View Article Online View Journal

# ChemComm

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Beil, S. Moehle, P. Enders and S. R. Waldvogel, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC02996B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

# **Chemical Communications**



## COMMUNICATION

### Electrochemical Instability of Highly Fluorinated Tetraphenyl Borates and the Syntheses of their Respective Biphenyls

Sebastian B. Beil,<sup>a,b,†</sup> Sabine Möhle,<sup>a,†</sup> Patrick Enders,<sup>a</sup> and Siegfried R. Waldvogel<sup>a,b</sup>

Received 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 16 May 2018. Downloaded by Kings College London on 17/05/2018 02:39:44.

Highly fluorinated tetraphenyl borate anions are of importance as weakly coordinating anions in metalorganic reactions. However, at high positive potentials their electrochemical stability in organic solvents is not sufficient. This was investigated by a comprehensive cyclic voltammetry study and can be used synthetically to generate highly fluorinated biphenyls.

The application of weakly coordinating anions plays an important role in various field of chemistry.<sup>1,2</sup> Due to their low nucleophilicity such salts exhibit a strong influence on redox processes of various organometallic complexes.<sup>3,4</sup> A prominent example of this type of anions is the tetraphenyl borate (**1**) and its fluorinated congeners  $[B(C_6F_5)_4]^-$  (**2**) and  $[B(C_6H_3(CF_3)_2)_4]^-$  (**3**), known as BArF anions (Figure 1).<sup>2</sup> Their electrochemical properties have been extensively studied by Geiger and Barrière in terms of providing a benign electrolyte system for the generation of organometallic radical cations.<sup>4,5</sup> Due to their comparably high solubility in less polar solvents, even perfluorinated solvents become accessible for electrochemical applications.<sup>5,6</sup>



Figure 1: Examples of commonly applied tetraphenyl borate anions.

First studies about the electrochemical stability of **1** were reported by Geske in the 1950s, who found the formation of the respective biphenyl as a product of degradation.<sup>7,8</sup> Despite intense mechanistic investigation it is still unclear, whether the biphenyl formation follows an inter- or intramolecular

mechanism. For an intermolecular mechanism, the presence of free phenyl radicals in solution is anticipated. Whereas a intramolecular mechanism can either follow a radical or an ionic pathway, forming cationic  $B(Ph)_2^+$  species.<sup>7,9</sup>

When using the highly fluorinated BArF salts **2** and **3** as supporting electrolyte, we observed by serendipity the anodic generation of the corresponding biphenyls decafluorobiphenyl (**4**) and 3,3',5,5'-tetrakis(trifluoromethyl)biphenyl (**5**) (Scheme 1). These types of highly fluorinated structures are usually obtained using palladium<sup>10</sup> or gold catalysts,<sup>11</sup> as well as by oxidative coupling of borate or halide precursors again catalyzed by palladium,<sup>12</sup> iron,<sup>13</sup> rhodium,<sup>14</sup> or copper.<sup>15</sup> Strong Lewis acids were also reported to degrade borate anions,<sup>16</sup> but never described the formation of the respective biphenyls.



Scheme 1: Direct electrochemical formation of highly fluorinated biphenyls 4 and 5 by electrolysis of BArF anions 2 and 3.

This unusual anodic conversion prompted us to further investigate the electrochemical stability of fluorinated tetraphenyl borates **2** and **3** as well as the electrochemical access to fluorinated biphenyls **4** and **5**. Initially, our recently reported active molybdenum anode in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) was applied.<sup>17</sup> The three biphenyls could be isolated in moderate yields ranging from 15% to 46% (Table 1, Entries 1-3). Nevertheless, a disadvantage of this protocol was the significant drop of the initial current density of 8.3 mA/cm<sup>2</sup> during electrolysis due to low conductivity and fouling at the molybdenum anode, resulting in high voltages. Furthermore, solubility of Na-**3** in HFIP was not sufficient. To overcome these issues, the elec-

<sup>&</sup>lt;sup>a.</sup> Institute of Organic Chemistry, Johannes Gutenberg University Mainz,

Duesbergweg 10-14, 55128 Mainz, Germany, waldvogel@uni-mainz.de.

<sup>&</sup>lt;sup>b.</sup> Graduate School of Excellence Material Science in Mainz (MAINZ), Staudingerweg 9, 55128 Mainz, Germany.

<sup>&</sup>lt;sup>+</sup> These authors contributed equally to this work.

