed.*, 2015, **54**, 11259–11264.
- 60 J. A. P. Sprenger, L. A. Bischoff, M. Drisch, L. Herkert, M. Finze, H. Willner, E. Bernhardt, N. Ignatyev and M. Schulte, WO2016058665, Merck Patent GmbH, 2016.
- 61 R. Bertermann, H. Braunschweig, R. D. Dewhurst, C. Hörl, T. Kramer and I. Krummenacher, *Angew. Chem., Int. Ed.*, 2014, **53**, 5453–5457.
- 62 D. P. Curran, A. Boussonnière, S. J. Geib and E. Lacôte, *Angew. Chem., Int. Ed.*, 2012, **51**, 1602–1605.
- 63 N. V. Ignat'ev, M. Finze, J. A. P. Sprenger, C. Kerpen, E. Bernhardt and H. Willner, *J. Fluorine Chem.*, 2015, **177**, 46–54.