Electronic Supplementary Information (ESI) available: XXX See DOI: 10.1039/x0xx00000x

### COMMUNICATION

trolysis conditions were optimized with regards to Na-3 as substrate (for details see SI). Different anode materials like platinum, boron-doped diamond (BDD), glassy carbon, and isostatic graphite were investigated. The best result, with a yield of 52% of 5, was obtained using a BDD anode, whereas graphite anodes gave only traces of 5 in HFIP. To increase the solubility of Na-3 different solvents and co-solvents were tested. At a BDD anode, the best result was obtained in acetonitrile with the addition of 2vol% of tert-butanol leading to a yield of 63% of 5. However, the highest yield of 5 (73%, Table 1, Entry 5) was observed in acetonitrile at an isostatic graphite anode, whereas in HFIP only traces of 5 were identified. Shifting from molybdenum/HFIP to BDD or isostatic graphite/acetonitrile the conductivity was drastically increased, resulting in a lower applied voltage according to instrumentation and the electrolysis could be performed at a constant current density of 8.3 mA/cm<sup>2</sup>. The isolated yield of 73% could not be further increased by varying applied charge, current density or electrolyte concentration (see SI). With this optimized reaction protocol in hand, biphenyl could be obtained in an isolated yield of 61% from Bu<sub>4</sub>N-1 (Table 1, Entry 4). However, when applying this electrolysis conditions to Li-2 only traces of the perfluorinated biphenyl 4 where found by GC-MS technique (Table 1, Entry 6). Despite fouling of the molybdenum anode and a high applied voltage according to instrumentation, for  $[B(C_6F_5)_4]^-$  (2) the highest yield (20%, Table 1, Entry 7) of the perfluorinated biphenyl 4 was obtained at molybdenum in HFIP + 1vol% methanol. Traces of methanol, identified in the recovered HFIP (see SI), were found to be advantageous for the formation of biphenyls 4 and 5 in HFIP.<sup>18</sup>

Table 1: Isolated yield of biphenyls obtained at various electrolytic conditions.

e	[BAr.]	anode    Pt						
	sol	solvent, 8.3 mA/cm <sup>2</sup> , 2.57 F						
Entry	Anode	Solvent	Anion	Yield [%] <sup>a</sup>				
<b>1</b> <sup>b</sup>	Mo <sup>c</sup>	HFIP <sup>d</sup>	[BPh₄]⁻	20				
<b>2</b> <sup>e</sup>	Mo <sup>c</sup>	HFIP <sup>d</sup>	[B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	15				
3	Mo <sup>c</sup>	HFIP <sup>d</sup>	$[B(C_6H_3(CF_3)_2)_4]^-$	46				
4	graphite	MeCN	[BPh <sub>4</sub> ] <sup>-</sup>	61				
5	graphite	MeCN	[B(C <sub>6</sub> H <sub>3</sub> (CF <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> ] <sup>-</sup>	73				
6	graphite	MeCN	[B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	traces <sup>f</sup>				
<b>7</b> <sup>g</sup>	Mo <sup>c</sup>	HFIP + 1%	[B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	20				
		MeOH						

anode || Pt

Electrolytic conditions: 0.5 mmol tetraphenylborate salt, 5 mL solvent (c(BAr4-) = 0.1 M), undivided cell, platinum cathode, 8.3 mA/cm², 2.57 F, 22 °C; a: isolated yield; b: Q = 0.68 F; c: initial current density of 8.3 mA/cm<sup>2</sup> decreased during electrolysis; d: water and methanol impurities were identified by <sup>1</sup>H NMR spectroscopy (see SI); e: Q = 1.86 F, f: observed by GC-MS; g: Q = 2.2 F.

After the optimization of the formation of highly fluorinated biphenyls 4 and 5, we focused on the investigation of the reaction mechanism to find evidence for either an inter- or intramolecular proceeding. Through addition of quenching agents ( $\alpha$ , $\alpha$ , $\alpha$ -trifluorotoluene, fluorobenzene, benzene or pyridine) we envisioned to trap free radical species in solution. As a test reaction, we chose the conversion of Na-3 on a BDD anode in MeCN. The isolated yield of 5 was 57% without any

additives (Table 2, Entry 1). The addition of 20 vol% of either  $\alpha, \alpha, \alpha$ -trifluorotoluene, fluorobenzene op Behzene/had had has seen a nificant effect onto the yield (Table 2, Entries 2-4). Only for pyridine, a decreased yield of 41% was obtained (Table 2, Entry 5). Traces of cross-coupling products 6 could be clearly identified by GC-MS, which proves the presence of limited amounts of free-radical species in the solution. However, the high surplus of additive had limited effect on the yield of 5 and only traces of

Table 2: Trapping experiments during the electrolysis of sodium tetrakis(3,5bis(trifluoromethyl)phenyl borate) (Na-3).

cross-coupling product 6 were found, which indicates an

intramolecular mechanism.



<b>F</b> . <b>1</b>		
Entry	Additive (Vol%)	Field of 5 [%]"
1	_	57
2	$\alpha, \alpha, \alpha$ -trifluorotoluene (20)	58
3	fluorobenzene (20)	57
4	benzene (20)	60
5	pyridine (20)	41

Electrolytic conditions: 0.5 mmol Na[B(C6H3(CF3)2)4], 4 mL MeCN, 1 mL additive,  $(c(Na[B(C_6H_3(CF_3)_2)_4]) = 0.1 \text{ M})$ , undivided cell, BDD anode, platinum cathode, 8.3 mA/cm<sup>2</sup>, 2.57 F, 22 °C; a: isolated yield.

Further evidence of an intramolecular mechanism was obtained by electrolyzing a 1:1 mixture of different tetraphenyl borates. When applying Li-2 and Na-3 as electrolytes at a Mo anode, we only observed and isolated homo-coupled biphenyls 4 and 5 in yields of 25% and 43% (Scheme 2a). Electrolyzing a 1:1 mixture of Bu<sub>4</sub>N-1 and Na-3 at isostatic graphite in MeCN, a mixture of biphenyl (82%) and biphenyl 5 (35%) was obtained (Scheme 2b). No mixed biphenyls, expected in an intermolecular process, were identified or traced. Finally, we subjected a non-symmetrical BArF salt 7, which exhibits a non-fluorinated phenyl, to electrolysis at an isostatic graphite anode. We anticipated the formation of the unsymmetrical biphenyl 8, which was clearly identified as the sole product of electrolysis by GC-MS (Scheme 2c). This finding also supports our hypothesis of an intramolecular reaction mechanism, since a first oxidation at the borate will be potentially localized at the phenyl moiety and a subsequent elimination with one fluorinated arene is most likely.

An intense cyclic voltammetry (CV) study was conducted to gain insight into the electrochemical stability of highly fluorinated tetraphenylborates (CV data see Figures S2-S33). To determine the anodic limit potential, CVs of 0.1 M solutions of Bu<sub>4</sub>N-1, Na-3 and Li-2 in MeCN were recorded at various working electrodes (Figures S2-S5). As expected, the anodic limit potentials of the fluorinated salts 2 and 3 were, due to different electronwithdrawing substituents, significantly higher, than that of Bu<sub>4</sub>N-1 (Table 3).

Page 2 of 5



Scheme 2: Control experiments to investigate the reaction mechanism; a/b) electrolysis of a 1:1 mixture of two different tetraphenylborate salts; c) electrolysis of an unsymmetrical BArF electrolyte.

 $\label{eq:linear_state} \begin{array}{l} \hline Electrolytic conditions: \\ undivided cell, platinum cathode, 8.3 mA/cm^2, 22 °C; \\ a) 0.25 mmol Li[B(C_6F_{3})_{4}], 0.25 mmol Na[B(C_6H_3(CF_3)_{2})_{4}], 5 mL HFIP, molybdenum \\ anode, 1.82 F, decreasing current density; b) 0.25 mmol Bu_4NBPh_4, 0.25 mmol \\ Na[B(C_6H_3(CF_3)_{2})_{4}], 5 mL MeCN, isostatic graphite anode, 2.57 F; c) 0.03 mmol \\ Bu_4NBPh(C_6F_{5})_{3}, 5 mL MeCN, isostatic graphite anode, 2.57 F; d) NMR-yield. \end{array}$ 

For Bu<sub>4</sub>N-**1** and Na-**3** the lowest anodic limit potential was observed at isostatic graphite, whereby also the highest yields of biphenyls were observed in the preparative electrolyses (Table 1). The anodic limit potentials (and oxidation potentials  $E^{Ox}$ ) vary depending on the electrode material, due to different overpotentials for the oxidation of BArF salts.

 Table 3: Anodic limit potential of tetraphenylborate salts 1-3 in acetonitrile at different working electrode materials.

Entry	Working Electrode	Bu₄NBPh₄ (Bu₄N-1)	Na[B(C₅H₃(CF₃)₂)₄] (Na-3)	Li[B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] (Li-2)
1	BDD	0.49 V	1.64 V	1.63 V
2	glassy carbon	0.28 V	1.52 V	1.78 V
3	platinum	0.37 V	1.51 V	1.68 V
4	isostatic graphite	0.17 V	1.25 V	-

Potentials given vs. FcH/FcH+.

In agreement with the E<sup>ox</sup> of **2** and **3** reported by Geiger *et al.*,<sup>5</sup> the highest anodic limit was determined for Li-**2**. At isostatic graphite, no anodic limit potential could be assigned, due to side reactions among the whole potential range. As traces of methanol were found to be advantageous for the formation of **4** (and **5**) in HFIP, the influence of 1vol% of MeOH on the oxidation of Li-**2** at molybdenum was studied.<sup>19</sup> In contrast to pure HFIP, an oxidation peak ( $E^{Ox} = 2.79$  V vs. Ag/AgCl) was observed, when 1vol% of MeOH was added (Figure S6). This oxidation is most likely the oxidation of Li-**2**, as no oxidation of MeOH was observed, employing Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte (Figure S7). Although recording CVs of 0.1 M

solutions of Bu<sub>4</sub>N-1, Li-2 or Na-3 is similar to the preparative electrolyses, the obtained anodic limit potentials are not classify comparable to the oxidation potentials ( $E^{Ox}$ ) reported by Geiger *et al.*<sup>5</sup> and Datta *et al.*<sup>9</sup> For comparable results, the oxidation potentials ( $E^{Ox}$ ) of tetraphenylborates 1-3 were determined measuring CVs of 3 mM solutions of Bu<sub>4</sub>N-1, Na-3 and Li-2 in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> or 0.1 M NaClO<sub>4</sub>/MeCN, thus adapting the reported conditions (Figures S8-S33, Table 4, Table S9 and S10).<sup>5,9</sup> As working electrodes BDD, glassy carbon, and platinum were used. At molybdenum anodes oxidation of 1-3 was not observed (Figures S11/S18) and isostatic graphite underwent fast corrosion.

COMMUNICATION

Гable	4:	Oxidation	potentials	(E <sup>Ox</sup> )	of	tetraphenylborate	salts	1-3	in	0.1 M
VaClO4/MeCN at different working electrodes.										

Entry	Substrate	BDD	glassy carbon	platinum	
1			0.48 V	0.57 V	
	Bu₄N- <b>1</b>	0.93 V	Lit.: 0.40 V <sup>[a]</sup>	Lit.: 0.47 V <sup>[a]</sup>	
			0.78 V vs. SCE <sup>9</sup>	0.85 V vs. SCE <sup>9</sup>	
2	Na- <b>3</b>	1.56 V	shoulder: 1.9 V	2.02 V	
3	Li- <b>2</b>	shoulder: 2.1 V	1.83 V	shoulder: 2.0 V	

Potentials given vs. FcH/FcH<sup>+</sup>; [a] conversion constant from SCE to FcH/FcH<sup>+</sup> according to Pavlishchuk and Addison: 380 mV.<sup>20</sup>

The oxidation potentials ( $E^{Ox}$ ) of Na-**3** strongly depend on the applied electrolyte (Figures S22-S27). In CH<sub>2</sub>Cl<sub>2</sub> the highest  $E^{Ox}$  was observed at BDD (shoulder at 2.0 V) and the lowest  $E^{Ox}$  at platinum (1.57 V), whereas in MeCN the picture was inversed. Geiger *et al.* report an  $E^{Ox}$  (**3**) of 1.55 V vs. FcH/FcH<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>. However, the working electrode is not clearly stated.<sup>5</sup> For Li-**2** (Figures S28-S33) oxidation potentials ( $E^{Ox}$ ) could only be determined in MeCN. In CH<sub>2</sub>Cl<sub>2</sub> oxidation of **2** was in the range of electrochemical decomposition of the electrolyte. Interestingly Geiger *et al.* report an  $E^{Ox}$ (**2**) of 1.84 V in CH<sub>2</sub>Cl<sub>2</sub>, again without reporting the material of working electrode.<sup>5</sup>

As expected, the lowest E<sup>Ox</sup> were obtained for Bu<sub>4</sub>N-1 and the values at platinum and glassy carbon are comparable to those reported by Datta et al.<sup>9</sup> Interestingly, the CVs of Bu<sub>4</sub>N-1 (e.g. Figure 2, red line) show a 2<sup>nd</sup> oxidation peak in a range from 1.5 V to 1.6 V. This 2<sup>nd</sup> peak has also been observed by Geske et al. at a rotating platinum disk electrode<sup>7</sup> and is most likely associated with the oxidation of biphenyl, generated via oxidation of 1 (Figure 2, blue line). This observation, together with the disappearance/decrease and shifting of the 1<sup>st</sup> peak, as well as the shape of the 2<sup>nd</sup> peak (fast decline of current density after the peak maximum) indicate film formation at the working electrode.<sup>21</sup> Film formation seems to be fast e.g. at BDD in CH<sub>2</sub>Cl<sub>2</sub> (Figure S8) and less pronounced at platinum in MeCN (Figure S17). Film formation was also visually observed for Na-3 and Li-2 on the electrode and via disappearance/decrease of the oxidation peak (e.g. Figure 3, red line). Oxidation of biphenyls 4 or 5 occurs beyond the electrochemical window of the employed electrolyte. However, no film formation was observed in the electrolyses at BDD or isostatic graphite.

Published on 16 May 2018. Downloaded by Kings College London on 17/05/2018 02:39:44.



**Figure 2**: Cyclic voltammograms of 0.1 M NaClO<sub>4</sub>/MeCN (black line), 3.0 mM Bu<sub>4</sub>NBPh<sub>4</sub> (red line) and 3.0 mM biphenyl (blue line), working electrode: glassy carbon, electrolyte: 0.1 M NaClO<sub>4</sub>/MeCN, scan rate: 50 mV/s.



**Figure 3**: Cyclic voltammograms of 0.1 M NaClO<sub>4</sub>/MeCN (black line), 3.0 mM Bu<sub>4</sub>NBPh<sub>4</sub> (red line, four consecutive cycles), working electrode: glassy carbon, electrolyte: 0.1 M NaClO<sub>4</sub>/MeCN, scan rate: 50 mV/s.

In this study we present the optimized syntheses of highly fluorinated biphenyls from the respective BArF anions and provide a comprehensive picture on the reaction mechanism of this unexpected degradation process. An intense CV study was performed to gain further insight into the electrochemical stability of BArF salts. Even though, high oxidation potentials were found for BArF anions, an intramolecular cleavage of tetraphenylborates is most likely the main reaction path and in agreement with preparative and CV data.

### **Conflicts of interest**

The authors declare no conflict of interest.

### Notes and references

- 1 S. H. Strauss, Chem. Rev., 1993, 93, 927.
- 2 I. M. Riddlestone, A. Kraft, J. Schaefer and I. Krossing, *Angew. Chem. Int. Ed.*, 2018, DOI: 10.1002/anie.201710782.
- a) I. Chávez, A. Alvarez-Carena, E. Molins, A. Roig, W. Maniukiewicz, A. Arancibia, V. Arancibia, H. Brand and J. Manuel Manríquez, J. Organomet. Chem., 2000, 601, 126; b) S. E. Creutz and J. C. Peters, J. Am. Chem. Soc., 2014, 136, 1105; c) J. DePasquale, I. Nieto, L. E. Reuther, C. J. Herbst-Gervasoni, J. J. Paul, V. Mochalin, M. Zeller, C. M. Thomas, A. W. Addison and E. T. Papish, Inorg. Chem., 2013, 52, 9175; d) H. J. Gericke, N. I. Barnard, E. Erasmus, J. C. Swarts, M. J. Cook and M. A.S. Aquino, Inorg. Chim. Acta, 2010, 363, 2222; e) M. G. Hill, W. M.

Lamanna and K. R. Mann, *Inorg. Chem.*, 1991, **30**, 4687; fj R. Jine LeSuer and W. E. Geiger, *Angew. Chem.* Art. Ed. 2000; **39**, 248; B g) G. Mistlberger, X. Xie, M. Pawlak, G. A. Crespo and E. Bakker, *Anal. Chem.*, 2013, **85**, 2983; h) M. Oyama, Y. Nitta and S. Okazaki, *J. Electroanal. Chem.*, 2001, **511**, 88; i) I. Raabe, K. Wagner, K. Guttsche, M. Wang, M. Grätzel, G. Santiso-Quiñones and I. Krossing, *Chem. - Eur. J.*, 2009, **15**, 1966; j) J. Shen, G. P. A. Yap, W. E. Barker, W. E. Geiger and K. H. Theopold, *Chem. Commun.*, 2014, **50**, 10626; k) E. P. Warnick, R. J. Dupuis, N. A. Piro, W. Scott Kassel and C. Nataro, *Polyhedron*, 2016, **114**, 156.

- 4 F. Barrière and W. E. Geiger, J. Am. Chem. Soc., 2006, **128**, 3980.
- 5 W. E. Geiger and F. Barrière, Acc. Chem. Res., 2010, 43, 1030.
- 6 E. J. Olson, P. G. Boswell, B. L. Givot, L. J. Yao and P. Bühlmann, *J. Electroanal. Chem.*, 2010, **639**, 154.
- 7 D. H. Geske, J. Phys. Chem., 1959, 63, 1062.
- 8 J. H. Morris, H. J. Gysling and D. Reed, Chem. Rev., 1985, 85, 51.
- 9 P. K. Pal, S. Chowdhury, M. G. B. Drew and D. Datta, *New J. Chem.*, 2002, 26, 367.
- 10 a) E. Gioria, J. del Pozo, J. M. Martínez-Ilarduya and P. Espinet, Angew. Chem. Int. Ed., 2016, 55, 13276; b) D. Peral, F. Gomez-Villarraga, X. Sala, J. Pons, C. J. Bayon, J. Ros, M. Guerrero, L. Vendier, P. Lecante, J. Garcia-Anton and K. Philippot, Catal. Sci. Technol., 2013, 3, 475.
- a) M. Hofer, E. Gomez-Bengoa and C. Nevado, *Organometallics*, 2014, **33**, 1328; b) H. Tran, T. McCallum, M. Morin and L. Barriault, *Org. Lett.*, 2016, **18**, 4308.
- 12 L. Zhou and W. Lu, Organometallics, 2012, 31, 2124.
- 13 X. Xu, D. Cheng and W. Pei, J. Org. Chem., 2006, 71, 6637.
- 14 T. Vogler and A. Studer, *Adv. Synth. Cat.*, 2008, **350**, 1963.
- S. A. R. Mulla, S. S. Chavan, M. Y. Pathan, S. M. Inamdar and T. M. Y. Shaikh, *RSC Adv*, 2015, **5**, 24675.
- a) Bochmann and M. J. Sarsfield, *Organometallics*, 1998, **17**, 5908; b) H. J. Frohn, A. Klose and V. V. Bardin, *J. Fluorine Chem.*, 1993, **64**, 201; c) K. Koppe, V. Bilir, H.-J. Frohn, H. P. A. Mercier and G. J. Schrobilgen, *Inorg. Chem.*, 2007, **46**, 9425.
- a) S. B. Beil, T. Müller, S. Sillart, P. Franzmann, A. Bomm, M. Holtkamp, U. Karst, W. Schade and S. R. Waldvogel, *Angew. Chem. Int. Ed.*, 2018, 57, 2450; b) C. Gütz, B. Klöckner and S. R. Waldvogel, *Org. Process Res. Dev.*, 2015, 20, 26.
- A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes and S. R. Waldvogel, *Angew. Chem. Int. Ed.*, 2018, DOI: 10.1002/anie.201711060.
- B. Elsler, A. Wiebe, D. Schollmeyer, K. M. Dyballa, R. Franke and S. R. Waldvogel, *Chem. - Eur. J.*, 2015, **21**, 12321.
- 20 V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, 298, 97.
- a) J. Ghilane, P. Martin, O. Fontaine, J.-C. Lacroix and H. Randriamahazaka, *Electrochem. Commun.*, 2008, **10**, 1060; b) L. T. Nielsen, K. H. Vase, M. Dong, F. Besenbacher, S. U. Pedersen and K. Daasbjerg, *J. Am. Chem. Soc.*, 2007, **129**, 1888.

cebted

Published on 16 May 2018. Downloaded by Kings College London on 17/05/2018 02:39:44.



The electrochemical instability of highly fluorinated tetraphenyl borates was studied by cyclic voltammetry and anodic formation of the respective biphenyls.